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Groundwater Investigation and Monitoring Plan for Portsmouth Naval Shipyard Kittery, Maine

Northern Division
Naval Facilities Engineering Command
Contract Number N62472-90-D-1298
Contract Task Order 0148

November 1996

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A Division f Halliburton NUS Corporation

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PITT-10-8-162
October 26, 1998
Project Number 5003

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Contract Task Order No. 201

Subject: PHASE I/PHASE II OFFSHORE DATA
COMPARATIVE ANALYSIS REPORT
FOR THE INSTALLATION RESTORATION PROGRAM
PORTSMOUTH NAVAL SHIPYARD, KITTERY, ME

Dear Ms. Cassidy/Mr. McLeod:

On behalf of the U.S. Navy, TetraTech NUS (TtNUS) is pleased to submit to the U.S. Environmental Protection Agency Region 1 (USEPA) [4 copies] and to Maine Department of Environmental Protection (MEDEP) [4 copies] of the Final Phase I/Phase II Offshore Data Comparative Analysis Report.

If additional information is required, please contact Mr. Fred Evans at 610-595-0567

Sincerely,

Deborah J. Cohen, P.E.
Project Manager

Attachment

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The Groundwater Investigation and Monitoring Plan for the Portsmouth Naval Shipyard has been reviewed and is satisfactory for final publication.

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GROUNDWATER INVESTIGATION AND MONITORING PLAN FOR PORTSMOUTH NAVAL SHIPYARD KITTERY, MAINE

COMPREHENSIVE LONG-TERM ENVIRONMENTAL ACTION NAVY (CLEAN) CONTRACT

Submitted to:
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1.0 GROUNDWATER MONITORING PLAN

1.1 INTRODUCTION

This Groundwater Investigation and Monitoring Plan for the Portsmouth Naval Shipyard (PNS) in Kittery, Maine was prepared for the U.S. Department of the Navy (Navy) by Brown & Root Environmental (B&R Environmental) under the Comprehensive Long-Term Environmental Action Navy (CLEAN), Contract Number N62472-90-D-1298, Contract Task Order (CTO) 0148.

This document has been prepared in accordance with the Navy Installation Restoration Laboratory Quality Assurance Guide (Interim Guidance) (NFESC, February 1996).

1.2 SCOPE AND OBJECTIVES

The purpose of this Groundwater Investigation and Monitoring Plan is to provide additional information (low-flow sampling) to be used in the offshore migration modeling effort and, additionally, to facilitate the implementation of a cost effective, long-term groundwater monitoring program for various sites of concern, if it should be necessary. The data will be used as input concentrations for the offshore migration modeling effort to determine the site's impact on the quality of groundwater in the aquifer and impact on State waters.

To meet this objective, a pilot study to evaluate the effects of low-flow purging in tidally influenced areas on field monitored groundwater quality parameters was conducted. Next, two rounds of sampling (referenced to herein as the first and second re-sampling event) will initially be conducted and incorporated into the existing database and for use in migration modeling. The pilot study is discussed in Section 4.2 of this Plan. All 70 existing RFI and RFI Data Gap monitoring wells, plus one monitoring well from the Stearns & Wheler investigation (Stearns & Wheler 1994) will be re-sampled as part of this effort; the suite of analytes is site-specific and is based on an evaluation of site history and previous analytical results. Subsequent to the planned re-sampling and upon evaluation of analytical results and groundwater contours, the number of monitoring wells sampled and the suite of analytes may be reduced in the future. Conversely, additional monitoring well locations for sampling may need to be defined. Also, source and groundwater remediation may be occurring in the next several years, which would impact the groundwater monitoring program.

The analytical results from the first and second re-sampling event will be utilized for contaminant transport modeling. The objective of the modeling is to assess whether current onsite conditions require remediation

in order to protect off-shore receptors. The groundwater sampling will provide a comprehensive and current set of facility-wide analytical results that can be utilized for the modeling. However, remedial action decisions will not be made based solely on the results of the contaminant fate and transport modeling. The modeling results will be considered together with the existing and proposed groundwater, seep, and sediment data.

1.3 APPROACH

Upon completion of the pilot study, two groundwater re-sampling events (referred to herein as first event, second event) are planned. Requirements for subsequent sampling, if necessary, will not be finalized until after the initial sampling rounds are evaluated. There are 55 existing monitoring wells installed as part of an initial RCRA Facilities Investigation (RFI) conducted in 1991 (McClaren/Hart, 1992). An additional 15 monitoring wells were installed in mid 1994 as part of the RFI Data Gap investigation (Halliburton NUS, 1995a). The subject groundwater investigation and monitoring program considers all these monitoring wells, as necessary. Monitoring wells previously installed throughout PNS (to evaluate groundwater parameters and geology) will be re-sampled. This sampling effort will be conducted and a qualitative assessment will be performed to determine if the spatial distribution of chemicals in groundwater have changed over the last several years. A quantitative comparison may not be possible when comparing historical water quality results with data generated from the current investigation due to differences in sampling techniques. In addition, these distributions (both past and present) will be utilized in a comprehensive migration model which will evaluate freshwater inputs from PNS groundwater to the adjacent sediments and marine environment. The following groundwater monitoring approach is proposed for the PNS:

(1) Re-sample all 55 existing monitoring wells installed as part of the initial RFI and the additional 15 monitoring wells installed during the RFI Data Gap investigation. Two of the monitoring wells installed during the RFI data gap investigation have recently become damaged and have been replaced. WOT-6 was replaced with new monitoring well HW-2 and WOT-1 was replaced with HW-3. Additionally, monitoring is included for MW-10-BW from the Stearns & Wheler investigation of the tank farm; this well is upgradient/crossgradient of the DRMO Salvage Yard. Conduct two rounds of sampling on a schedule agreed upon by the Navy, EPA and MEDEP after work plan approval. The sampling and analysis program was developed based on an evaluation of site history and previous analytical data. However, the first event analytical results may identify "hot spots" or other interest zones where more frequent monitoring is required in the future. At a maximum, monitoring wells may be analyzed for full Target Compound List (TCL) organics and SW inorganics, which is consistent with the analytical methods used for the RFI and RFI Data Gap investigations. Where applicable, freon will be included with TCL volatile organics analysis. Qualitative information on tentatively identified compounds (TICs) will be

provided with the TCL analytical package in accordance with EPA Region I guidance. Also, indicator parameters are included but without replicate sampling since the sampling/analysis program includes TCL organics and SW inorganics, resulting in less reliance on indicator parameters. Indicator parameters will include pH, specific conductance, total organic carbon (TOC), total organic halogen (TOX), nitrate, bromide, alkalinity, chloride, iron, manganese, sodium, phenols and sulfate. In addition, pH testing will be performed in the laboratory. Gasoline range and diesel range petroleum hydrocarbon compounds will also be included for analysis where appropriate.

(2) Conduct subsequent groundwater monitoring for selected monitoring wells. Not all existing monitoring wells installed at the facility will require long-term monitoring. It is anticipated that those wells installed solely to investigate site hydrogeology and those wells in excess of that required for adequate upgradient and downgradient monitoring of a site will be excluded from subsequent long-term monitoring. Also, where one site lies within another site (or adjacent to another site), monitoring at the outer boundary of the combined sites is deemed sufficient. Specific monitoring wells selected for groundwater monitoring are preliminarily identified as follows. These identified wells, frequency of monitoring, and analytical methods are subject to change following evaluation of the first and second event analytical results, evaluation of the groundwater flow maps, and consultation with the regulators. As an example, a change to SW-846 analytical methods could be appropriate.

- Three on-site background wells for the facility will be selected for subsequent monitoring following establishment of background conditions. Two of the selected wells will be overburden wells and the third will be a bedrock monitoring well. If no on-site wells are suitable for background, off-site wells would be considered in the future. An extensive survey of existing information from nearby water utilities/wells, State, and CERCLA records would need to be conducted to further aid in establishing groundwater background conditions.

- At the DRMO Salvage Yard, where groundwater flow direction is known, two near upgradient wells and five overburden and two bedrock wells located along the downgradient DRMO perimeter are anticipated for monitoring. Additionally, monitoring of upgradient MW-10-BW from the Stearns & Wheler investigation at the tank farm is anticipated. No farther downgradient wells can be installed since this site borders the Piscataqua River.

- At the Jamaica Island Landfill (JILF), where groundwater flow direction appears to be in several directions, perimeter wells will be monitored. Nineteen overburden and eight bedrock wells are anticipated for monitoring.

- The Mercury Burial Sites are located within the JILF and therefore can be included with the JILF. Monitoring will be in accordance with the JILF perimeter monitoring program. The inclusion of the Mercury Burial Sites within the JILF Landfill for groundwater monitoring does not preclude remediation activities specific to these sites.

- The Former Waste Oil Tanks also are located in close proximity to the JILF. Monitoring will be in accordance with the JILF perimeter monitoring program. The inclusion of the Former Waste Oil Tanks within the JILF for groundwater monitoring does not preclude remediation activities specific to these sites.

- At the Berth 6 Industrial Area, all six existing overburden wells will be monitored.

Groundwater samples will be analyzed for TCL organics/TAL inorganics, which is consistent with the analytical methods used for the RFI and RFI Data Gap investigations. Also, several indicator parameters are included but without replicate sampling since TCL organics and SW inorganics analysis is planned, resulting in less reliance on indicator parameters. Sampling/analysis will likely be conducted on a semi-annual basis; frequency of sampling/analysis will be determined based on consultation with the Navy, EPA, and MEDEP.

(3) Revise the monitoring program on a yearly basis, as necessary. It is the intent of the Navy to conduct sampling and analyses only as necessary. Therefore, after the first two re-sampling events are established, analytes which are not expected and not detected will be deleted from the analytical program for subsequent years. Similarly, different analytical methods may be requested.

(4) Water-level measurements will occur during each sampling round for all RFI and RFI Data Gap monitoring wells and not just those wells being sampled and analyzed at the time. Both high tide and low tide measurements will take place. In the future, additional rounds of water level data may be required to better characterize groundwater flow patterns and dynamics. If so, piezometers could be installed to provide additional groundwater level information.

1.4 PROJECT ORGANIZATION AND RESPONSIBILITIES

B&R Environmental will be responsible for the overall management of the project, including the field inspection and implementation of all sampling activities. Personnel from Navy will be actively involved in the investigation and will coordinate with personnel from B&R Environmental in a number of areas.

1.4.1 Project Organization

The key firms and personnel involved in the investigation, as well as the chain of communication and responsibility of the project personnel, are as follows:

The Navy Remedial Project Manager (RPM) is:

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Program Manager
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The Project Manager has the primary responsibility for project and technical management of this project. He is responsible for the coordination of all onsite personnel, and for providing technical assistance for all activities that are directly related to the determination of the hydrogeologic conditions and the environmental quality of the site. The review of all environmental and hydrogeologic data will also be conducted by the Project Manager. If quality assurance problems or deficiencies requiring special action are identified, the Project Manager and project QA/QC advisor will identify the appropriate corrective action.

1.4.2 Field Organization

The B&R Environmental field investigation team will be organized according to the activities planned. For onsite sampling, the sampling team members will be selected based upon the type and extent of effort required. The team will consist of a combination of the following personnel:

- Field Team Leader (FTL)
- Field hydrogeologist/geologist
- Health and Safety specialist

The FTL will be responsible for the coordination of all onsite personnel and for providing technical assistance when required. The FTL, or his or her designee will coordinate and be present during all sampling activities and will assure the availability and maintenance of all sampling materials/equipment. The FTL will be responsible for the completion of all sampling, and chain-of-custody documentation, and will assume custody of all samples and ensure the proper handling and shipping of samples.

The QA Manager, although not formally part of the field team, will be responsible for the adherence of all guidelines as defined in the QAPP. Strict adherence to these procedures is critical to the collection of acceptable and representative data.

A site safety officer will be designated prior to field activities and will be responsible for assuring that all team members adhere to the designated health and safety requirements.

2.0 BACKGROUND INFORMATION

2.1 GEOLOGY/HYDROGEOLOGY

2.1.1 Site Location and Description

Situated within the town of Kittery, Maine, the Portsmouth Naval Shipyard (PNS) is located as an island in the Piscataqua River. The Piscataqua River is a tidal estuary which forms the southern boundary between New Hampshire and Maine.

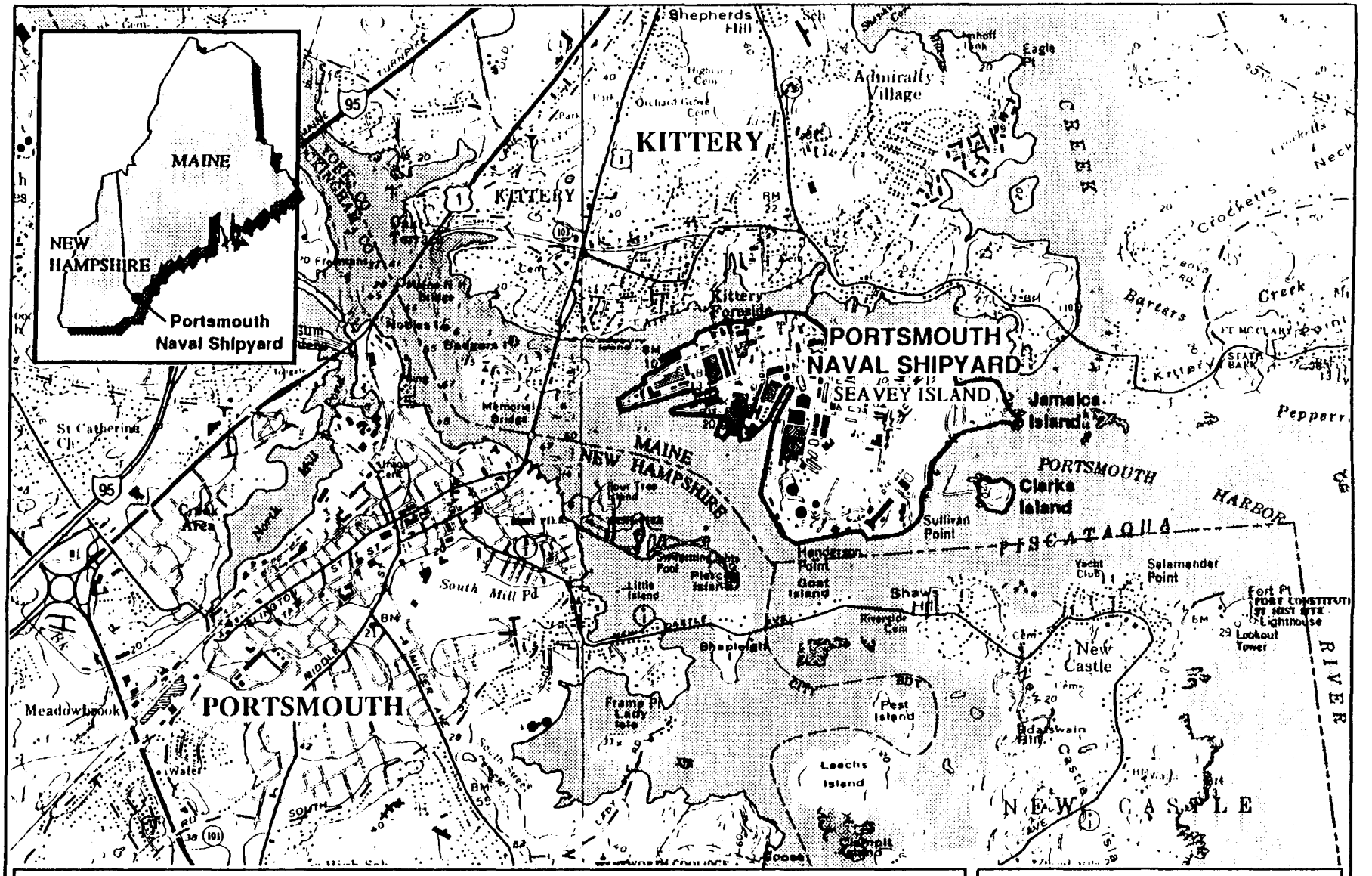
PNS is engaged in the overhaul and repair of submarines for the U.S. Navy. The shipyard has a long history dating back to 1690 when the first warship launched in North America, the *Falkland*, was built. PNS was first established as a government facility in 1800. PNS served as a repair and building facility for ships during the Civil War. The first government-built submarine was designed and built at the shipyard during World War I and a large number of submarines were designed and constructed at the yard from 1917 to the present. PNS has continued servicing submarines to this day.

As the workload at PNS expanded, fill material was used to create man-made-land adjacent to the original islands. Today PNS is composed of 376 buildings on 278 acres of continuous land surface that extends between the original islands. Much of PNS is built on fill overlying former tidal flats as shown in Map A (located at the end of the text).

2.1.2 Physiography

The PNS is located on Seavey Island in the Piscataqua River immediately south of the town of Kittery, Maine. The location of the shipyard is shown in Figure 2-1. PNS is built on an area comprising Dennett's, Seavey, Jamaica and Pumpkin Islands, as well as man-made land between these islands. Approximate elevations on-site range from sea level to a maximum of sixty feet above mean sea level (MSL). Two-thirds of the site is high-density industrial area containing 376 buildings, while the remaining areas are flat-lying to gently sloping grass-covered fields. Minor wooded areas exist on the east side of Jamaica Island.

The shoreline in the Portsmouth area is described as an embayed coast produced by partial submergence of a fluvially eroded land mass. This type of shoreline is closely associated with the drowned river valley type estuary. The Great Bay Estuary would be considered a drowned river valley in a geomorphological



Source: USGS Quads Portsmouth, N.H. - ME., 1988; Kittery, ME. - N.H., 1989.

FIGURE 2-1
Vicinity Map
Portsmouth Naval Shipyard
Kittery, Maine

classification. Valleys show some degree of straightening and deepening by ice; hilltops are blunted by ice erosion and deposits of till block smaller valleys.

2.1.3 Surface Water

The Piscataqua River hydrology is not characteristic of traditional inland fluvial hydrology. The Piscataqua River, Little Bay and Great Bay, and seven converging rivers form the Great Bay Estuary. Seavey Island is located in the mouth of the Great Bay Estuary, commonly referred to as the Portsmouth Harbor. The harbor's main channel is approximately 75 feet deep (mean low water) and the back channel is approximately 20 feet deep (mean low water) in the vicinity of Seavey Island.

Additional surface water information can be found in the RCRA Facilities Investigation Report (McLaren/Hart, 1992).

2.1.4 Geology and Stratigraphy

The islands composing the PNS are formed on bedrock highs with thin veneers of glacial till, recent alluvium, and/or fill materials. Bedrock consists of tectonically deformed Middle Ordovician volcanic rocks and highly fractured, metamorphosed sandstones, shales, and siltstone of Silurian age belonging to the Kittery Formation. Metamorphism has destroyed original interparticle porosity in the sedimentary rocks. Therefore, groundwater flow is controlled by fractures.

The bedrock of this area has undergone at least three periods of deformation; the Taconic Orogeny (440 million years before present (mybp)), Acadian (360 mybp), and the Appalachian (260 mybp)), resulting in multiple rock cleavages, planes of foliation, faults of various ages and types, and varied fold orientations and geometries. The resulting bedrock fracture pattern therefore is highly complex.

Additional geologic information can be found in the RCRA Facilities Investigation Report (McLaren/Hart, 1992) and the RFI Data Gap Report (Halliburton NUS, 1995a).

2.1.5 Hydrogeology

Groundwater is encountered within both the unconsolidated materials and bedrock at the facility. In general, the unconsolidated materials appear to be moderately to highly permeable. Bedrock permeability is generally less than that of the unconsolidated materials.

Groundwater levels at the PNS are shallow and appear to be controlled by the bedrock surface topography and by the thickness of glacial till and fill material overlying bedrock or former tidal flat areas. Groundwater flow directions on-site vary depending on ground surface topography, the thickness and composition of overburden, bedrock-overburden contact-surface dip, and tidal influence, but overall groundwater flow directions are from the original island interiors toward the island coastline. Recharge to groundwater is derived from local precipitation and tidal effects.

Kittery's potable water supply originates from surface reservoirs located in the vicinity of York, Maine. The shipyard is not currently using on-site groundwater.

Additional information can be found in the RFI Data Gap Report (Halliburton NUS, 1995a).

2.1.6 Topography

Detailed topographic maps of the DRMO and JILF Landfill can be found in the RCRA Facility Investigation Report (McLaren/Hart, 1992). Also, a topography map of the facility is provided as Map B of the RFI Data Gap Report (Halliburton NUS, 1995a). Interim remediation measures at the DRMO Salvage Yard were conducted in late 1993. A cap was installed, consisting of a geocomposite clay liner and gravel cover choked with concrete to prevent direct contact with contaminated soils and reduce infiltration of precipitation.

2.1.7 Climatology

Precipitation is fairly evenly distributed over the year, with 2.7 to 4.6 inches falling per month for a 42.6 inch annual total. On the average there are about 130 days each year having more than a trace of precipitation. Most summer precipitation results from showers and, infrequently, thunderstorms. Winter precipitation is generally associated with stormy conditions caused by air masses moving up along the coast. Heavy precipitation events are usually caused by storm centers that form along the east coast and move northeastward through the New England area.

3.0 GROUNDWATER MONITORING SYSTEM

3.1 MONITORING WELL LOCATIONS

The location of all existing wells proposed for monitoring can be found on the enclosed Map A. Additional information about the location of existing RFI monitoring wells can be found in Sections 4.0 and 5.0 of the RCRA Facility Investigation Report (McLaren/Hart, 1992). Additional information about the location of RFI Data Gap wells can be found in the RFI Data Gap Report (Halliburton NUS, 1995a). The first event water level measurements may identify areas where piezometers should be installed to more completely characterize groundwater levels and flow patterns.

Two existing monitoring wells at the former waste oil site have been damaged and have been replaced with overburden monitoring well HW-2 (replacement for WOT-6) and shallow bedrock monitoring well HW-3 (replacement for WOT-1), respectively. These two additional monitoring wells will be identified and located during the implementation of the Groundwater Investigation and Monitoring Plan."

3.2 MONITORING WELL CONSTRUCTION DETAILS

3.2.1 RFI Data Gap Monitoring Wells

The 15 RFI Data Gap monitoring wells (both overburden and bedrock) and HW-2 and HW-3 were constructed of 2-inch-diameter PVC well screen and casing. HW-2 and HW-3 were both drilled to a depth of 12 feet. HW-2 is an overburden well and HW-3 was advanced into bedrock. Bedrock was encountered at a depth of 8 feet. Five foot screens were installed in these wells. Table 3-1 summarizes RFI Data Gap monitoring well construction details. Additional information can be found in the RFI Data Gap Work Plan (Halliburton NUS, 1994) and the RFI Data Gap Report (Halliburton NUS, 1995a). Information on the two replacement wells HW-2 and HW-3 can be found in the Groundwater Monitoring Plan (C.T. Male, 1995).

3.2.2 RFI Monitoring Wells

A summary of the construction details for the 55 monitoring wells installed during the RFI is shown in Table 3-2. Additional information on existing well installation and construction can be found in Section 5.0 (and Appendix IV) of the RCRA Facility Investigation Report (McLaren/Hart, 1992).

TABLE 3-1

RFI DATA GAP (PHASE VI) MONITORING WELL CONSTRUCTION DETAILS
PNS, KITTERY, MAINE

Well I.D.	Ground Elevation (ft)	Top of Riser Elevation[c] (ft)	Top/Bottom of Screen (ft BGS)	Screened Formation[a]	Total Depth (ft BGS)	Depth to Bedrock (ft BGS)	K from Slug Test (ft/day)
DI-01B	112.40	113.88	24.0-34.0	BR	35.0	3.5	0.08
DI-01DB	113.06	114.89	79.0-94.0	BR	95.0	5.0	4.1
FA-01	107.13	109.13	4.0-14.0	F	14.0	14.0	1313
FA-01B	107.05	108.80	40.0-55.0	BR	55.0	23.5	0.06
FA-01DB	107.03	108.72	137.5-157.5	BR	157.5	22.0	0.028
SI-01B	117.89	119.70	20.5-35.5	BR	35.0	5.0	NT
SI-01DB	118.25	119.95	130.0-150.0	BR	150.0	3.5	NT
DW-07DB	110.20	111.89	130.0-150.0	BR	150.0	8.5	0.021
JW-13DB	108.92	110.54	131.0-151.0	BR	152.0	21.5	0.0006
WOT-1[b]	106.60	108.33	3.0-7.0	F	7.0	7.0	NT
WOT-2	106.59	106.07	3.0-8.0	F	8.0	8.0	41.6
WOT-3	106.65	106.34	3.0-12.0	F	12.0	12.0	8.9
WOT-4	105.91	105.24	4.0-14.0	F	14.0	14.0	3.8
WOT-5	108.05	107.60	8.0-15.0	F	15.0	15.0	4.2
WOT-6[b]	106.33	108.46	12.0-20.0	F	20.0	20.0	0.27

[a] F = fill and BR = bedrock.
[b] New monitoring well HW-2 replaces damaged monitoring well WOT-6. New monitoring well HW-3 replaces monitoring well WOT-1; the screened interval extends into shallow bedrock.
[c] Vertical elevations of all monitoring wells will be resurveyed after retrofitting for installation of low flow sampling pumps.

NOTES:
All wells are constructed of 2" PVC and well screens are also of PVC construction.
BGS means below ground surface.
NA means information is not available.
NT means not tested.

DI = Dennett's Island area wells.
FA = Fill Area wells.
SI = Seavey Island area wells.
DW = DRMO Salvage Yard area wells.
JW = JILF area wells.
WOT = Former Waste Oil Tank area wells.

TABLE 3-2

RFI (PHASE I, II, III, IV, IVA) MONITORING WELL CONSTRUCTION DETAILS
PNS, KITTERY, MAINE

Well I.D.[a]	Material of Construction	Ground Elevation (ft)	Top of Riser Elevation[b] (ft)	Top/Bottom of Screen (ft BGS)	Screened Formation[b]	Total Depth (ft BGS)	Depth to Bedrock (ft BGS)	K from Slug Test (ft/day)
JW-3	Teflon	108.46	110.09	7.0-17.0	BR	17.0	6.3	1.16
JW-4[c]	Teflon	106.13	105.80	7.0-12.0	WB.BR	13.0	7.0-8.0	12.04
	Teflon	106.07	108.60					
JW-5	Teflon	106.96	106.74	10.0-15.0	TF,BE,WB	20.0	12.0-15.0	12.67
JW-6	Teflon	108.31	107.78	11.0-21.0	F,TF,BE	33.0	26.3-28.0	4.68
JW-7	Teflon	107.14	108.94	6.8-11.8	BE,WB,BR	15.0	8.0-10.0	38.27
JW-7B	Teflon	107.32	108.87	18.0-23.0	BR	23.0	4.3	6.4
JW-8	Teflon	111.06	112.73	9.0-14.0	BE	19.5	14.5	47.53
JW-8B	Teflon	111.12	114.00	20.0-25.0	BR	25.5	12.0-14.5	0.14
JW-9	Teflon	105.09	106.42	7.0-15.0	F	19.5	15.5	245.68
JW-9B	Teflon	105.07	106.88	19.0-29.0	BR	30.5	14.3	0.17
JW-10	Teflon	106.43	108.40	7.0-12.0	F	21.7	19.0	171.99
JW-12S	Teflon	106.66	108.67	8.0-13.0	F	13.0	NA	Too Fast
JW-12D	Teflon	106.71	108.24	18.0-23.0	F	25.0	NA	Too Fast
JW-12B	Teflon	106.49	108.42	36.0-41.0	BR	41.0	25.0-25.5	60.69
JW-13S	Teflon	108.66	111.38	7.0-12.0	F	12.0	NA	Too Fast
JW-13D	Teflon	108.67	110.79	15.0-20.0	F	22.0	NA	Too Fast
JW-13B	Teflon	108.46	110.24	33.0-38.0	BR	40.0	28.0	Too Fast
JW-14	Teflon	109.57	111.13	10.0-15.0	F	15.0	15.0	Too Fast
JW-14B	Teflon	109.38	111.00	20.5-25.5	BR	25.5	14.5	Too Slow
JW-15[c]	Teflon	107.60	107.42	7.0-12.0	F	12.5	12.5	200.8
	Teflon	107.67	107.34					
JW-15B	Teflon	107.47	107.29	19.5-24.5	BR	24.5	14.5	0.33
JW-16[c]	Teflon	106.70	106.38	5.0-10.0	F	11.0	NA	NT
	Teflon	106.75	106.50					
JW-16B[c]	Teflon	106.73	106.40	14.5-19.5	BR	20.5	10.5	NT
	Teflon	106.73	106.57					
JW-17B[c]	Teflon	107.87	107.47	21.0-26.0	BR	26.5	17.0	1.16
	Teflon	107.98	107.66					

TABLE 3-2
RFI MONITORING WELLS CONSTRUCTION DETAILS
PNS, KITTERY, MAINE
PAGE 2

Well I.D.[a]	Material of Construction	Ground Elevation (ft)	Top of Riser Elevation[a] (ft)	Top/Bottom of Screen (ft BGS)	Screened Formation[b]	Total Depth (ft BGS)	Depth to Bedrock (ft BGS)	K from Slug Test (ft/day)
JW-18[a]	Teflon	108.54	108.29	8.0-13.0	F	14.0	NA	31.15
	Teflon	108.63	108.31					
JW-18B[a]	Teflon	108.56	107.86	24.7-29.7	BR	30.2	20.1	NT
JW-19	Teflon	111.88	114.14	12.0-22.0	F,TF	28.8	28.8	27.67
JW-19B[a]	Teflon	111.90	114.48	66.5-71.5	BR	72.0	62.0	NT
	Teflon	112.22	114.64					
MW-2	PVC	115.98	118.15	10.0-20.0	F	22.0	NA	252.3
MW-3	PVC	116.41	116.14	10.0-20.0	F	21.0	NA	NT
MW-4	PVC and Teflon	111.45	113.08	8.9-18.9	F	22.0	NA	85.89
MW-5	PVC	111.57	113.45	10.0-20.0	F	22.0	NA	NT
MW-6	Teflon	116.50	116.17	20.0-25.0	F,TF	28.0	NA	NT
MW-7	Teflon	111.66	113.86	16.5-21.5	F	24.5	NA	NT
DW-1	PVC	109.42	111.44	7.0-12.0	F,WB	16.5	11.5	42.49
DW-1B	Teflon	109.53	111.36	17.0-22.0	BR	22.0	11.5	2.09
DW-2	PVC	108.84	108.34	10.0-15.0	F	22.0	16.0-17.0	Too Fast
DW-2B	Teflon	109.93	111.77	21.0-26.0	BR	26.0	14.0	Too Fast
DW-3	PVC	108.48	110.69	10.0-20.0	F	36.5	26.3-35.0	Too Fast
DW-4	PVC	110.16	109.69	10.0-15.0	WB	18.5	9.5-15.0	172.33
DW-5	PVC	109.09	111.14	7.0-12.0	F,BR	16.0	11.0	37.43
DW-6	PVC	110.17	112.06	8.0-15.0	F,WB	20.5	10.0-15.5	226.06
DW-7	PVC	109.93	111.52	10.0-20.0	F	28.0	23.0	99.74
DW-7B	Teflon	110.41	112.33	28.0-33.0	BR	33.0	17.0-22.0	8.39
DW-8	Teflon	107.38	109.86	10.0-20.0	F	20.5	NA	39.22
DW-8B	Teflon	107.39	109.03	48.7-53.7	BR	54.5	42.0	0.27
DW-9	Teflon	108.42	110.14	10.0-20.0	F	23.5	NA	52.56
DW-10B	Teflon	111.62	112.83	13.0-18.0	BR	21.0	5.3	184.25
FW-1[a]	Teflon	NA	NA	10.5-15.5	F,BR	17.5	12.0	NT
	Teflon	106.22	105.77					
FW-2[a]	Teflon	NA	NA	10.0-15.0	F,BR	17.0	12.0	NT
	Teflon	104.91	104.59					

TABLE 3-2
RFI MONITORING WELLS CONSTRUCTION DETAILS
PNS, KITTERY, MAINE
PAGE 3

Well I.D.[a]	Material of Construction	Ground Elevation (ft)	Top of Riser Elevation[c] (ft)	Top/Bottom of Screen (ft BGS)	Screened Formation[b]	Total Depth (ft BGS)	Depth to Bedrock (ft BGS)	K from Slug Test (ft/day)
FW-3[a]	Teflon	NA	NA	8.0-13.0	F,BR	13.5	11.0	NT
	Teflon	104.73	104.21					
FW-4[a]	Teflon	NA	NA	10.0-15.0	F,BR	16.0	11.0	NT
	Teflon	105.69	105.41					
FW-5[a]	Teflon	NA	NA	11.0-16.0	BR	17.0	10.0	NT
	Teflon	105.07	104.82					
FW-6[a]	Teflon	NA	NA	5.0-15.0	F,BR	17.0	10.0	NT
	Teflon	105.32	104.78					
GW-1	Unknown	NA	119.48	12.0-27.0	NA	32.0	NA	

[a] These wells were repaired and/or re-surveyed during the RFI Data Gap Investigation. New ground surface and top of riser elevations are shown in the subsequent line.
[b] F=fill, TF=tidal flats, BE=beach deposits, WB=weathered bedrock, and BR=bedrock.
[c] Vertical elevations of all monitoring wells will be resurveyed after retrofitting for installation of low flow sampling pumps.

NOTES:
BGS means below ground surface.
NA means information is not available.
NT means not tested.

DW = DRMO Salvage Yard area wells.
JW = JILF area wells.
MW = Mercury Burial Site area wells.
FW = Berth 6 Industrial area wells.

3.2.3 Stearns & Wheler Monitoring Wells

As part of the Oil Terminal Facility Permit renewal process, PNS conducted a hydrogeologic investigation of the tank farm area at their facility. Stearns & Wheler, under contract to the Navy, conducted the work. The tank farm consists of five aboveground storage tanks (ASTs), as follows, with a total estimated petroleum capacity of 11,350,000 gallons.

Tank Number	Contents	Status
Tank 1	No. 6 Fuel Oil	Active
Tank 2	No. 6 Fuel Oil	Active
Tank 3	No. 2 Fuel Oil	Empty
Tank 4	Waste Oil	Empty
Tank 6	No. 2. Fuel Oil	Active

Sixteen new monitoring wells were installed during the Stearns & Wheler investigation (Stearns & Wheler, 1994). Split-spoon samples were collected from the borings for the monitoring wells, and were obtained continuously, every two feet, through the overburden. Soil gas was used to approximate the extent of volatile organic compounds (VOCs) present, and an ENSYS Immunoassay Test Kit provided information on petroleum product contamination. Soil samples were also collected for laboratory analysis of volatile organics, semi-volatile organics, total petroleum hydrocarbons (TPH), and the eight RCRA metals (i.e., arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver), plus beryllium. Five of the sixteen new monitoring wells could not be sampled because the wells were dry. Laboratory analysis for groundwater included volatile organics, semi-volatile organics, TPH, the eight RCRA metals, and beryllium.

Monitoring well MW-10BW, slated for inclusion in the monitoring program, is 12 feet in depth; depth to bedrock is 2 feet at this location. The well screen is 8 feet in length. The well is constructed of 2-inch diameter PVC with a PVC well screen.

Groundwater contamination is associated with No. 6 fuel oil, with lesser amounts of No. 2 fuel oil constituents. Impacts are primarily limited to Tank 2 and 4 in the containment area. Maximum TPH concentration was 20 mg/l detected in a shallow monitoring well (MW-5BW). Concerning metals, there were isolated elevated concentrations of arsenic, chromium, lead, and beryllium in various monitoring wells. Volatile organics at significant concentrations consisted of TICs. Semi-volatile organics at significant concentrations also were mainly TICs. Generally, the TICs were detected at significant concentrations in the wells where elevated TPH in soil (TPH exceeding 100 mg/kg) were observed. Although a trace of free product, evident as a sheen, was observed in one well, no significant occurrence of free product was detected during the 1994 investigation. However, petroleum product on the groundwater surface [in

MW-5BW] was measured at a thickness of 3-inches and 1.5-inches during the February and March 1995 sampling series, respectively.

3.3 SURVEYING

All monitoring well locations have been surveyed. Monitoring well horizontal locations are surveyed to the nearest 0.10 foot. Vertical elevations are referenced to the 1929 North American Datum. Monitoring well elevations are surveyed to the nearest 0.01 foot at the measuring point where the uncapped riser pipe is notched. Ground surface elevations at the well locations are surveyed to the nearest 0.10 foot.

Vertical elevations of all monitoring wells will be resurveyed after retrofitting for installation of low flow sampling pumps. All wells will be surveyed vertically to the nearest 0.01 foot at measuring point where the uncapped well riser is notched, and at the top of the protective casing. For all locations, ground surface elevations will be surveyed to the nearest 0.10 foot.

3.4 EXISTING DATA

3.4.1 Available Groundwater Monitoring Data

Complete groundwater monitoring data is included in the data base provided in Appendix D of the Draft Feasibility Study Report (Halliburton NUS, 1995b). The data base has since been updated to incorporate data validation. Copies of the updated data base have been provided to the regulatory agencies (letter of 10/13/95) and will be presented in future feasibility study reports.

Appendix D herein of the Groundwater Investigation and Monitoring Plan summarizes pertinent information for those sites of concern for groundwater. Evaluation of this information is the basis for selecting the suites of analytes for baseline monitoring of the 70 wells proposed for analysis. Note that in Appendix D all groundwater is compared with on-shore media protection standards (MPSs) for residential use because these are the only remediation goals currently available. Nevertheless, on-shore MPSs are likely a good indicator of potential contaminants of concern for off-shore receptors; however, since the on-shore MPS are reflective of protection of human health and do not take into account the potential impacts to the off-shore environment, other criteria will be evaluated as well. Off-shore preliminary remediation goals (PRGs) are currently in preparation. Where groundwater is not a potential drinking water source, off-shore preliminary remediation goals (PRGs) will govern. Moreover, other criteria may be used for the selection of analytical parameters, not just MPS/PRG related ones. The following summarizes the known nature and extent of contamination:

DRMO Salvage Yard (Site 6)

Elevated concentrations of metals were consistently detected in groundwater samples from the DRMO Salvage Yard wells. For the most part, metals were detected at high concentrations in the unfiltered groundwater samples and low concentrations in the filtered samples, indicating that the metals were largely in the particulate (or colloidal), rather than the dissolved, form. Lead is the primary contaminant of concern.

The measured concentration of several total metals (lead, arsenic, aluminum, antimony, cadmium, chromium, copper, manganese, nickel and zinc) exceeded residential MPSs. The maximum lead (total) concentration of 49,200 ug/l was observed at DW-02. The corresponding filtered concentration for lead of 213 ug/l was much lower. In general, total (particulate/colloidal) concentrations were higher and more prevalent than for filtered (dissolved) concentrations. Lead concentration in the bedrock well at DW-02 was present at 25.7 ug/l total (particulate/colloidal) concentration. No exceedences occurred for the corresponding filtered (dissolved) sample. In general, overburden wells had higher analyte concentrations than did bedrock wells. Also of note, total lead concentrations east of the DRMO (Old Incinerator Area) are elevated. An exceedence of 4,4'-DDD occurred once and polychlorinated biphenyl (PCB) exceedences occurred sporadically (Aroclor 1254). One slight exceedence of the residential MPS for bis(2-ethylhexyl)phthalate (BEHP) occurred in the old incinerator area. Petroleum ID fingerprinting occurred at 3 locations during the Phase IV investigation. Monitoring well DW-06 was nondetect. DW-02B indicated 1.6 mg/l of No. 6 Fuel Oil and DW-08 indicated No. 6 fuel oil (0.8 mg/l) and compressor oil (0.4 mg/l). In addition, during the RFI Data Gap investigation, total diesel (EPA Method 8100, modified) was present in monitoring well DW-07DB groundwater at a concentration of 160J ug/l.

Groundwater in and around the DRMO had elevated levels of metals (lead, arsenic, aluminum, antimony, cadmium, chromium, copper, manganese, nickel and zinc) at concentrations in excess of residential MPSs. This includes the Old Incinerator Area east of the DRMO, which is scheduled for additional investigation by the Navy. Monitoring wells slightly upgradient of the DRMO (DW-1, DW-1B, DW-5, DW-4, and DW10B) are contaminated as well, likely because of tidal effects.

Jamaica Island Landfill (Site 8)

Elevated concentrations of metals have been detected in numerous wells. For the most part, metals were detected at high concentrations in the unfiltered groundwater samples and low concentrations in the filtered samples, indicating that the metals were in the particulate (or colloidal), rather than the dissolved, form. Additionally, elevated levels of volatile and semi-volatile organics are sporadically present in several JILF monitoring wells (Halliburton NUS, 1995b). Petroleum product encountered has been largely attributed to the former waste oil storage tanks located in close proximity to the JILF Landfill.

The measured concentration of several total metals (lead, arsenic, aluminum, antimony, beryllium, cadmium, chromium, copper, manganese, nickel and zinc) exceeded residential MPSs. In general, total (particulate/colloidal) concentrations were higher and more prevalent than for filtered (dissolved) concentrations. Also, in general, shallow wells had higher analyte concentrations than did bedrock wells. Of note, arsenic in soils did not exceed the soils MPS; other inorganics were present in both soils and groundwater. Mercury was present in groundwater but an MPS for groundwater was not developed for this analyte.

Organics were sporadically detected, including BEHP, methylene chloride, benzene, 4,4'-DDD and PCBs. Organic contamination was generally present associated with the Former Waste Oil Tanks and the west corner of the JILF near Mercury Burial Site II. Petroleum hydrocarbon fingerprinting was conducted at 8 locations during the Phase IV investigation. Monitoring wells JW-07B, JW-12S, and JW13D indicated nondetects. No. 5 fuel oil (1.9 mg/l) was present at JW-14; No. 4 fuel oil existed at JW-15 and JW-16 (8.2 mg/l and 5.3 mg/l respectively); No. 6 fuel oil was also present at JW16 (14.0 mg/l); lube oil (1.2 mg/l) and compressor oil (1.8 mg/l) were present at JW-18; and gasoline (6.3 mg/l) occurred at JW-19.

In terms of extent of contamination, contaminants within the entire JILF, as well as nearby areas upgradient and side-gradient of the JILF, have exceeded the residential MPSs.

Mercury Burial Sites (Site 9)

Elevated groundwater concentrations of metals have been detected. For the most part, metals were detected in the unfiltered groundwater samples, indicating that the metals were in the particulate (or colloidal), rather than the dissolved, form. Additionally, volatile organics and semi-volatile organics sporadically detected in wells located near Mercury Burial Site II are associated with petroleum. Additional investigation of groundwater in this area during the RFI Data Gap Investigation did not indicate the presence of an organics plume.

No MPS was developed for mercury in groundwater. However, the maximum detection of total mercury was 1.5 ug/l at MW-02 (MBII), with a corresponding nondetect concentration for the filtered sample. This maximum concentration is below the final Maximum Contaminant Level (MCL) for mercury of 2 ug/l and the State of Maine Maximum Exposure Guideline (MEG) also of 2 ug/l. Petroleum hydrocarbon fingerprinting results identified gasoline (49.4 mg/l) and lube oil (1.0 mg/l) in MW-3 and No. 4 fuel oil (1.1 mg/l) and No. 6 fuel oil (4.1 mg/l) in MW-7, which is consistent with the volatile and semivolatile compounds detected in the wells.

- Mercury Burial Site I (MBI): Primary MPS exceedences in all 3 wells were comprised of numerous inorganics. Inorganics were primarily present in the unfiltered form. Only single exceedences of benzo(a)anthracene, chrysene, benzene, and methylene chloride occurred and were of low concentrations.

- Mercury Burial Site II (MBII): Primary exceedences in all 3 wells were comprised of numerous inorganics (up to several orders of magnitude exceedences of residential MPSs). Inorganics were primarily present in the unfiltered form. Benzene, pesticides (4,4'-DDD and 4,4'-DDE), PCBs, polycyclic aromatic hydrocarbons (PAHs), and BEHP were also present.

In summary, contamination is primarily attributed to JILF rather than the Mercury Burial Sites. No releases to date have occurred from the buried concrete blocks and the concrete pipe that were found at MBI. The concrete pipe, perceived to have lesser structural integrity than the concrete blocks, was removed during the RFI Data Gap Investigation (Halliburton NUS, 1995a). Although the soil sampling in the vicinity of MBI and MBII did not indicate mercury contamination, inorganic and organic contamination indicative of contamination found at the JILF was noted.

Former Waste Oil Tanks (Site 11)

Manganese exceedences in groundwater occurred consistently. Other inorganics (cadmium, lead, and aluminum) were sporadically present at concentrations above MPSs. Of note, the maximum detection of manganese occurred upgradient of the former waste oil tanks. Benzene was present in groundwater at location JW-16. TICs were present predominantly in monitoring wells WOT-02, WOT-03, WOT-04, and WOT-05. Although total diesel (dissolved), using EPA Method 8100 Modified, was detected in groundwater at significant concentrations, measurable free product was not encountered in the six permanent monitoring wells installed as part of the RFI Data Gap investigation. However, results of a supporting direct drive point investigation, to set the locations for the six permanent monitoring wells, indicated the presence of free product at WOT-DP-10. The WOT-DP-10 location is located near monitoring well JW-16 installed during the RFI. The RFI Report indicated the presence of a sheen during development/purging at this well, which is located closest to the former waste oil tanks. However, no measurable free product layer was encountered at either the overburden well JW-16 or the bedrock well JW-16B. It is unlikely that free product would be observed in monitoring well JW-16B because the top of the well screen is approximately 10 feet below the water table. The top of the well screen for JW-16 is at an elevation of 101.7', the approximate elevation of the water table is 101.4'. If free product is present in the area this well should intercept it.

The extent of groundwater contamination, except for potential upgradient contributions, has been defined. Note that PAH contamination in groundwater is limited to WOT-02 and WOT-03, with no exceedences of

groundwater MPSs for PAHs at these locations. This indicates that PAHs are adsorbing to soils and not significantly impacting groundwater.

Berth 6 Industrial Area (Site 27)

There were isolated exceedences of groundwater MPSs for numerous metals including arsenic, aluminum, cadmium, chromium, lead, manganese, copper, and beryllium. Inorganics were primarily detected in the particulate, or possibly colloidal, form. It is uncertain whether these constituents are site related since soils did not exceed MPSs for any metals. Also, the maximum concentrations of metals were consistently located in monitoring wells FW-05 and FW-06 which are cross-gradient of the site. Petroleum hydrocarbon fingerprinting (conducted for FW-06 only) indicated the presence of No. 4 fuel oil (4.8 mg/l) and lube oil (2.9 mg/l). In support of the fingerprinting, semivolatile TICs were encountered in FW-06. Free product, at a thickness not specified, was observed in monitoring wells FW-02 and FW-06. TPH analysis was performed for samples in wells FW-04 (non detect) and FW-06 (5.0 mg/l).

The source of the contamination was not identified but is not believed to be solely from the Fuel Oil Spillage Area fuel spill. Lateral and vertical extent of TPH groundwater contamination was not delineated during RFI but was further refined during the Oil Terminal Investigation by Stearns & Wheler. Plans for further investigation is underway to determine the source of metals contamination.

Non-Site Related Areas

Included with the non-site related monitoring wells are those wells installed solely in support of the hydrogeology investigation, as presented in the RFI Data Gap Report. Analytes exceeding the residential MPSs for groundwater consisted of metals (aluminum, beryllium, lead, and manganese). Diesel fuel was present in the Seavey's Island wells at concentrations of potential concern (5.0 mg/l at SI-1B and 0.930J at SI-1DB).

3.4.2 Available Groundwater Level Data

Groundwater elevations were measured for all RFI wells and RFI Data Gap wells on July 26th, 1994, at low tide and high tide. For each well, Table 3-3 lists the well number, reference point elevation (top of inner casing), depth to water, calculated groundwater elevation, and time of measurement. Monitoring well locations are provided in Map A. Measurements were collected within a 2-hour interval and in the same order during low tide in the morning and high tide in the afternoon.

TABLE 3-3

GROUNDWATER-LEVEL ELEVATIONS
RFI DATA GAP INVESTIGATION
PNS, KITTERY, MAINE

Date: 7-26-94		Low Tide			High Tide			Tidal Range (Ft.)[a]	Salinity[c]
Well No.	Ref. PT. Elev. (Ft.)[b]	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time		
GW-1	119.48	10.18	109.30	0817	10.16	109.32	1436		F
MW-2	118.15	14.92	103.23	0807	14.71	103.44	1428	0	F
MW-3	116.14	13.51	102.63	0815	13.45	102.69	1432	NT	F/B
MW-4	113.08	14.44	98.64	0805	14.60	98.48	1426	0.8	F/B
MW-5	113.45	15.02	98.43	0807	15.05	98.40	1428	NT	F/B
MW-6	116.17	13.27	102.90	0813	13.23	102.94	1429	NT	F/B
MW-7	113.86	15.39	98.47	0806	15.58	98.28	1430	NT	B
SI-01B*	119.70	26.65[d]	93.05[d]	0926	26.17[d]	93.53[d]	1531	0	F
SI-01DB*	119.95	73.92[d]	46.03[d]	0928	72.28[d]	47.67[d]	1536	0	F
DI-01B*	113.88	13.78	100.10	0937	13.75	100.13	1545	0	F
DI-01DB*	114.89	14.80	100.09	0936	14.74	100.15	1547	0	F
FA-01*	109.13	10.34	98.79	0945	10.30	98.83	1603	0.5	S
FA-01B*	108.80	11.03	97.77	0947	8.88	99.92	1605	2.1	B
FA-01DB*	108.72	11.50	97.22	0943	10.19	98.53	1600	0.9	S
DW-1	111.44	13.79	97.65	0953	10.25	101.19	1513	4.1	B/S
DW-1B	111.36	15.23	96.13	0951	10.33	101.03	1510	5.7	B
DW-2B	111.77	19.32	92.45	0934	10.62	101.15	1507	10.3	S
DW-3	110.69	17.13	93.56	1003	8.68	102.01	1524	10.3	S

TABLE 3-3 (Continued)
GROUNDWATER-LEVEL ELEVATIONS
RFI DATA GAP INVESTIGATION
PNS, KITTERY, MAINE

Date: 7-26-94		Low Tide			High Tide			Tidal Range (Ft.)[a]	Salinity[a]
Well No.	Ref. PT. Elev. (Ft.)[b]	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time		
DW-4	109.69	12.19	97.50	0947	8.68	101.01	1512	4.4	B
DW-5	111.14	11.33	99.81	0954	10.16	100.98	1518	2.3	F/B
DW-6	112.06	10.36	101.70	0920	10.10	101.96	1522	9.0	S
DW-7	111.52	18.94	92.58	0931	9.95	101.57	1503	10.5	B/S
DW-7B	112.33	18.92	93.41	0929	11.45	100.88	1459	8.7	B
DW-7DB*	111.89	18.61	93.28	0925	11.95	99.94	1501	5.8	B
DW-8	109.86	15.99	93.87	1009	8.92	100.94	1532	9.1	B
DW-8B	109.03	15.80	93.23	1010	7.74	101.29	1530	9.7	B
DW-9	110.14	15.95	94.19	1010	9.37	100.77	1527	8.6	B/S
DW-10B	112.83	15.37	97.46	1007	11.82	101.01	1525	4.6	B/S
JW-3	110.09	7.94	102.15	0818	7.99	102.10	1448	0	F
JW-4	108.60	7.57	101.03	0847	7.67	100.93	1509	0	F
JW-5	106.74	7.18	99.56	0851	5.60	101.14	1508	1.5	B
JW-6	107.78	7.24	100.54	0842	7.27	100.51	1450	0	F
JW-7	108.94	7.10	101.84	0834	7.08	101.86	1453	0	F/B
JW-7B	108.87	7.03	101.84	0835	7.03	101.84	1455	0	F/B
JW-8	112.73	9.60	103.13	0824	9.65	103.08	1446	0	F
JW-8B	114.00	11.20	102.80	0825	11.25	102.75	1447	0	F
JW-9	106.42	6.95	99.47	0805	7.06	99.36	1424	1.6	B/S

TABLE 3-3 (Continued)
GROUNDWATER-LEVEL ELEVATIONS
RFI DATA GAP INVESTIGATION
PNS, KITTERY, MAINE

Date: 7-26-94		Low Tide			High Tide			Tidal Range (Ft.)[a]	Salinity[a]
Well No.	Ref. PT. Elev. (Ft.)[b]	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time		
JW-9B	106.88	7.33	99.55	0804	7.42	99.46	1422	1.5	F/B
JW-10	108.40	11.88	96.52	0905	7.69	100.71	1451	5.5	S
JW-12S	108.67	13.68	94.99	0845	7.45	101.22	1503	7.1	S
JW-12D	108.24	16.52	91.72	0850	6.87	101.37	1458	10.3	S
JW-12B	108.42	16.84	91.58	0855	6.83	101.59	1501	10.1	B
JW-13S	111.38	14.57	96.81	0835	10.07	101.31	1433	4.2	S
JW-13D	110.79	18.11	92.68	0840	9.84	100.95	1435	9.1	S
JW-13B	110.24	16.52	93.72	0830	9.46	100.78	1438	4.1	B
JW-13DB*	110.54	23.14[d]	87.40[d]	0825	24.75[d]	85.79[d]	1442	0	B
JW-14	111.13	9.93	101.20	0803	9.86	101.27	1420	0	B
JW-14B	111.00	11.18	99.82	0801	10.84	100.16	1422	1.3	B
JW-15	107.34	10.17	97.17	0835	6.46	100.88	1445	4.5	S
JW-15B	107.29	11.04	96.25	0833	6.85	100.44	1441	6.3	S
JW-16	106.50	5.11	101.39	0813	5.08	101.42	1433	NT	
JW-16B	106.57	5.04	101.53	0812	5.03	101.54	1430	NT	FB
JW-17B	107.66	6.78	100.88	0845	6.70	100.96	1453	0.4	B
JW-18	108.31	8.44	99.87	0830	8.41	99.90	1451	0	B
JW-19	114.14	13.48	100.66	0823	13.47	100.67	1443	0	B
JW-19B	114.64	14.42	100.22	0822	14.80	99.84	1442	NT	B

TABLE 3-3 (Continued)
GROUNDWATER-LEVEL ELEVATIONS
RFI DATA GAP INVESTIGATION
PNS, KITTERY, MAINE

Date: 7-26-94		Low Tide			High Tide			Tidal Range (Ft.)[c]	Salinity[d]
Well No.	Ref. PT. Elev. (Ft.)[b]	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time	Depth to Water (Ft.)	Groundwater Elev. (Ft.)	Time		
WOT-1*	108.33	6.55	101.78	0841	6.63	101.70	1503	0	F
WOT-2*	106.07	4.20	101.87	0821	4.19	101.88	1434	0	F
WOT-3*	106.34	5.02	101.32	0818	5.02	101.32	1437	0	F
WOT-4*	105.24	3.66	101.58	0800	3.74	101.50	1430	0	F
WOT-5*	107.60	6.21	101.39	0826	6.22	101.38	1439	0	F
WOT-6*	108.46	6.17	102.29	0843	6.28	102.18	1506	0	F
FW-1	105.77	8.33	97.44	0950	5.32	100.45	1540	NT	B/S
FW-2	104.59	10.32	94.27	0952	3.73	100.86	1545	NT	S
FW-3	104.21	10.51	93.70	0955	3.43	100.78	1549	NT	S
FW-4	105.41	11.84	93.57	1000	4.66	100.75	1552	NT	S
FW-5	104.82	10.80	94.02	1004	4.21	100.61	1555	NT	S
FW-6	104.78	12.21	92.57	0920	3.67	101.11	1525	7.0	S
TG-1	106.60	14.58	92.02	0858	5.26	101.34	1509	8.06	S
TG-2	105.15	12.88	92.27	0930	4.22	100.93	1520	7.2	S
SG-1	118.43	3.20	115.23	0921	3.21	115.22	1526	NT	S
SG-2	119.09	2.50	116.59	0916	2.54	116.55	1520	NT	S

TABLE 3-3 (Continued)
GROUNDWATER-LEVEL ELEVATIONS
RFI DATA GAP INVESTIGATION
PNS, KITTERY, MAINE

NOTE:

- * Denotes RFI Data Gap installed well June, July 1994 (15 total).
- ** Wells not completely recovered.
- *** Elevation 100.00' = Mean High Tide, Portsmouth Naval Shipyard System is equal to 3.804' USGS System.
- **** Tidal range data taken from RFI Data Gap Report, 1995.
- ***** Salinity Identifiers - F = Fresh; B = Brackish; S = Seawater; NT = Not Tested

4.0 SAMPLING AND ANALYSIS

4.1 SELECTION OF MONITORING WELLS FOR SAMPLING AND ANALYSIS

4.1.1 Groundwater Monitoring - First Two Events Re-Sampling

Re-sampling will be conducted at all 55 existing monitoring wells installed as part of the RFI and 15 monitoring wells installed during the RFI Data Gap investigation. Additionally, monitoring is included for MW-10-BW from the Stearns & Wheler investigation of the tank farm; this well is upgradient of the DRMO Salvage Yard. Two rounds of sampling are initially planned. Future sampling events, as required, will build on the existing database and be used in migration modeling efforts. Analysis primarily consists of TCL organics and SW inorganics which is consistent with the analytical methods used for the RFI and RFI Data Gap investigations. Freon will be quantitated by the laboratory, and included with the TCL volatiles analysis. Qualitative information on TICs will be provided with the TCL analytical package in accordance with EPA Region I guidance. Also indicator parameters will be analyzed; however replicate sampling will not be conducted, since sampling/analysis includes TCL organics and SW inorganics, resulting in less reliance on indicator parameters. Gasoline range and diesel range petroleum hydrocarbons will also be analyzed, where appropriate.

In addition to the groundwater sampling, two surface water samples will be collected from the Piscataqua River and analyzed for SW metals, chloride, sulfate and alkalinity during each of the proposed sampling events. These surface water samples will aid in assessing the dilution effects within the tidal portions of the aquifer. Given the fact the Piscataqua River is part of a tidal estuary, ionic concentrations in the surface water should change based on the tidal stage due to the relative mixing of fresh and salt water.

Analytes for the first two events of groundwater monitoring were established based on an evaluation of the complete database for the PNS facility (Halliburton NUS, 1995b). Rationale for inclusion/ omission of analytes at the DRMO, JILF/Mercury Burial Sites, Former Waste Oil Storage Tanks, Fuel Oil Spillage Area and non-site related monitoring wells is provided in Tables 4-1 through 4-5. Table 4-6 provides analytical methods, containers, preservation, and holding times for each parameter. Tables 4-7 and 4-8 present the anticipated number of samples, with and without QA/QC samples, for the first and second sampling event. Table 4-6 also presents the Navy Installation Restoration Laboratory Quality Assurance Guide (NFESC, 1996) levels of QC to be utilized. Level D quality assurance/quality control (QA/QC) will be applied for the TCL organics and SW inorganics analysis. Level C QA/QC will be applied for water quality parameters (i.e.,

TABLE 4-1

RATIONALE FOR SELECTION OF ANALYTES - DRMO SALVAGE YARD GROUNDWATER MONITORING PNS, KITTERY, MAINE

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
TCL Volatiles plus Freon	CLP OLM03.1	No	No exceedences of on-shore MPSs occurred for groundwater. On-shore MPSs were not included for soils. Concentrations of volatiles in soils and in groundwater were sporadic and present at low concentrations compared to regulatory standards.
TCL Semi-volatiles	CLP OLM03.1	No	Base/neutral semivolatiles and phenols (total) are included elsewhere as separate analyses. Note that there were no detections of acid extractables [i.e., phenols] in site groundwater (on-shore MPSs were not included for acid extractables).
TCL Base/Neutral Semi-volatiles	CLP OLM03.1	Yes	There was one exceedence of the on-shore MPS for BEHP in groundwater near the Old Incinerator Area east of the DRMO. For soils, there were on-shore MPS exceedences for PAHs and one surface soil on-shore MPS exceedence for BEHP.
TCL Pesticides/PCBs	CLP OLM03.1	Yes	There were exceedences of on-shore MPSs for both PCBs and pesticides in groundwater. There was one exceedence of the groundwater on-shore MPS for pesticides at monitoring well DW-06 located just outside the DRMO boundaries. Both pesticides and PCBs exceeded on-shore MPSs for soils.
SW Inorganics (Total)	SW3010/6010	Yes	Exceedences of on-shore MPSs occurred for both groundwater and soils. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
SW Inorganics (Filtered)	SW3010/6010	Yes	Exceedences of on-shore MPSs occurred. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
Cyanide	SW3010/6010	No	Cyanide was not detected in either groundwater or soils.
TPH (Gasoline Range)	Modified SW846/8015	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils. Baseline conditions monitoring results may indicate that TPH is present solely in the diesel range, in which case TPH (Gasoline Range) could be omitted from analysis in the future.
TPH (Diesel Range)	Modified SW846/8100	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils.
Total Organic Carbon (TOC)	EPA 415.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Total Organic Halogen (TOX)	SW9020	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Chloride	EPA 325.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.

TABLE 4-1
RATIONALE FOR SELECTION OF ANALYTES - DRMO SALVAGE YARD
GROUNDWATER MONITORING
PNS, KITTERY, MAINE
PAGE 2

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
Nitrate	EPA 352.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Bromide	EPA 320.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Sulfate	EPA 375.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
pH	EPA 150.1	Yes	Include with baseline conditions monitoring and future monitoring to obtain general water quality information. Both field and laboratory analysis to be conducted.
Iron, Manganese, Sodium	EPA 200.7	No	Included with TAL inorganics analysis.
Phenols	EPA 420.2	Yes	On-shore MPSs for phenols in soils or groundwater were not included. However, include this analysis with baseline conditions monitoring to obtain general water quality information. Detections of phenols occurred in soil near the Old Incinerator Area east of the DRMO. Baseline conditions monitoring results may warrant omitting phenols from analysis in the future or including at select monitoring well locations.
Alkalinity	EPA 310.1	Yes	Include with baseline conditions monitoring to obtain general water quality information in support of potential groundwater treatment system design.
Salinity	---	Yes	Include as a field measurement only. There was good correlation between field and laboratory measurements from previous investigations.
Specific Conductance	---	Yes	Include as a field measurement only.
Oxidation Reduction Potential	---	Yes	Include as a field measurement only.

BEHP - Bis(2-ethylhexyl)phthalate
CLP - Contract Laboratory Procedure
MPS - Media Protection Standard
PAH - Polycyclic Aromatic Hydrocarbons
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons
TPH analyses is being conducted at the request of Maine Department of Environmental Protection.

TABLE 4-2

RATIONALE FOR SELECTION OF ANALYTES - JAMAICA ISLAND LANDFILL AND MERCURY BURIAL SITES GROUNDWATER MONITORING PNS, KITTERY, MAINE

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
TCL Volatiles plus Freon	CLP OLM03.1	Yes	Exceedences of on-shore MPSs occurred for groundwater. Both chlorinated and nonchlorinated volatiles are present. Known solvent disposal at landfill warrants continued monitoring in the future. On-shore MPSs were not included for soils.
TCL Semi-volatiles	CLP OLM03.1	No	Base/neutral semivolatiles and phenols (total) are included elsewhere as separate analyses. Note that on-shore MPSs for acid extractables (i.e., phenols) in groundwater were not included.
TCL Base/Neutral Semi-volatiles	CLP OLM03.1	Yes	There were exceedences of on-shore MPSs for both PAHs and BEHP in groundwater. PAH exceedences of on-shore MPSs also occurred for site soils.
TCL Pesticides/PCBs	CLP OLM03.1	Yes	There were exceedences of on-shore MPSs for both PCBs and pesticides in groundwater. PCB exceedences of on-shore MPSs also occurred for site soils.
SW Inorganics (Total)	SW3010/6010	Yes	Exceedences of on-shore MPSs occurred for both groundwater and soils. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
SW Inorganics (Filtered)	SW3010/6010	Yes	Exceedences of on-shore MPSs occurred. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
Cyanide	SW3010/6010	No	There were sporadic detections of cyanide. No on-shore MPS was developed for cyanide. Cyanide was detected at low concentrations compared to regulatory standards.
TPH (Gasoline Range)	Modified SW846/8015	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils. Baseline conditions monitoring results may indicate that TPH in the gasoline range is present only at select monitoring well locations.
TPH (Diesel Range)	Modified SW846/8100	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils.
Total Organic Carbon (TOC)	EPA 415.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Total Organic Halogen (TOX)	SW9020	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Chloride	EPA 325.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Sulfate	EPA 375.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Nitrate	EPA 352.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
chloride		Yes	

TABLE 4-2
RATIONALE FOR SELECTION OF ANALYTES - JAMAICA ISLAND LANDFILL AND MERCURY BURIAL SITES GROUNDWATER MONITORING PNS, KITTERY, MAINE PAGE 2

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
Bromide	EPA 320.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
pH	EPA 150.1	Yes	Include with baseline conditions monitoring and future monitoring to obtain general water quality information. Both field and laboratory analysis to be conducted.
Iron, Manganese, Sodium	EPA 200.7	No	Included with TAL inorganics analysis.
Phenols	EPA 420.2	Yes	On-shore MPSs for phenols in soils or groundwater were not included. However, include this analysis with baseline conditions monitoring. Baseline conditions monitoring results may warrant omitting phenols from analysis in the future or including at select monitoring well locations.
Alkalinity	EPA 310.1	Yes	Include with baseline conditions monitoring to obtain general water quality information in support of potential groundwater treatment system design.
Salinity	---	Yes	Include as a field measurement only. There was good correlation between field and laboratory measurements from previous investigations.
Specific Conductance	---	Yes	Include as a field measurement only.
Oxidation Reduction Potential	---	Yes	Include as a field measurement only.

BEHP - Bis(2-ethylhexyl)phthalate
CLP - Contract Laboratory Procedure
MPS - Media Protection Standard
PAH - Polycyclic Aromatic Hydrocarbons
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons
TPH analyses is being conducted at the request of Maine Department of Environmental Protection.

TABLE 4-3

RATIONALE FOR SELECTION OF ANALYTES - FORMER WASTE OIL STORAGE TANKS GROUNDWATER MONITORING PNS, KITTERY, MAINE

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
TCL Volatiles plus Freon	CLP OLM03.1	Yes	Exceedences of on-shore MPSs occurred for groundwater. Both chlorinated (including Freon) and nonchlorinated volatile organics were detected although generally sporadic and at low concentrations compared to regulatory standards. Elevated concentrations of 2-butanone also occurred. On-shore MPSs were not included for soils.
TCL Semi-volatiles	CLP OLM03.1	Yes	Although no on-shore MPSs were exceeded for groundwater, base/neutral semivolatiles exceedences of PAHs occurred for SWMU soils. No on-shore MPSs were included for acid extractables; however, phenols were consistently present. Include acid extractables with baseline conditions sampling although acid extractables may be omitted from analysis in the future or included at select monitoring well locations.
TCL Base/Neutral Semi-volatiles	CLP OLM03.1	No	Included with TCL Semi-volatiles analysis.
TCL Pesticides/PCBs	CLP OLM03.1	No	Pesticides or PCBs were not detected in site groundwater. Although detected in soils, pesticides and PCBs did not exceed on-shore MPSs for soils.
SW Inorganics (Total)	SW3010/6010	Yes	Exceedences of on-shore MPSs. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
SW Inorganics (Filtered)	SW3010/6010	Yes	Exceedences of on-shore MPSs. Complete inorganics analysis also supports groundwater treatment system design that may be implemented (Refer to the Feasibility Study Report [Halliburton NUS 1995b]).
Cyanide	SW3010/6010	No	An MPS was not included for cyanide. Cyanide was detected sporadically in groundwater at low concentrations.
TPH (Gasoline Range)	Modified SW846/8015	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater. Baseline conditions monitoring results may indicate that TPH is present in the gasoline range only at select monitoring wells.
TPH (Diesel Range)	Modified SW846/8100	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater.
Total Organic Carbon (TOC)	EPA 415.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Total Organic Halogen (TOX)	SW9020	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Chloride	EPA 325.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.

TABLE 4-3
RATIONALE FOR SELECTION OF ANALYTES - FORMER WASTE OIL STORAGE TANKS
GROUNDWATER MONITORING
PNS, KITTERY, MAINE
PAGE 2

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
Nitrate	EPA 352.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Bromide	EPA 320.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Sulfate	EPA 375.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
pH	EPA 150.1	Yes	Include with baseline conditions monitoring and future monitoring to obtain general water quality information. Both field and laboratory analysis to be conducted.
Iron, Manganese, Sodium	EPA 200.7	No	Included with TAL inorganics analysis.
Alkalinity	EPA 310.1	Yes	Include with baseline conditions monitoring to obtain general water quality information in support of potential groundwater treatment system design.
BOD_5	EPA 405.1	Yes	Include with baseline conditions monitoring to obtain general water quality information in support of potential groundwater treatment system design.
Phenols	EPA 420.2	Yes	Phenols were consistently detected at this site.
Salinity	---	Yes	Include as a field measurement only. There was good correlation between field and laboratory measurements from previous investigations.
Specific Conductance	---	Yes	Include as a field measurement only.
Oxidation Reduction Potential	---	Yes	Include as a field measurement only.

BOD_5 - Biochemical Oxygen Demand (5 day)
CLP - Contract Laboratory Procedure
MPS - Media Protection Standard
PAH - Polycyclic Aromatic Hydrocarbons
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons
TPH analyses is being conducted at the request of Maine Department of Environmental Protection.

TABLE 4-4

RATIONALE FOR SELECTION OF ANALYTES - BERTH 6 INDUSTRIAL AREA GROUNDWATER MONITORING PNS, KITTERY, MAINE

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
TCL Volatiles plus Freon	CLP OLM03.1	No	No exceedences of on-shore MPSs occurred for groundwater and on-shore MPSs were not included for soils. Concentrations of volatiles in soils and in groundwater were sporadic and present at low concentration.
TCL Semi-volatiles	CLP OLM03.1	No	There were no exceedences of semi-volatiles in groundwater. MPSs were not included for acid extractables (i.e., phenols) and acid extractables were not detected in either soils or groundwater. Base/neutral semi-volatile detections, BEHP and PAHs, were sporadic; there was one slight exceedence of one PAH (benzo(a)anthracene) for soils.
TCL Base/Neutral Semi-volatiles	CLP OLM03.1	No	Refer to the comment for TCL Semi-volatiles.
TCL Pesticides/PCBs	CLP OLM03.1	No	There were no detections of PCBs or pesticides in either soils or groundwater.
SW Inorganics (Total)	SW3010/6010	Yes	Exceedences of on-shore MPSs for groundwater occurred but no exceedences occurred for soils.
SW Inorganics (Filtered)	SW3010/6010	Yes	Exceedences of on-shore MPSs for groundwater occurred.
Cyanide	SW3010/6010	No	Cyanide was not detected in either groundwater or soils.
TPH (Gasoline Range)	Modified SW846/8015	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils. Baseline conditions monitoring results may indicate that TPH is present solely in the diesel range, in which case TPH (Gasoline Range) could be omitted from analysis in the future.
TPH (Diesel Range)	Modified SW846/8100	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater and soils.
Total Organic Carbon (TOC)	EPA 415.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Total Organic Halogen (TOX)	SW9020	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Chloride	EPA 325.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Sulfate	EPA 375.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
pH	EPA 150.1	Yes	Include with baseline conditions monitoring and future monitoring to obtain general water quality information. Both field and laboratory analysis to be conducted.
Iron, Manganese, Sodium	EPA 200.7	No	Included with TAL inorganics analysis.

TABLE 4-4
RATIONALE FOR SELECTION OF ANALYTES - BERTH 6 INDUSTRIAL AREA
GROUNDWATER MONITORING
PNS, KITTERY, MAINE
PAGE 2

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
Nitrate	EPA 352.1	Yes	Include with baseline conditions monitoring to obtain general water quality information.
Bromide	EPA 320.1	Yes	Include with baseline conditions monitoring to obtain general water quality information.
Alkalinity	EPA 310.1	Yes	Include with baseline conditions monitoring to obtain general water quality information.
Phenols	EPA 420.2	No	Phenols were not detected in either soils or groundwater.
Salinity	—	Yes	Include as a field measurement only. There was good correlation between field and laboratory measurements from previous investigations.
Specific Conductance	—	Yes	Include as a field measurement only.
Oxidation Reduction Potential	—	Yes	Include as a field measurement only.

BEHP - Bis(2-ethylhexyl)phthalate
CLP - Contract Laboratory Procedure
MPS - Media Protection Standard
PAH - Polycyclic Aromatic Hydrocarbons
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons
TPH analyses is being conducted at the request of Maine Department of Environmental Protection.

TABLE 4-5

RATIONALE FOR SELECTION OF ANALYTES - NON-SITE MONITORING WELLS
GROUNDWATER MONITORING
PNS, KITTERY, MAINE

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
TCL Volatiles plus Freon	CLP OLM03.1	No	No exceedences of on-shore MPSs occurred for groundwater. On-shore MPSs were not included for soils. There was one occurrence of a volatile organic (toluene at DI-01DB) at low concentration compared to regulatory standards.
TCL Semi-volatiles	CLP OLM03.1	No	Base/neutral semivolatiles were detected in one instance (BEHP at FA-01DB) at a concentration less than the on-shore MPS for groundwater. Acid extractables (i.e., phenols) were not detected in groundwater.
TCL Base/Neutral Semi-volatiles	CLP OLM03.1	No	Refer to the comment for TCL Semi-volatiles.
TCL Pesticides/PCBs	CLP OLM03.1	Yes	PCBs and pesticides were not analyzed for in previous investigations. The presence of TPH contamination warrants analysis for pesticides/PCBs. Include with baseline conditions sampling although may be omitted from analysis in the future or included at select monitoring well locations.
SW Inorganics (Total)	SW3010/6010	Yes	Exceedences of On-shore MPSs for both groundwater and soils.
SW Inorganics (Filtered)	SW3010/6010	Yes	Exceedences of On-shore MPSs for both groundwater and soils.
Cyanide	SW3010/6010	Yes	Cyanide was not analyzed for in previous investigations. Only include with unfiltered (total) inorganic analysis.
TPH (Gasoline Range)	Modified SW846/8015	No	No MPS developed. However, TPH (Gasoline Range) was analyzed at each non-site monitoring location during the RFI Data Gap investigation and found to be nondetect.
TPH (Diesel Range)	Modified SW846/8100	Yes	No MPS developed. However, TPH is present at significant concentrations in groundwater at locations DI-01DB, SI-1B, and SI-1DB.
Total Organic Carbon (TOC)	EPA 415.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Total Organic Halogen (TOX)	SW9020	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Chloride	EPA 325.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Sulfate	EPA 375.3	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
pH	EPA 150.1	Yes	Include with baseline conditions monitoring and future monitoring to obtain general water quality information. Both field and laboratory analysis to be conducted.
Iron, Manganese, Sodium	EPA 200.7	No	Included with TAL inorganics analysis.

TABLE 4-5
RATIONALE FOR SELECTION OF ANALYTES - NON-SITE MONITORING WELLS
GROUNDWATER MONITORING
PNS, KITTERY, MAINE
PAGE 2

ANALYSIS	ANALYTICAL METHOD	YES/NO	RATIONALE FOR INCLUSION OR OMISSION
Alkalinity	EPA 310.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Nitrate	EPA 352.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Bromide	EPA 320.1	Yes	Include with baseline conditions monitoring results to obtain general water quality information.
Phenols	EPA 420.2	No	Phenols were not detected in groundwater.
Salinity	—	Yes	Include as a field measurement only. There was good correlation between field and laboratory measurements from previous investigations.
Specific Conductance	—	Yes	Include as a field measurement only.
Oxidation Reduction Potential	—	Yes	Include as a field measurement only.

BEHP - Bis(2-ethylhexyl)phthalate
CLP - Contract Laboratory Procedure
MPS - Media Protection Standard
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons
TPH analyses is being conducted at the request of Maine Department of Environmental Protection.

TABLE 4-6

SAMPLE CONTAINERS, PRESERVATION METHODS, AND HOLDING TIMES
PNS, KITTERY, MAINE

Method	Parameter	Container Material	Sample Volume	Preservation	Holding Time (a)	Data Quality Objective (DQO) Level
GROUNDWATER						
CLP OLM03.1	TCL Volatiles + Freon	Glass, Teflon-lined septa	(2) 40 ml	4 C; 4 drops HCl, pH < 2	14 days	D
CLP OLM03.1	TCL Semi-volatiles	Glass, Teflon-lined septum	2,500 ml	Cool, 4 C	Extract 7 days; Analyze 40 days	D
CLP OLM03.1	Pesticides/PCBs	Glass, Teflon-lined septum	2,500 ml	Cool, 4 C	Extract 7 days; Analyze 40 days	D
CLP ILM03.0	TAL Metals (Total)	Plastic, glass	1 liter	4 C; HNO_3 to pH < 2	6 months Hg- 28 days	D
CLP ILM03.0	TAL Metals (Dissolved)	Plastic, glass	1 liter	4 C; HNO_3 to pH < 2	6 months Hg- 28 days	D
CLP ILM03.0	Cyanide (Total)	Plastic	1 liter	4 C NaOH to pH>12	14 days	D
EPA 415.1 SW 9020	Total Organic Carbon (TOC) Total Organic Halogen (TOX)	Polyethylene	500 ml	H_2SO_4 to pH<2	28 days	C
EPA 320.1 EPA 325.3 EPA 375.3 EPA 150.1 EPA 310.1	Bromide Chloride Sulfate pH Alkalinity	Polyethylene	1 liter	Cool, 4 C	28 days (Bromide, Chloride, Sulfate, pH) 14 days (Alkalinity)	C
EPA 200.7	Iron Manganese Sodium	Polyethylene	1 liter	HNO_3 to pH<2 Cool, 4 C	6 months	C
EPA 420.1	Phenols	Amber glass	1 liter	H_2SO_4 to pH<2 Cool, 4C	28 days	C

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TABLE 4-6
SAMPLE CONTAINERS, PRESERVATION METHODS, AND HOLDING TIMES
PNS, KITTERY, MAINE
PAGE 2

Method	Parameter	Container Material	Sample Volume	Preservation	Holding Time (a)	Data Quality Objective (DQO) Level
Modified SW846/8015	TPH (Gasoline Range)	Glass	(3) 40 ml	4 C; HCl to pH<2	14 days	C
EPA/352.1	Nitrate	Polyethylene	500 ml	Cool to 4 C	48 hours	C
Modified SW846/8100	TPH (Diesel Range)	Glass	1 liter	Cool, 4 C	Extract 14 days Analyze 40 days	C
EPA 405.1	BOD_5	Polyethylene	300 ml	Cool, 4 C	6 hours	C

(a) Holding times are measured from time of collection.

Notes:
1) Additionally Oxidation Reduction Potential (ORP), pH, specific conductance, temperature, dissolved oxygen (DO), salinity and eH will be measured in the field.
2) For the determination of dissolved metals the sample is field filtered to 0.45 μ before acidification according to Section 5.2.5 of SOP-SF-1.2 attached in Appendix B.

TABLE 4-7

SUMMARY OF GROUNDWATER MONITORING ANALYSIS BY SITE (EXCLUDING QA/QC SAMPLES) FIRST AND SECOND EVENT GROUNDWATER SAMPLING PNS, KITTERY, MAINE

ANALYSIS[a,b,c]	DRMO SALVAGE YARD	JAMAICA ISLAND LANDFILL/MERCURY BURIAL SITES	FORMER WASTE OIL STORAGE TANKS	BERTH 6 INDUSTRIAL AREA	NON-SITE RELATED WELLS	TOTAL NUMBER OF SAMPLES
TCL Volatiles plus Freon	0	36	6	0	0	42
TCL Semi-volatiles	0	0	6	0	0	6
TCL Base/Neutral Semi-volatiles	16	36	0	0	0	52
TCL Pesticides/PCBs	16	36	0	0	7	59
SW Inorganics (Total)	16	36	6	6	7	71
SW Inorganics (Filtered)	3	4	1	1	1	10
Cyanide	0	0	0	0	7	7
TPH (Gasoline Range)	16	36	6	6	0	64
TPH (Diesel Range)	16	36	6	6	7	71
Total Organic Carbon (TOC)	16	36	6	6	7	71
Total Organic Halogen (TOX)	16	36	6	6	7	71
Chloride	16	36	6	6	7	71
Sulfate	16	36	6	6	7	71
pH	16	36	6	6	7	71
Iron, Manganese, Sodium	0	0	0	0	0	0
Phenols	16	36	6	0	0	58

TABLE 4-7
SUMMARY OF GROUNDWATER MONITORING ANALYSIS BY SITE (EXCLUDING QA/QC SAMPLES)
FIRST AND SECOND EVENT GROUNDWATER SAMPLING
PNS, KITTERY, MAINE
PAGE 2

ANALYSIS[a,b]	DRMO SALVAGE YARD	JAMAICA ISLAND LANDFILL/MERCURY BURIAL SITES	FORMER WASTE OIL STORAGE TANKS	BERTH 6 INDUSTRIAL AREA	NON-SITE RELATED WELLS	TOTAL NUMBER OF SAMPLES
Alkalinity[c]	16	36	6	6	7	71
BOD_5[c]	0	0	6	0	0	6
Nitrate, Bromide	16	36	6	6	7	71

BOD_5 - Biochemical Oxygen Demand (5 day)
TAL - Target Analyte List
TCL - Target Compound List
TOC - Total Organic Carbon
TOX - Total Organic Halogen
TPH - Total Petroleum Hydrocarbons

Notes:

(a) The number of monitoring wells at each site is summarized as follows:

DRMO Salvage Yard -	16
Jamaica Island Landfill -	30
Mercury Burial Sites I and II -	6
Former Waste Oil Tanks -	6
Berth 6 Industrial Area -	6
Non-Site Related Wells -	7
Total	71

The 16 monitoring wells at the DRMO includes monitoring well MW-10-BW from the Stearns & Wheler investigation.

(b) In addition to the analytes shown, pH, salinity, specific conductance, and oxidation reduction potential will be determined by field measurement

(c) Included in support of potential groundwater treatment design.

TABLE 4-8

GROUNDWATER MONITORING ANALYTICAL PROGRAM SUMMARY (INCLUDING QA/QC SAMPLES)
FIRST AND SECOND EVENT GROUNDWATER SAMPLING
PNS, KITTERY, MAINE

Media	Analysis	Method	No. Samples	Trip Blank[1]	Rinsate Blank[2]	Field Blank[3]	Duplicate[4]	Total Samples
Groundwater	TCL volatiles + Freon	CLP OLM03.1	42	12	2	-	5	61
	TCL semi-volatiles	CLP OLM03.1	6	-	2	-	1	9
	TCL base/neutral semi-volatile	CLP OLM03.1	52	-	2	-	6	60
	TCL pesticide/PCBs	CLP OLM03.1	59	-	2	-	6	67
	TAL inorganics[5] (Total)	RCRA SW3010/6010	71	-	2	-	8	81
	TAL inorganics[5] (Filtered)	RCRA SW3010/6010	10	-	-	-	1	11
	Total organic carbon (TOC)	EPA 415.1	71	-	2	-	8	81
	Total organic halogen (TOX)	SW9020	71	-	2	-	8	81
	Chloride	EPA 325.3	71	-	2	-	8	81
	Sulfate	EPA 375.3	71	-	2	-	8	81
	pH	EPA 150.1	71	-	2	-	8	81
	Alkalinity	EPA 310.1	71	-	2	-	8	81
	Nitrate	EPA 352.1	71	-	2	-	8	81
	Bromide	EPA 320.1	71	-	2	-	8	81
	BOD_5	EPA 405.1	6	-	2	-	1	9
	Cyanide	RCRA SW3010/6010	7	-	2	-	1	10
	Phenols	EPA 420.1	58	-	2	-	7	67
	TPH (Gasoline Range)	Modified SW 846/8015	64	-	-	-	7	71
	TPH (Diesel Range)	Modified SW846/8100	71	-	-	-	8	79
Surface Water	Total Metals	RCRA SW3010/6010	2	-	1	-	1	4
	Chloride	EPA 325.3	2	-	1	-	1	4
	Sulfate	EPA 375.3	2	-	1	-	1	4
	Alkalinity	EPA 310.1	2	-	1	-	1	4
	Nitrate	EPA 352.1	2	-	1	-	1	4

TABLE 4-8
GROUNDWATER MONITORING ANALYTICAL PROGRAM SUMMARY (INCLUDING QA/QC SAMPLES)
FIRST AND SECOND EVENT GROUNDWATER SAMPLING
PNS, KITTERY, MAINE
PAGE 17

(1) Trip Blanks - Samples which originate from analyte-free water taken from the laboratory to the sampling site and returned to the laboratory with the volatile organic (VOA) samples. One trip blank per each cooler containing volatile organics.

(2) Rinsate Blank - Samples obtained by pouring analyte-free water over sample collection equipment (bailer, etc.) after decontamination. Assesses the effectiveness of field decontamination procedure. Obtained at a frequency of 1/day/media/analysis unless dedicated or precleaned equipment is used. Number of samples reflects the number of actual laboratory analyses performed. Only samples from every other day will be analyzed. Only two rinsate blanks are included for the subject groundwater monitoring program based on the use of dedicated sampling equipment.

(3) Field Blank - Samples consisting of the source water used in (1) steam cleaning and/or (2) decontamination. Obtained at a frequency of 1/event/media. Field blanks are not included for the subject groundwater monitoring program based on the use of dedicated sampling equipment.

(4) Duplicates - A single sample split into two portions during a single act of sampling. Assess the overall precision of the sampling and analysis program. Obtained at a frequency of 10 percent of the number of samples.

(5) Total Metals - For the determination of total metals the sample is not filtered before acidification.

(6) Dissolved Metals - For the determination of dissolved metals the sample is field filtered to 0.45μ before acidification according to Section 5.2.5 of SOP-SF-1.2 attached in Appendix B. 10 to 15 percent of the total metals samples are planned.

(7) One of the samples to be collected during high tide and one during low tide.

Note: Additionally, specific conductance, pH, salinity, turbidity, temperature, eH and Oxidation Reduction Potential (ORP) will be measured in the field.

chloride, sulfate, carbonate/bicarbonate, salinity, and gasoline/fuel oil. Subsequent to the first sampling event, design-related parameters may be included in the future to expedite any groundwater remediation design, if any. It is currently unknown whether any groundwater remediation is required; this decision depends on the results of the contaminant fate and transport modeling.

In selecting analytes for a given site, it is also important to consider upgradient contamination that could migrate and impact the site. The following evaluation shows that the planned analysis is adequate to address this concern.

DRMO Salvage Yard - The Oil Terminal Facility, specifically the tank farm area, is upgradient of the DRMO. This was taken into account in developing the monitoring plan. Monitoring well MW-10-BW from the Stearns and Wheler investigation of the Oil Terminal Facility is included in the Groundwater Investigation and Monitoring Plan as an upgradient well. Also, both TPH (gasoline range) and TPH (diesel fuel range) are included in the suite of analyses for the DRMO. During the evaluation effort, data from other Stearns & Wheler monitoring wells should be looked at in evaluating upgradient contamination. These wells should include MW-13-BW and MW-13BD.

Jamaica Island Landfill - The former waste oil tanks are upgradient and adjacent to the JILF; no other sites are upgradient. The former waste oil tank contamination will be evaluated in conjunction with the JILF contamination; the FS Report considered the potential impacts of the upgradient former waste oil tanks. The FS Report develops alternatives that encompass both sites together. Free product (if present) removal at the former waste oil tanks is the only condition believed to potentially warrant a separate action. Similar to the FS Report, the Groundwater Investigation and Monitoring Report will evaluate impacts of the former waste oil tanks on the JILF.

Mercury Burial Sites I and II - The mercury burial sites are located within the JILF.

Former Waste Oil Tanks - No sites are upgradient of the former waste oil tanks.

Berth 6 Industrial Area - The tank farm is upgradient of fuel oil spill area. Both the fuel oil spill area and the tank farm are considered part of the Oil Terminal Facility. No other known sites are upgradient of the fuel oil spill area; however, there are indications that there may be an unidentified upgradient source of inorganics contamination.

The current monitoring well listing, on a site-by-site basis, and operable unit (OU) designation noted in parentheses is as follows:

DRMO Salvage Yard (OU2 - Site 6)

DW-1, DW-1B, DW-2, DW-2B, DW-3, DW-4, DW-5, DW-6, DW-7, DW-7B, DW-7DB, DW-8, DW-8B, DW-9, DW-10B, MW-10-BW (upgradient non-DRMO well)

Jamaica Island Landfill (JILF) (OU3 - Site 8)

JW-3, JW-4, JW-5, JW-6, JW-7, JW-7B, JW-8, JW-8B, JW-9, JW-9B, JW-10, JW-12S, JW-12D, JW-12B, JW-13S, JW-13D, JW-13B, JW-13DB, JW-14, JW-14B, JW-15, JW-15B, JW-16, JW-16B, JW-17B, JW-18, JW-18B, JW-19, JW-19B, GW-1

Mercury Burial Sites MBI & MBII (OU3 - Site 9)

MW-2, MW-3, MW-4, MW-5, MW-6, MW-7

Berth 6 Industrial Area (OU5 - Site 27)

FW-1, FW-2, FW-3, FW-4, FW-5, FW-6

Former Waste Oil Tanks (OU3 - Site 11)

HW-3, WOT-2, WOT-3, WOT-4, WOT-5, HW-2 (As footnoted on Table 3-1, new monitoring well HW-2 replaces damaged monitoring well WOT-6. New monitoring well HW-3 replaces monitoring well WOT-1; the screened interval of the new well extends into shallow bedrock).

Non-Site Related Wells

DI-01B, DI-01DB, FA-01, FA-01B, FA-01DB, SI-01B, SI-01DB

4.1.2 Subsequent Groundwater Monitoring

Following the first two sampling events, subsequent groundwater monitoring may continue for selected monitoring wells, as follows. These identified monitoring wells are preliminary and subject to change following evaluation of the analytical results from the first two sampling events, evaluation of the groundwater flow maps, and consultation with the regulatory agencies.

- Two overburden background wells are anticipated for monitoring, plus one bedrock monitoring well. Three background wells are recommended to provide a higher level of confidence concerning corresponding concentrations, considering the variability of the overburden (freshwater vs. saline water; fill material vs. native material). Analytical results will be used for comparison purposes with other wells selected for monitoring such that contaminants can be identified as site related or indicative of background conditions. Analytical results and soil boring logs will be used in determining background wells. Ideally, one freshwater well and one saline well will be selected. Selection of these wells will be determined upon completion of the first and second sampling event. It is possible, based on facility conditions that no on-site wells are suitable for background purposes. If this is the case, the inclusion of off-site wells would be considered in the future, with the owner's permission and upon evaluation of the well construction. An extensive survey of existing information from nearby water utilities/wells, State, and CERCLA records will be conducted to further aid in establishing groundwater background conditions.

- At the DRMO Salvage Yard, where groundwater flow direction is certain, two upgradient wells and five overburden/three bedrock wells located at the DRMO Salvage Yard downgradient perimeter will likely be monitored, plus upgradient monitoring well MW-10-BW from the Stearns & Wheler investigation at the tank farm area. True downgradient wells cannot be installed since this site borders the Piscataqua River. The ~~nine~~ 10 wells anticipated for monitoring include DW-4, DW-10B, DW-3, DW-8/DW-8B, DW-2/DW-2B, DW-9, and DW-7/DW-7B. Map A herein presents the monitoring well locations. Map B of the RFI Data Gap Report (Halliburton NUS, 1995a) supports the selection of monitoring wells DW-4 and DW-10B as being slightly upgradient.

- At the JILF, where groundwater flow direction appears to be in several directions, perimeter wells are anticipated for monitoring. Fifteen overburden/ten bedrock wells are anticipated for monitoring. The 25 wells to be monitored include JW-6, JW-17B, JW-15/JW-15B, JW-5, JW-4, JW-3, JW-14/JW-14B, MW-4, JW-13S/JW-13B/JW-13D, JW-12S/JW-12B/JW-12D, JW-10, JW-9/JW-9B, MW-6, GW-1, JW-8/JW-8B, and JW-7/JW-7B. Map A presents monitoring well locations.

- The Mercury Burial Sites are located within the JILF Landfill. Therefore, monitoring will likely be in accordance with the JILF perimeter monitoring program. The JILF monitoring program currently includes monitoring well MW-6 at MBII. Monitoring wells at JW-10, JW-12 cluster and JW-13 cluster, although much further downgradient, provide information at the potential point of exposure (at Clark's Cove).

- The Former Waste Oil Tanks also are located within the JILF Landfill. Therefore, monitoring will likely be in accordance with the JILF perimeter monitoring program. Monitoring of immiscible layers will continue.

- At the Berth 6 Industrial Area, all six existing wells will be monitored, including FW-1, FW-2, FW-3, FW-4, FW-5, and FW-6. Monitoring of immiscible layers will continue.

Samples will be analyzed for TCL organics and SW inorganics, as appropriate, which is consistent with the analytical methods used for the RFI and RFI Data Gap investigations. Data will be reviewed and a revised analytical suite will be proposed if appropriate. Any changes to the monitoring program will be reviewed and approved by the regulatory agencies. Also, indicator parameters will be included; however, no replicate sampling will be conducted. Sampling/analysis will likely occur on a semi-annual basis. The actual months selected for sampling may vary from year to year to gain information associated with seasonal changes. Sampling/analysis frequency will be determined with concurrence from the regulatory agencies.

Refer to Tables 4-2 through 4-6 for a summary of specific parameters of concern to be sampled for each site. These tables are subject to refinement based on an evaluation of analytical results from baseline conditions monitoring. Table 4-7 presents analytical methods, containers, preservation, and holding times for each parameter.

4.2 SAMPLING AND ANALYSIS PROCEDURES

Katahdin Analytical Services has been selected to perform the analytical services for the groundwater monitoring. Refer to Appendix C of the Groundwater Investigation and Monitoring Plan for the Analytical Laboratory NFESC Quality Assurance Guide for Katahdin.

In accordance with standard Navy CLEAN procedures, all field team members will be cleared by the CLEAN Health and Safety Manager prior to working on this (or any) project. Refer to Appendix E for the Health and Safety Plan (HASP).

4.2.1 Inspection of Existing Monitoring Wells

Prior to sampling each monitoring well, a brief inspection will be conducted, evaluating the following conditions:

- Condition of the protective casing
- Condition of the cement seal surrounding the protective casing

- Presence of any standing water around the protective casing
- Presence of dedicated sampling equipment
- Determination of static water level
- Determination of total depth of well, including a check to determine if well is obstructed
- Determination of the presence of immisible layers
- Well security evaluation

Comparisons will be made between baseline conditions and sampling date conditions to determine if significant changes have occurred which may indicate well damage. A record of all field observations will be recorded in a field log book.

4.2.2 Water-Level Measurement

Two comprehensive rounds of water-level measurements will be collected, before purging and sampling activities are conducted, for each event to provide semi-annual information regarding groundwater flow patterns and flow gradients across the PNS facility. Water-levels will be obtained from all 70 RFI and RFI Data Gap facility wells; one round during mean high tide and one round during mean low tide. Additionally, water-level measurements will be conducted from monitoring well MW-10-BW from the Stearns & Wheler investigation at the tank farm. Each set of water-level measurements will be obtained within an 2-hour period, and no sooner than 24 hours after a significant precipitation event, to minimize the precipitation effects, on the data sets.

Measurements will be taken with an M-Scope (electrical water-level indicator) using the top of the inner well casing as the reference point for determining depths to water. This well casing shall be notched and marked so that the same point will be referenced for all measurements. Water-level measurements will be recorded to the nearest 0.01 foot in the field logbook and on a groundwater level measurement form, attached in Appendix A. Section 5.0 of SOP-GH-2.5 (refer to Appendix B) provides a description of Water Level Measurement procedures.

M-scopes will be calibrated prior to each sampling event by comparison of M-scope markings with a steel tape measure.

4.2.3 Measurement of Immiscible Layers

During installation of the low-flow pumps, floating free product may be encountered at a few wells, particularly the FW wells at the Berth 6 Industrial Area. To address this problem wells containing light non-aqueous phase liquids (LNAPL) will be purged using a peristaltic pump before the submersible pump is installed. The peristaltic pump will be lowered to the top of the LNAPL, and purged moving the tube increasingly downward until the pump begins to extract water. At that point the tubing will be removed and the pump lowered into well and installed. Since pump installation will be permanent, this procedure only applies to the initial installation.

Measurement of light phase floating product, which is less dense than water, will take place before purging of a given monitoring well for sampling purposes. Free product measurement will be accomplished with an interface probe. Thickness of the free product layer, detected at the potentiometric surface, will be recorded in the field logbook. All monitoring wells at the Former Waste Oil Tanks including JW-16 and JW-16B and the Berth 6 Industrial Area will be checked for floating product using the interface probe.

Measurement of dense non-aqueous phase layer (DNAPL) will also occur before purging of a given monitoring well for sampling purposes and will be accomplished with an interface probe. Thickness of the free product layer, detected by lowering the instrument to the bottom of the monitoring well will be recorded in the field logbook. All monitoring wells at the Former Waste Oil Tanks including JILF monitoring wells JW-16 and JW-16B will be checked for DNAPL using the interface probe.

4.2.4 Well Purging

It is anticipated that dedicated 1.66 inch diameter low-flow bladder type pumps (teflon-lined, PVC) will be installed in all of the monitoring wells prior to the baseline sampling. However, it is anticipated that four wells will require the use of peristaltic pumps: HW-3, JW-12S, JW-13S, and DW-1. The pumps will be certified contaminant free; this certification as well as lot numbers will be provided in an appendix of the initial groundwater monitoring report. Purging and sampling will be accomplished by using low-flow purging techniques in accordance with SOP-SA-1.1 (Groundwater Sample Acquisition) and US EPA Region I Low-Flow Purging and Sampling Procedure found in Appendix B. Low-flow purging and sampling is being implemented because this method will provide the least disturbance to the surrounding formation (i.e., less turbulence in sampling and hence less turbidity) allowing for a more representative sample to be collected. Results fromthe September 1996 low-flow pilot test are incorporated herein (B&R Environmental, 1996).

Prior to obtaining groundwater samples, water levels will be measured using an electric water-level indicator (M-Scope) capable of 0.01-foot accuracy. Water levels will be monitored every 3 to 5 minutes as purging

occurs. Each monitoring well will be purged and sampled using a dedicated, low-flow 1.66-inch diameter bladder pump and dedicated teflon or teflon-lined polyethylene tubing. The pump will be placed at the midpoint of the low tide saturated well screen and if possible no less than 2 feet above the bottom of the well so as to not disturb any sediment which may be located near the bottom of the well. Initially, the pumping rate will be set at approximately 0.2 liters per minute, or lower if possible. The pumping rate will be reduced if turbidity is greater than 5 NTUs after all other field parameters have stabilized. The pumping rates will be adjusted so as to not allow drawdown to exceed 0.3 feet, in wells that are not impacted by the tide, during the purging. If groundwater is drawn down below the top of the well screen, in wells that are not impacted by the tide, purging will cease and the well will be allowed to recover before purging continues. Slow recovering wells will be identified and purged at the beginning of the work day. If possible samples will be collected from these wells within the same 8-hour work day.

During purging, water quality parameters (pH, turbidity, specific conductance, temperature, eH, salinity, and dissolved oxygen) will be measured and recorded every 5-minutes using a flow-through cell until all of the parameters have stabilized and the minimum purge volume has been removed (stabilized purge volume plus the extraction tubing volume). Stabilization of the above parameters is defined as follows:

- pH $\pm$ 0.1 standard units
- turbidity $\pm$ 10% for value greater than 1 NTU
- specific conductance $\pm$ 3%
- temperature $\pm$ 3%
- eH $\pm$ 10 millivolts
- dissolved oxygen $\pm$ 10%

For tidally influenced wells, purging should begin 2-1/2 hours prior to low tide. If the parameters have not stabilized within one and one-half hours, then sampling will be initiated. Samples will be collected between one hour before low tide of the well and before the end of the slack tide for the well. Prior to sampling, the turbidity reading will be confirmed with a HORIBA water quality meter or other visible light source turbidity probe. Those wells which have excessive turbidity even after low-flow purging will be scheduled for redevelopment and resampling.

Calibration and standards checks will be conducted on the flow-through cell in accordance with the manufacturer. The cell will be cleaned at each well prior to purging and during purging, as needed (e.g., when fluctuating turbidity readings are observed and confirmed by collection of a turbidity sample before the cell for comparison). A tee connector with a valve will be inserted into the pump's tubing prior to the cell for collection of the turbidity sample. If the cell needs to be cleaned during purging operations, continue

pumping and disconnect cell for cleaning, then reconnect after cleaning and continue monitoring activities. The cell will be cleaned by rinsing with deionized water.

Precautions will be taken to prevent air entrapment and/or air leaks in the purging system so that potential problems with stabilizing dissolved oxygen are minimized. Precautions will include: 1) taking care to fill the cell with water, while minimizing air entrapment, prior to initiating purging and 2) maintaining a full cell of water by pinching the discharge line shut of keeping the tubing from the pump to the cell elevated above the cell.

Purge water will be containerized and labeled by B&R Environmental. The empty containers will be provided by PNS. The containerized water will be turned over to PNS for disposal. Refer to Section 4.2.7 concerning residue management.

Section 5.0 of SOP-SF-1.1, attached in Appendix B, provides additional requirements for groundwater sample acquisition.

4.2.5 Sampling of Wells

Monitoring wells will be sampled during each event using a low-flow 1.66-inch diameter low flow bladder-type pump and dedicated teflon or teflon-lined polyethylene tubing. After purging is completed the flow-through cell will be disconnected and samples will be collected directly from the discharge of the pump. In the event that static-water level conditions do not allow for the installation of a pump, a peristallic pump will be used. It is anticipated that four wells will require the use of peristaltic pumps: HW-3, JW-12S, JW-13S, and DW-1.

All sample containers should be filled by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence. Samples to be analyzed for volatile constituents will be taken first and immediately sealed in a pre-preserved container so that no head space exists. For filtered inorganic samples, an in-line 0.45 micron filter will be used. The filter will be pre-rinsed with approximately 400 ml of deionized water and attached to the discharge end of the pump tubing.

For monitoring wells that are tidally influenced, groundwater samples will be collected at low tide. At low tide, contaminant concentrations are expected to be at maximum concentration, therefore, providing conservative data (at high tide, inflow of "clean" water would potentially dilute the contaminants in tidally influenced wells). Wells that are not tidally influenced will be sampled independent of the tide. A list of wells that will be sampled independent of the tide is presented in Table 4-9.

TABLE 4-9

TIDALLY AFFECTED WELLS[1]
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

Well No.	Tidally Affected	Water Level Low Tide[2] (feet)	Water Level High Tide[2] (feet)	Difference (feet)
DI-01B	No	12.22	12.25	-0.03
DI-01DB[3]	No	13.18	13.18	0.0
FA-01	No	8.38	8.40	-0.02
FA-01B	Yes	9.48	8.05	1.43
FA-01DB	Yes	9.97	8.42	1.55
SI-01B	No	1.82	1.85	-0.03
SI-01DB	No	5.92	5.85	0.07
DW-07DB	Yes	15.46	10.69	4.77
JW-13DB[4]	Yes	11.57	11.36	0.21
HW-3[5][6]	No	---	---	---
WOT-2	No	4.20	4.19	0.01
WOT-3	No	5.02	5.02	0.0
WOT-4	No	3.66	3.74	-0.08
WOT-5	No	6.21	6.22	-0.01
JW-3	No	6.31	6.36	-0.05
JW-4	No	7.57	7.67	-0.1
JW-5	Yes	7.18	5.60	1.58
JW-6	No	6.71	6.74	-0.03
JW-7	No	5.30	5.28	0.02
JW-7B	No	5.48	5.48	0.0
JW-8	No	7.93	7.98	-0.05
JW-8B	No	8.32	8.37	-0.05
JW-9	No	5.62	5.73	-0.11
JW-9B	No	5.52	5.61	-0.09
JW-10	Yes	9.91	5.72	4.19
JW-12S[6]	Yes	11.67	5.44	6.23
JW-12D	Yes	14.99	5.34	9.65

TABLE 4-9
TIDALLY AFFECTED WELLS[1]
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE
PAGE 2

Well No.	Tidally Affected	Water Level Low Tide[2] (feet)	Water Level High Tide[2] (feet)	Difference (feet)
JW-13S[6]	Yes	11.85	7.35	4.5
JW-13B	Yes	14.74	7.68	7.06
JW-14[4]	Yes	8.37	8.30	0.07
JW-14B[4]	Yes	9.56	9.22	0.34
JW-15	Yes	10.17	6.46	3.71
JW-15B	Yes	11.04	6.85	4.19
JW-16	No	5.11	5.08	0.03
JW-16B	No	5.04	5.03	0.01
JW-17B	No	6.78	6.70	0.08
JW-18[7]	No	8.44	8.41	0.03
JW-18B[5][7]	No	---	---	---
JW-19	No	11.22	11.21	0.01
JW-19B[3]	No	11.84	12.22	-0.38
MW-2	No	12.75	12.54	0.21
MW-3	No	13.51	13.45	0.06
MW-4	No	12.81	12.97	-0.16
MW-5	No	13.14	13.17	-0.03
MW-6	No	13.27	13.23	0.04
MW-7	No	13.51	13.70	-0.19
DW-1[6]	Yes	11.77	8.23	3.54
DW-1B	Yes	13.40	8.50	4.9
DW-2[5][7]	Yes	---	---	---
DW-2B	Yes	17.48	8.78	8.7
DW-4	Yes	12.19	8.68	3.51
DW-5	Yes	9.28	8.11	1.17
DW-6[4]	Yes	8.47	8.21	0.26
DW-7	Yes	17.35	8.37	8.98
DW-8	Yes	13.51	6.44	7.07
DW-8B	Yes	14.16	6.10	8.06

TABLE 4-9
TIDALLY AFFECTED WELLS[1]
PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE
PAGE 3

Well No.	Tidally Affected	Water Level Low Tide[2] (feet)	Water Level High Tide[2] (feet)	Difference (feet)
DW-9	Yes	14.23	7.65	6.58
DW-10B[3]	Yes	14.16	10.65	3.51
FW-1	Yes	8.33	5.32	3.01
FW-2	Yes	10.32	3.73	6.59
FW-3	Yes	10.51	3.43	7.08
FW-4	Yes	11.84	4.66	7.18
FW-5	Yes	10.80	4.21	6.59
FW-6[3]	Yes	12.21	3.67	8.54
GW-1	No	10.18	10.16	0.02
DW-3	Yes	14.92	6.47	8.45
DW-7B	Yes	17.00	9.53	7.47
JW-12B	Yes	14.91	4.90	10.01
JW-13D	Yes	15.99	7.72	8.27
MW-10-BW[5]	Yes	---	---	---
HW-2[5]	No	---	---	---

NOTES:

1. The monitoring wells shown in **BOLD** are considered to be tidally influenced (e.g., difference between low and high tide greater than 1 foot) and therefore should be sampled at low tide.

2. Low tide/high tide water level data were obtained on July 26, 1994. The low tide was -0.4 feet.

3. Four wells (DI-01DB, DW-10B, JW-19B, and FW-6) are damaged and cannot be sampled until they are replaced.

4. Although the difference between low and high tide is less than one foot, the location indicates that the well may be tidally affected and therefore the well will be sampled at low tide.

5. Water level data was not available. The tidally influenced determination was made based on the well location and the tidal impact on nearby wells.

6. Peristaltic pumps will be used in four wells (HW-3, DW-1, JW-12S, and JW-13S) where water depth is not sufficient for pump installation.

7. Three wells (JW-18, JW-18B, and DW-2) have not been located.

After sampling, the discharge piping will be drained to prevent possible freezing. Care will be taken not to contaminate the exterior of the tubing (via contact with the ground or clothing) while conducting this activity.

4.2.6 Decontamination

Nondedicated equipment involved in field sampling activities will be decontaminated prior to and during sampling activities. Since dedicated sampling equipment will be used at each well location to the extent possible, little to no decontamination water will be generated. Any decontamination water that is generated will be handled in the same manner as purge water, described in Section 4.2.7.

For any nondedicated sampling equipment used for collecting groundwater samples, the equipment will be decontaminated both prior to beginning field sampling and between samples. The following decontamination steps will be conducted.

- Potable water rinse
- Alconox or Liquinox detergent wash
- Potable water rinse
- Analyte-free water rinse
- Air dry

4.2.7 Residue Management

Two types of potentially contaminated residues are expected to be generated during the groundwater monitoring program, namely Personal Protective Equipment (PPE) and purge water. Based on the activities and types of contaminants present, none of these residues are expected to represent a significant risk to human health or the environment if properly managed. Planned management of each of these residues is provided below:

PPE - B&R Environmental will place uncontaminated PPE in the trash receptacles at the facility. If contaminated, PPE will be containerized, labeled and disposed of by B&R Environmental.

Purge Water - It is recommended that purge water be containerized in large plastic/polyethylene tanks staged near the industrial treatment plant or containerized in 55-gallon drums provided by PNS. Purge water generated during monitoring well sampling will be containerized and stored until analytical results are received. Purge water will be disposed of by B&R Environmental.

- If analytical results indicate that purge water concentrations for any constituent in the container exceed MCLs or MEGs but are less than RCRA hazardous waste concentrations, the contents will be disposed in accordance with Federal, State, and local regulations.

- If analytical results indicate that purge water concentrations for any constituent exceed RCRA Toxicity Characteristic Leachate Procedure (TCLP) criteria for a given analyte, then treatment at an offsite treatment facility is warranted, in accordance with Federal, State, and local regulations.

4.2.8 Sample Identification System

Each sample collected will be assigned a unique sample tracking number. The sample tracking number will consist of a two-segment, alpha-numeric code that identifies the sample medium and location, and sample round identifier (in the case of groundwater samples). Any other pertinent information regarding sample identification will be recorded in the field log books.

The alpha-numeric coding to be used in the sample system is explained in the diagram and the subsequent definitions:

(AAAA[N])	-	**(AANN)**	-	**(AANN)**
(Site ID)		(Location)		(Medium & Round Identifier)

Character Type:

A = Alpha

N = Numeric

Site ID:

JILF	=	Jamaica Island Landfill (JILF)
MBS1	=	Mercury Burial Site 1 (MBI)
MBS2	=	Mercury Burial Site 2 (MBII)
DI	=	Dennett's Island (non-site related wells)
SI	=	Seavey Island (non-site related wells)
FA	=	Fill Area (non-site related wells)
DRMO	=	DRMO Salvage Yard (DRMO)
WOT	=	Former Waste Oil Tanks
FW	=	Berth 6 Industrial Area

SW = Stearns & Wheler (Tank Farm Area)

HW = HWSF (Hazardous Waste Storage Facility, Building 357)

Sample Location:

Groundwater sample = Monitoring well number

Media:

GW = Groundwater from monitoring well

Sample Round Identifier:

For all samples = sampling round

- First event, Round 7
- Second event, Round 8
- Subsequent Sampling, Round 9, 10, etc.

For example, a groundwater sample collected from monitoring well 13DB at Jamaica Island Landfill during establishment of second event baseline conditions would be designated as: JILF-13DB-GW-08.

Note that the McLaren/Hart RFI encompassed Phases 1 through 4A (sometimes referred to as Phase 5) and the Halliburton NUS RFI Data Gap consisted of Phase 6. Therefore the proposed first event sampling, will be considered Round 7.

Field quality control (QC) samples are described in Section 4.4.3. They will be designated using a different coding system. The QC code will consist of a two-segment, alpha-numeric code that identifies the sample medium (for duplicates only), QC type, and date. The same sample medium codes will be used as for the standard environmental samples (i.e., GW). The QC types are identified as:

RB = Rinsate Blanks

TB = Trip Blanks

FB = Field Blanks

FD = Field Duplicates

For example, a duplicate of a groundwater sample obtained on June 3, 1996 would be designated as: GWFD-060396. This allows duplicates to be submitted as "blind" samples to the analytical laboratory. Sample log sheets, not received by the analytical laboratory, will document duplicate sample location.

Matrix Spike and Matrix Spike Duplicate (MS/MSD) samples will be designated on the field documentation forms and sample labels. MS/MSDS are collected at a frequency of 1 per 20 samples per matrix and double or triple volumes of sample are required for analytical purposes. Due to the large volume of sample required for MS/MSDS samples, only those wells exhibiting high hydraulic conductivities will be selected whenever possible. MS/MSD samples should be collected for salt, brackish and freshwater wells to assess matrix effects for each of these scenarios.

The sampling time recorded on the chain-of-custody form for duplicate and matrix spike/matrix spike duplicate samples will be 00:00 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded in the field log book and on sample log sheets. A separate sample log sheet will be completed for duplicate samples sent blind to the laboratory.

4.2.9 Sample Handling

Sample handling includes the field related considerations connected with the selection of sample containers, preservatives, allowable holding times, and analyses requested. Table 4-6 provides a summary of all sample handling considerations. Section 5.0 of SOP-SF-1.2, attached in Appendix B, provides a description of Sample Preservation Requirements.

4.2.10 Chain-of-Custody

Sample custody procedures are designed to provide documentation of preparation, handling, storage, and shipping of all samples collected. An example of the chain-of-custody form, which will be used during this investigation, is included in Appendix A. A copy of the procedure is included in Appendix B.

Integrity of the samples collected during the site investigation will be the responsibility of identified persons from the time they are collected until they, or their derived data, are incorporated into the final report. Stringent chain-of-custody procedures will be followed to document sample possession.

Field Custody

- The Field Team Leader (FTL) is responsible for the care and custody of the samples collected until they are delivered to the analyzing laboratory or entrusted to a carrier.

- Sample logs or other records will be signed and dated.

- Chain-of-custody sample forms will be completed to the fullest extent possible prior to sample shipment. They will include the following information: project name, sample number, time collected, source of sample and location, sample salinity, description of sample location, matrix, type of sample, grab or composite designation, preservative, and name of sampler (see attached form). Sample salinities are included to aid the analytical laboratory in establishing dilution requirements for metals analyses were salinity could present an interference concern.

  These forms will be filled out in a legible manner, using waterproof ink, and will be signed by the sampler. Similar information will be provided on the sample label which will be securely attached to the sample bottle. The label will also include the general analyses to be conducted. In addition, sampling forms will be used to document collection, filtration, and preparation procedures. Copies of all forms used during field activities are provided in Appendix A.

Transfer of Custody and Shipment

The following procedures will be used when transferring custody of samples:

- Samples will be accompanied by a chain-of-custody record. When transferring samples, the individuals relinquishing and receiving them will sign, date, and note the time of the chain-of-custody record. This record documents the sample custody transfer from the sampler to the laboratory, often through another person or agency (common carrier). Upon arrival at the laboratory, internal sample custody procedures will be followed.

- Prior to shipment to the laboratory for analysis, samples will be properly packaged. Individual custody records will accompany each shipment. Shipping containers will then be sealed for shipment to the laboratory. The methods of shipment, courier name, and other pertinent information, will be entered in the remarks section of the custody record.

- All shipments will be accompanied by the chain-of-custody record identifying the contents. The original record will accompany the shipment; and a copy will be retained by the field sampler.

- Proper documentation will be maintained for shipments by common carrier.

Sample Shipment Procedures

The following procedures will be followed when shipping samples for laboratory analysis:

- Samples requiring cooling to 4°C will be promptly chilled with ice or Blue Ice and will be packaged in an insulated cooler for transport to the laboratory. A temperature blank will be included in each cooler to be used as a temperature indicator. Each temperature blank will be clearly identified by the field sampling team. Ice will be sealed in containers to prevent leakage of water. Samples will not be frozen.

- Only shipping containers that meet all applicable state and Federal standards for safe shipment will be used.

- Shipping containers will be sealed with nylon strapping tape, custody seals will be signed, dated, and affixed, in a manner that will allow the receiver to quickly identify any tampering that may have occurred during transport to the laboratory.

- The field chain-of-custody document will be placed inside the shipping container in a sealed plastic envelope.

- Shipment will be made by a public courier. After samples have been taken, they will be sent to the laboratory within 24 hours.

Field Documentation Responsibilities

It will be the responsibility of the FTL to secure all documents produced in the field (e.g., sampling logs, calibration forms) at the end of each work day. A copy of all forms used during field activities are included in Appendix A. Copies of all field logbooks will be sent to NORTHDIV monthly, to the attention of Fred Evans. Additionally, field notes will be included as an appendix to the report.

At the completion of field activities, the FTL will send the Project Manager all field records, data, field notebooks, logbooks, chain-of-custody receipts, sample log sheets, daily logs, etc. The Project Manager will ensure that these material are entered into the B&R Environmental document control system in accordance with appropriate administrative guidelines.

Changes in project operating procedures may be necessary as a result of changed field conditions or unanticipated events. A summary of the sequence of events associated with field changes is as follows:

- The FTL notifies the Project Manager of the need for the change.

- If necessary, the Project Manager will discuss the change with the pertinent individuals (e.g., Navy Remedial Project Manager, B&R Environmental Quality Assurance Manager) and will provide a verbal approval or denial to the FTL for the proposed change. The EPA and MEDEP will be consulted of any scope changes that may occur while fieldwork is ongoing.

- The FTL will document the change on a Task Modification Request form and forward the form to the B&R Environmental Project Manager at the earliest convenient time (e.g., end of the workweek).

- The B&R Environmental Project Manager will sign the form and distribute copies to the Navy Remedial Project Manager, Quality Assurance Manager, FTL, and project file.

- A copy of the completed Task Modification Request form will be attached to the field copy of the affected document.

The possession of all records will be documented; however, only the project FTL or designee may remove field data from the site for reduction and evaluation.

Laboratory Sample Custody

To ensure the integrity of a sample from collection through analysis, it is necessary to have an accurate, written record that traces the possession and handling of the sample. This documentation is referred to as the sample chain-of-custody.

A sample is under custody if:

- The sample is in the physical possession of an authorized person.

- The sample is in view of an authorized person after being in his/her possession.

- The sample is placed in a secure area by an authorized person after being in his/her possession.

- The sample is in a secure area, restricted to authorized personnel only.

Sample custody during collection and shipping is discussed in Section 5.3 of SOP SA-6.1, attached in Appendix B. Laboratory sample custody is discussed in the following sections.

When samples are received, the shipping manifest is signed and dated to acknowledge sample receipt. The sample custodian must examine the shipping containers and verify that the correct number of containers was received. The shipping containers are then opened and the enclosed sample paperwork is removed. Samples are removed from the shipping containers and the bottle condition, cooler temperature and sample salinity must be noted. The information on the chain-of-custody, the airbill, the containers, and the laboratory request is reviewed to note any discrepancies.

All samples received by the laboratory must be stored at 4°C until analysis. Laboratory holding times are specified by the contract and are presented in Table 4-6.

4.3 QUALITY ASSURANCE OBJECTIVES

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and reporting that will provide environmental monitoring data of known and acceptable quality. Specific procedures to be used for sampling, chain-of-custody, calibration of field instruments, laboratory analysis, reporting, internal quality control, audits, preventative maintenance, and corrective actions are described in later sections of this plan. The purpose of this section is to address the data quality objectives in terms of the (PARCC) parameter, quantitation and detection limits, field blanks, rinsate blanks, duplicates, and bottleware cleanliness.

4.3.1 Data Quality Objectives

Data quality Objectives (DQOs) are qualitative and/or quantitative statements regarding the quality of data needed to support the field activities. The sampling rationale provided in the Work Plan explains the choice of sample locations and media which will supply information needed for the site investigation.

4.3.2 PARCC Parameters

The quality of data set is measured by certain characteristics of the data, namely the PARCC parameters. Some of the parameters are expressed quantitatively, while others are expressed qualitatively. The objectives of the investigation and the intended use of the data define the PARCC goals.

4.3.2.1 Precision

Precision characterizes the amount of variability and bias inherent in a data set. Precision describes the reproducibility of measurements of the same parameter for a sample under the same or similar conditions. Precision is expressed as a range (the difference between two measurements of the same parameter) or

as a relative percent difference (the range relative to the mean, expressed as a percent). Range and Relative Percent Difference (RPD) values are calculated as follows:

$$Range = OR - DR$$

$$RPD = \frac{[OR - DR]}{1/2\ (OR + DR)} \times 100\%$$

where: **OR** = original sample result

DR = duplicate sample result

The internal laboratory control limits for precision are three times the standard deviation of a series of RPD or range values. RPD values may be calculated for both laboratory and field duplicates, and can be compared to the control limits as a QA check. Laboratory duplicates will be analyzed at the rate required by NEESA. Field duplicates will be collected for 10 percent of all samples collected.

4.3.2.2 Accuracy

Accuracy is the comparison between experimental and known or calculated values expressed as a percent recovery (%R). Percent recoveries are derived from analysis of standards spiked into deionized water (standard recovery) or into actual samples (matrix spike or surrogate spike recovery). Recovery is calculated as follows:

$$\%R = E/T \times 100\%$$

where: **E** = experimental result

T = true value (theoretical result)

and

$$T = \frac{(Sample\ Aliquot)\ (SampleConc.) + (Spike\ Aliquot)\ (Spike\ Conc.)}{Sample\ Alquot + Spike\ Aliquot}$$

Control limits for accuracy are set at the mean plus or minus three times the standard deviation of a series or %R values.

Accuracy for aqueous and solid samples will be evaluated by use of surrogate and matrix spikes. Out-of-criteria results will be reviewed for data applicability as a part of data validation.

4.3.2.3 Representativeness

All data obtained should be representative of actual conditions at the sampling location. The Work Plan is designed so that the samples taken will present an accurate representation of actual site conditions. The rationales discussed int he Work Plan are designed to ensure this. All sampling activities will conform to the protocols given in Section 4.0 of this Work Plan. The use of NFESC approved analytical protocols and data deliverables will ensure that analytical results and deliverables are representative, and both consistently performed and reported.

4.3.2.4 Comparability

Comparability will be achieved by utilizing standardized sampling and analysis methods and data reporting format. Both analytical procedures and sample collection techniques will maximize the comparability of this new data to previous data. Additionally, consideration will be given to seasonal conditions and other environmental conditions that could influence analytical results.

4.3.2.5 Completeness

Completeness is a measure of the amount of valid data obtained from the measurement program, compared to the total amount collected. For relatively clean, homogeneous matrices, 100 percent completeness is expected. However, as matrix complexity and heterogenicity increase, completeness may decrease. Where analysis is precluded or where DQOs are compromised, effects on the overall investigation must be considered. Whether any particular sample is critical to the investigation will be evaluated in terms of the sample location, the parameter in question, the intended data use, and the risk associated with the error.

Critical data points may not be evaluated until all the analytical results are evaluated. If in the evaluation of results it becomes apparent that the data for a specific medium are of insufficient quality (95 percent), either with respect to the number of samples or an individual analysis, resampling of the deficient data points may be necessary.

4.3.3 Quality Control Samples

Field Blanks

Field blanks are not anticipated for the interim monitoring program unless new monitoring wells are installed or non-dedicated bailers are used for sampling. Field blanks are obtained by sampling the water(s) used in decontamination during the field investigation activities. Samples consist of the source water used in: (1) steam cleaning of large equipment and (2) analyte-free water used for decontamination of sampling equipment. Field blanks will be used to confirm the effectiveness of decontamination procedures, and to determine if the analyte-free water or the potable water (used for steam cleaning) may be contributing to sample contamination. Field blanks will be collected for each type of water used for decontamination and will be submitted at a frequency of one per sampling event. Field blanks will be obtained during the early days of the sampling activities.

Rinsate Blanks

Minimal equipment rinsate blanks are anticipated for the interim monitoring program unless new monitoring wells are installed or non-dedicated bailers are used for sampling. Equipment rinsate blanks are obtained under representative field conditions by running analyte-free water through sample collection equipment (bailer, split-spoon, corer, etc.) after decontamination and placing it in the appropriate sample containers for analysis. Equipment rinsate blanks will be used to assess the effectiveness of decontamination procedures. Equipment rinsate blanks will be collected for each type of non-dedicated sampling equipment used and will be submitted at a frequency of one per day per media. Equipment rinsate blanks, however, will only be analyzed every other day unless positive detections are recorded in the prior rinsate blank. Rinsate blanks are collected on a daily basis and are analyzed at a frequency of every other day in accordance with NFESC requirements. The analytical laboratory will receive all rinsate blanks. If contamination is encountered in the rinsate blanks, and the contamination is not attributed to internal laboratory contamination, the laboratory must notify the project manager and analyze the remaining rinsate blanks. For dedicated or precleaned equipment, rinsate blanks will be collected and analyzed at a frequency of one per lot for a specific equipment type. It will be the responsibility of the FTL to communicate to the laboratory whether an equipment blank is, or is not, to be analyzed as stated above.

Field Duplicates

Field duplicates are two samples collected: (1) independently at a sampling location in the case of groundwater or surface water, or (2) a single sample split into two portions in the case of soil or sediment. Duplicates are obtained during a single act of sampling and are used to assess the overall precision of the

sampling and analysis program. Ten percent of all samples for each media will be field duplicates. Duplicates will be analyzed for the same parameters in the laboratory and will be labeled so as to make the identity of the duplicate unknown to the laboratory.

Trip Blanks

Trip blanks are samples which originate from analyte-free water taken from the laboratory to the sampling site and returned to the laboratory with the volatile organic analysis samples (such as TCL volatiles). One trip blank will be collected per each cooler containing volatile organics. Trip blanks are only analyzed for the volatile constituents that are being shipped in a given cooler.

4.4 ANALYTICAL LABORATORY CAPACITY

Careful coordination with the analytical laboratory will be required throughout the project so as not to exceed the capacity of the laboratory to perform the analysis. A detailed schedule will be included in the analytical laboratory specification to aid in the planning/coordination effort and to ensure that project requirements are achieved.

4.5 CALIBRATION PROCEDURES AND FREQUENCY

Instrument used in the field and in the laboratory will be calibrated according to the procedures described below. Several monitoring instruments will be used during field activities, including:

- In-line flow-through cell
- Electronic water-level meter
- HNu/OVA organic vapor detector

The electronic water-level meter will be calibrated prior to field use and periodically at the discretion of the Field Team Leader (FTL). The remaining instruments will be calibrated daily or according to the manufacturer's operating manual.

Calibration will be documented on an Equipment Calibration Log (Appendix A). During calibration, an appropriate maintenance check will be performed on each piece of equipment. If damaged or defective parts are identified during the maintenance check and it is determined that the damage could have an impact on the instrument's performance, the instrument will be removed from service until the defective parts are repaired or replaced.

Calibration of equipment at the analytical laboratory will comply with the specified analytical method.

4.6 INTERNAL QUALITY CONTROL CHECKS

Quality control samples generated by B&R Environmental will include the collection of field duplicates, the preparation of field blanks, trip blanks, and the preparation of equipment/rinsate blanks. An approximate 10 percent duplication (one per 10 samples or one per sample matrix if less than 10 samples) will be collected. See Table 4-8 for the required number of sample duplicates.

Trip blanks will be prepared on a one per day frequency. Rinsates, prepared by running distilled water through the sampling equipment, will be analyzed to determine whether the sampling procedures may be biasing the data. Field blanks are not included based on the use of dedicated sampling equipment. Procedures for collecting these samples are contained in the Section 4.4 of this Plan.

There are two types of quality assurance mechanisms used to ensure the production of analytical data of known and documented quality. The internal quality control procedures for the analytical services are specified under NFESC guidelines and Table 4-8. These specifications include the types of control samples required (sample spikes, surrogate spikes, controls, and blanks), the frequency of each control, the compounds to be used for sample spikes and surrogate spikes, and the quality control acceptance criteria. It will be the laboratory's responsibility to document, in each package, that both initial and ongoing instrument and analytical QC criteria are met. This documentation will be included int he data packages generated by the contract laboratory.

Analytical results of field-collected quality control samples will also be compared to acceptance criteria, and documentation will be performed showing that criteria have been met. Any samples in nonconformance with the QC criteria will be identified and reanalyzed by the laboratory, if possible. The following procedures will be employed for the samples:

- Proper storage of samples.
- Use of qualified and/or certified technicians.
- Use of calibrated equipment.
- Formal independent confirmation of all computation and reduction of laboratory data and results.

- Use of standardized test procedures.

- Inclusion of replicate samples at a frequency of one replicate per 10 samples or one per sample matrix if less than 10 samples are collected.

4.7 PERFORMANCE AND SYSTEM AUDITS

System audits will be performed as appropriate, to assure that the work is being implemented in accordance with the approved project SOPs and in an overall satisfactory manner.

- The FTL will supervise and check on a daily basis that the monitoring wells are installed and developed correctly, field measurements are made accurately, equipment is thoroughly decontaminated, samples are collected and handled property, and the field work is accurately and neatly documented.

- The data validator will review (on a timely basis) the data packages submitted by the laboratory. The data validator will check that the data was obtained through the approved methodology, that the appropriate level of QC effort and reporting was conducted, that holding times were met, and that the results are in conformance with the QC criteria. On the basis of these factors, the data validator will evaluate the data quality and limitations.

- The project manager will oversee the FTL and data validator, and check that management of the acquired data proceeds in an organized and expeditions manner.

- System audits for the laboratory are conducted by NFESC on a regular basis as required.

- A formal audit of the field sampling procedures may be conducted in addition to the auditing that is an inherent part of the daily project activities.

- The auditors will check that sample collection, sample handling, decontamination protocols, and instrument calibration and use are in accordance with the approved project SOPs. The auditors will also check that the field documentation logs and chain-of-custody forms are being filled out properly.

The subcontracted analytical laboratory must be approved by NFESC, be eligible to perform the required analysis under NFESC protocols, and must have site-specific approval prior to commencement of work.

4.8 PREVENTATIVE MAINTENANCE

B&R Environmental has established a program for the maintenance of field equipment to ensure the availability of equipment in good working order when and where it is needed. This program consists of the following elements.:

- The equipment manager keeps an inventory of the equipment in terms of items (model and serial number) quantity and condition. Each item of equipment is signed out when in use, and its operating condition and cleanliness checked upon return.

- The equipment manager conducts routine checks on the status of equipment and is responsible for the stocking of spare parts and equipment readiness.

- The equipment manager maintains the equipment manual library and trains field personnel in the proper use and care of equipment.

- The FTL is responsible for working with the equipment manager to make sure that the equipment is tested, cleaned, charged, and calibrated in accordance with the manufacturer's instructions and B&R Environmental SOPs before being taken to the job site and during field activities.

4.9 CORRECTIVE ACTION

The QA program will enable problems to be identified, controlled, and corrected. Potential problems may involved nonconformance with the SOPs and/or analytical procedures established for the project or other unforseen difficulties. Any person identifying an unacceptable condition will notify the project manager. The project manager with the assistance of the project QA/QC officer, will be responsible for developing and initiating appropriate corrective action and verifying that the correction action has been effective. Corrective actions may include the following: resampling and/or reanalysis of sample, amending or adjusting project procedures. If warranted by the severity of the problem (for example, if a change in the approved work plan is required), the Navy will be notified in writing and their approval will be obtained prior to implementing any change. The EPA and MEDEP will be consulted of any scope changes that may occur while fieldwork is ongoing. Minor changes will be documented to the main file by the B&R Environmental project manager. Additional work that is dependent on a nonconforming activity will not be performed until the problem has been eliminated.

The laboratory maintains an internal closed-loop corrective action system that operates under the direction of the laboratory QA coordinator.

4.10 QUALITY ASSURANCE REPORTS

The QA/QC advisor will review all aspects of the implementation of the Plan on a regular basis and prepare a summary report. Also, monthly progress reports will be sent to NFESC's subcontractor for QA/QC review. Reviews will be performed at the completion of each field activity and reports will be completed at this time. These reports will include an assessment of data quality and the results of system and/or performance audits. Any significant QA deficiencies will be reported and identified, and corrective action possibilities discussed. The laboratory will issue monthly progress reports.

5.0 PREPARATION, EVALUATION, AND RESPONSE FOR GROUNDWATER MONITORING

5.1 DATA ASSESSMENT PROCEDURES

5.1.1 Representativeness, Accuracy, and Precision

All data generated in the investigation will be assessed for its representativeness, accuracy, and precision. The completeness of the data will also be assessed by comparing the valid acquired data to the project objectives to see that these objectives are being addressed and met. The specific procedures used to determine data precision, accuracy, and completeness will be provided in the analytical reports. Accuracy will be determined using laboratory spiked samples and laboratory field blanks.

The representativeness of the data will be assessed by determining if the data are consistent with known or anticipated hydrogeologic or chemical conditions and accepted principles. Field measurements will be checked for completeness of procedures and documentation of procedures and results.

Precision and accuracy will be determined using replicate samples and blank and spiked samples, respectively. The specific procedures for determining PARCC parameters are outlined in Section 4.0.

5.1.2 Data Validation

The Navy will perform full data validation in accordance with current Region I guidelines of ten percent of the samples. Depending on the findings from validating ten percent of the samples, further validation may be conducted if warranted.

5.2 PROCEDURES FOR DETERMINING SIGNIFICANT INCREASES FOR MONITORED CONTAMINANTS AND INDICATOR PARAMETERS

Compliance criteria will be in accordance with the on-shore MPSs and where applicable, the off-shore preliminary remediation goals which are currently under development. The more stringent of on-shore MPSs and off-shore preliminary remediation goals for groundwater will be the basis for identifying contaminants of concern, as a preliminary screening step. Ultimately, groundwater/surface water modelling underway will be the basis for identifying contaminants of concern and contaminant concentrations considered protective.

In the future, if there is an exceedence, the PNS may resample within one month and repeat the analysis for those compounds that exceed the criteria, to confirm the elevated concentration.

Where groundwater is not a potential drinking water source, offshore MPSs for surface water will hopefully be available and evaluated. It is anticipated that, at the time of "subsequent sampling", the analytical results would be compared with both on-shore MPSs and off-shore MPSs as a preliminary screening of the data. This strategy serves as a conservative basis for identifying all potential contaminants of concern by considering the most stringent standard regardless of whether the given site groundwater is fresh or saline/brackish. The evaluation will ultimately consider whether water is fresh or saline/brackish in making recommendations for further monitoring and/or determining the effectiveness of remedial actions (if any). Also, it is unknown at this time whether on-shore or off-shore MPSs are more stringent for a given contaminant. Furthermore, at the JILF some monitoring wells are fresh water wells while others are brackish/saline. Therefore, it is logical to consider both on-shore and off-shore MPSs in the evaluation. In summary, it is premature to propose strict evaluation criteria for "subsequent sampling" at this time. Migration modeling results will also be a key factor in establishing subsequent sampling requirements.

Joint efforts between the Navy, EPA and MEDEP will determine the usefulness of statistical analyses. Upon evaluation of the analytical data, statistical evaluation may be utilized to determine temporal and spatial trends in the data; however, compliance criteria is based on MPSs. Based on existing conditions at the facility, however, statistics are not expected to be utilized in determining variance because 1) contaminant migration has already occurred, 2) complexity of facility hydrogeology, and 3) expectation that contaminants are not normally distributed. In the event that statistical evaluation is performed, variance among samples will be performed using tolerance levels based on normal distribution (or perhaps log normal distribution for data skewed to the left) in accordance with the USEPA's Addendum to the Statistical Guidance Document for Groundwater Monitoring (1992). With this method, a tolerance interval is established for the background well(s) for each monitored constituent of concern. Sample analyses from downgradient wells are then compared to the established tolerance interval, with those values falling above the upper limit of the tolerance interval being considered statistically significant evidence of contamination. A coverage of the tolerance interval of 95% will be used, with tolerance coefficient of 95%. This combination results in a 95% certainty that the results from a well unaffected by the unit operations will not exceed the upper 95% tolerance limit. The procedure for applying this statistical method to the monitoring data is as follows:

(1) Calculate the mean (M) and standard deviation (SD) of the background data set, for each monitored constituent.

(2) Calculate the upper tolerance limit (TL) as follows: TL=M+ (SD)(K), where K is the one sided tolerance factor found in Table 5, Appendix B of EPA's "Guidance Document for Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities" (EPA/530SW89-026).

(3) Compare the data from the downgradient wells to the tolerance limit for each constituent.

Background ranges of values for monitored constituents have not been established yet. Tolerance limits cannot be established until after the collection of four rounds of water quality data from the monitoring wells.

For already contaminated wells, the first two sampling events would first be established as already specified. Then, rather than comparing data solely to the background well(s) for each monitored constituent of concern, data will be further evaluated by calculating a percent change, examining groundwater contours, examining data from nearby monitoring wells, examining the contaminant concentration versus the media protection standard, examining the location of the well with respect to the site boundaries, comparing data to data from previous monitoring events, and any other pertinent data. All these factors will be employed in determining whether an increase/decrease in contaminant concentration represents a fluctuation or a trend. In summary, emphasis is on qualitative evaluation. Statistical analysis will be conducted only if determined to be useful.

The results of each sampling round, along with the applicable data evaluation information, will be forwarded to the appropriate EPA and MEDEP personnel for evaluation. The sampling data for each well will be provided in a table format, with the tolerance limit also presented for each constituent (where statistical evaluation is warranted) for comparative purposes. Downgradient well samples that exhibit statistically significant increases in monitored constituents will be identified and the constituent exceedence levels identified. A project file and computer database will also be kept by the PNS and provided to the EPA and MEDEP with all of the groundwater monitoring data and statistical evaluations.

If future sampling results reveal evidence of significant contaminant increases in any of the monitoring wells, the regulatory authorities will be notified in writing as to:

(1) Identification and concentrations of contaminants of concern

(2) Any proposed changes to the groundwater monitoring system at the facility

(3) Any proposed additions or changes to the monitoring frequency, sampling and analysis procedures or methods

If the number, location, or depth of monitoring wells needs to be modified or evaluation of analytical data is required (e.g., risk assessment calculations), the necessary modifications will be made to bring the groundwater monitoring system into compliance with this requirement. If vertical migration of contaminants is suspected to be a problem, existing deep bedrock monitoring wells DW-7DB at the DRMO and JW-13DB at the JILF will be added to the monitoring program.

If warranted in the future, analytes which are not expected and not detected will be deleted from the analytical program, upon written request by the Navy and approval by the regulatory authorities. Similarly, written request and approval will be obtained in the future prior to switching to other analytical methods which are less expensive, yet include the primary contaminants of concern. One particular modification that could be considered following completion of the first two sampling events may be the reduction of the number of samples analyzed for both filtered and unfiltered metals.

5.3 PROCEDURES FOR ANNUAL DETERMINATION OF AQUIFER FLOW RATE AND DIRECTION

Monitoring wells have been measured for hydraulic conductivity via rising-head or falling-head slug tests. Water levels will be measured twice during each sampling round (to represent high tide and low tide conditions) to determine groundwater flow directions and assess seasonal fluctuations in the water table. The high tide and low tide measurements will provide the maximum range of tidal influence for the given day of testing; conducting two rounds of GW sampling monitoring provide additional information on seasonal fluctuations. Overall average groundwater flow directions and gradients were established during the RFI Data Gap investigation. Additionally, based on water level elevations, potentiometric surface groundwater maps will be prepared for both low tide and high tide conditions for each groundwater report issued.

5.4 REMEDIAL ACTION

A Draft Feasibility Study (FS) (Halliburton NUS, 1995b) has been prepared, and reviewed by the regulatory agencies, to address any remedial action necessary to alleviate existing contamination problems. Migration modeling is now in the planning phase to evaluate the need for remediation, if any. It is currently planned to develop new feasibility studies specific to each Operable Unit; therefore, remedial action will be re-evaluated in the future.

6.0 RECORDKEEPING

6.1 RECORDKEEPING

Records to be maintained for the groundwater monitoring program include well purging/sampling forms, groundwater sample forms, chain-of-custody forms, laboratory analysis results, and static water level records. These records will be maintained by NORTHDIV.

Field personnel will use bound logbooks with sequentially numbered pages for the maintenance of all field records pertaining to sampling activities. These records will be maintained onsite and will document all visual observations, calculations and equipment adjustments. Every entry will be dated, and the time for each entry will be noted. The logbooks are controlled documents that will be properly maintained and retained as part of the project files.

Field notes will be maintained in the following manner:

- Entries into the field notebook will be legibly written in indelible ink.
- A new page will be used at the beginning of each day's activities. This page will identify the date, time, location, onsite personnel, and observed weather conditions.
- Sketches or maps will be included to identify well, sample and/or photograph locations. Maps should include a north arrow and scale.
- Information for water-level measurements will include well numbers, date, time span, and weather conditions.
- Upon sample completion, notes will include date, time, sample locations, and sample ID numbers.
- None of the documents are to be destroyed or thrown away, even if they are illegible or contain inaccuracies.

6.2 DATA MANAGEMENT AND REPORTING

Appropriate data sheets will be used by the laboratory to record analysis data. Records of the groundwater analytical data will be kept in a computer database. A project file will also be kept which will include a copy of the groundwater monitoring data and field notes.

The following information will be reported to the EPA and the Maine Department of Environmental Protection (MEDEP):

- During the first two sampling events and for subsequent sampling/analysis events, concentrations of the analytical parameters for each well will be reported as part of the report, and will be available for regulatory review upon completion of Navy review. In addition, any parameters that exceed the established MPSs will be identified. The data will be presented as a database in an appendix by site. Field parameters will be incorporated into the database also, as requested by the MEDEP. Where an analyte was not detected, the detection limit will be shown with a "U" qualifier. Statistics and tag maps illustrating exceedences of on-shore MPSs are also included.

- If applicable, the Navy will request in writing that certain analytes be deleted from subsequent sampling/analysis events.

- Groundwater contour maps will be produced from each round of water level measurements and submitted to the regulatory agencies as part of the report submittal. Water levels will be measured twice during each sampling round (to represent high tide and low tide conditions) to determine groundwater flow directions and assess seasonal fluctuations in the water table.

A single report will be prepared after the second sampling event is completed. The results of the first sampling event will be provided in the form of tables, maps, and field notes. The groundwater monitoring reports will be presented in the following format:

1.0 Introduction
- 1.1 Purpose
- 1.2 Project Organization and Responsibilities
- 1.3 Scope of Work

2.0 Groundwater Sampling Procedures

- 2.1 Sample Locations and Analytical Methods
- 2.2 Sample Collection Procedures
- 2.3 Water Level Measurements
- 2.4 Measurement of Immiscible Layers

3.0 Results and Data Evaluation

- 3.1 Analytical Results
  - 3.1.1 Analytical Results and Exceedences of Media Protection Standards
  - 3.1.2 Statistical Evaluations
  - 3.1.3 Comparison with Previous Results
- 3.2 Groundwater Flow Directions
  - 3.2.1 Current Groundwater Flow Directions
  - 3.2.2 Comparison with Previous Results

4.0 Recommendations

Maps (Tag Maps and Groundwater Contour Maps)

Appendix A - Field Investigation Forms
Appendix B - Chain of Custody Forms
Appendix C - Field Notes
Appendix D - Analytical Data Base (Limited Data Validation) and Exceedences of Media Protection Standards
Appendix E - Statistical Calculations (if warranted)
Appendix F - Certification for Low-flow Sampling Pumps (first report only)

Letters, reports, etc. requiring geologic interpretation of hydrogeologic data will be signed and stamped by a Maine Certified Geologist. To expedite submittal of information to the regulatory agencies, concurrent review by the regulatory agencies and the Maine Certified Geologist will be conducted. Also, any changes to the monitoring program will be subject to review and comment by the regulators prior to finalization.

7.0 SCHEDULE

The pilot test to determine stabilization of field parameters for low-flow purging was conducted in September of 1996. The groundwater sampling is expected to occur during December, 1996 (first event). Other sampling events will be scheduled at a later date, as necessary. Frequency of monitoring will be determined based on consultation with the Navy, EPA, MEDEP; it is expected that monitoring may occur semi-annually until such time that remedial decisions are made pursuant to CERCLA. A detailed field sampling schedule will be developed and provided to the regulatory agencies.

REFERENCES

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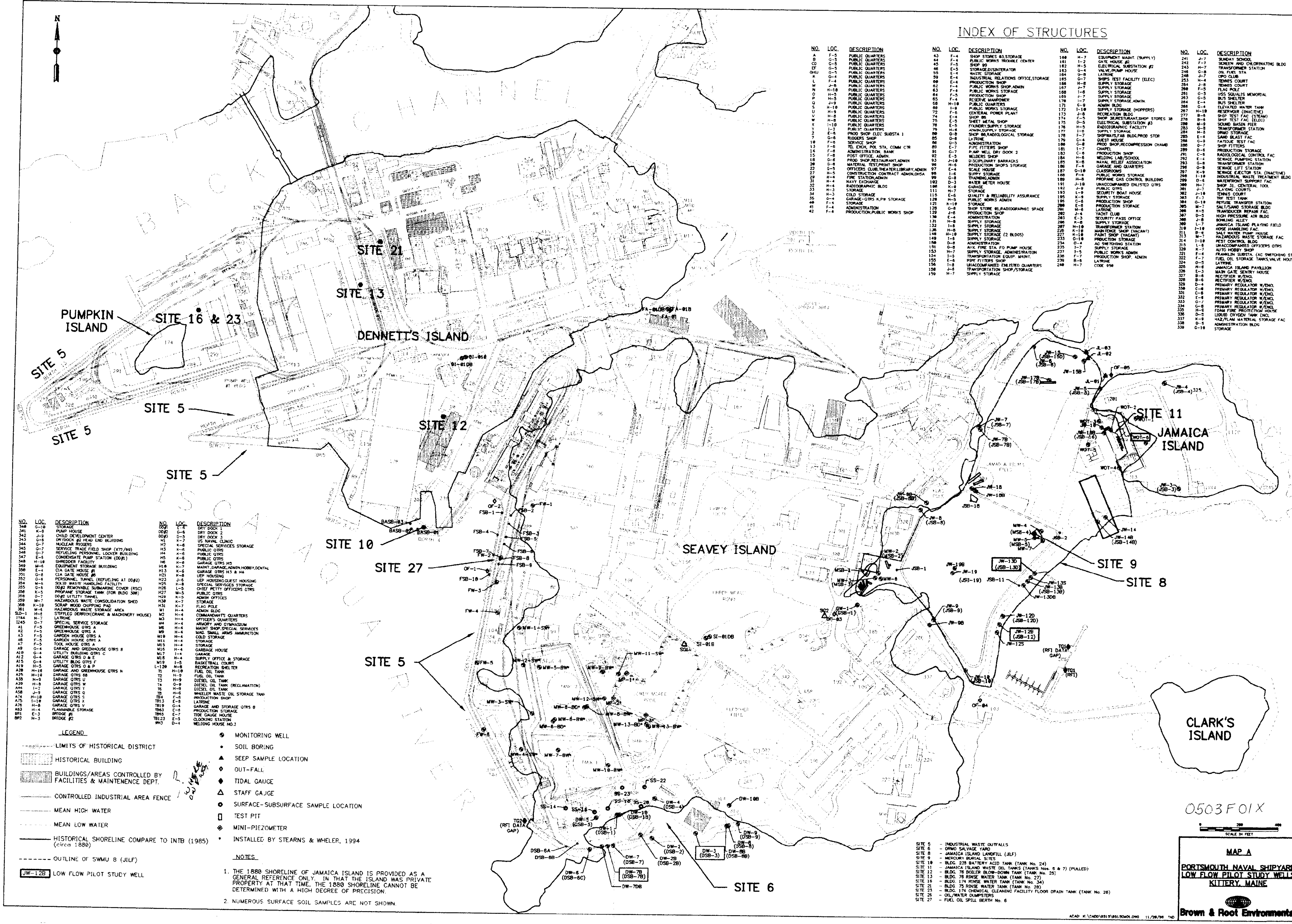
United States Environmental Protection Agency (U.S. EPA), 1989; "Guidance Document for Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities," Table 5, Appendix B (EPA/530SW89-026).



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GHIJ	G-5	PUBLIC QUARTERS
K	G-4	PUBLIC QUARTERS
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336	D-5	LIQUID OXYGEN TANK ENCL
337	K-9	HAZ/FLAM MATERIAL STORAGE FAC
338	D-5	ADMINISTRATION BLDG
339	G-10	STORAGE

NO.	LOC.	DESCRIPTION
340	G-10	STORAGE
341	K-9	PUMP HOUSE
342	J-9	CHILD DEVELOPMENT CENTER
343	G-6	DRYDOCK #2 HEAD END BLUIDING
344	G-7	NUCLEAR RIGGERS
345	G-7	SERVICE TRADE FIELD SHOP (X72/99)
346	G-7	REFUELING PERSONNEL LOCKER BUILDING
347	E-6	CONDENSATE PUMP STATION (DD#1)
348	H-10	SHREDDER FACILITY
349	M-6	EQUIPMENT STORAGE BUILDING
350	E-4	CIA GATE HOUSE #1
351	G-8	CIA GATE HOUSE #6
352	G-8	PERSONNEL TUNNEL (REFUELING AT DD#2)
354	M-6	SOLID WASTE HANDLING FACILITY
355	G-6	DD#2 REMOVABLE SUBMARINE COVER (RSC)
356	K-5	PROPANE STORAGE TANK (FOR BLDG 306)
358	G-7	DD#2 UITLITY TUNNEL
359	M-7	HAZARDOUS WASTE CONSOLIDATION SHED
360	K-10	SCRAP WOOD CHIPPING PAD
361	M-6	HAZARDOUS WASTE STORAGE AREA
SLD-1	H-8	STIFFLEG DERRICK(CRANE & MACHINERY HOUSE)
IY44	N-7	LATRINE
IZ45	O-7	SPECIAL SERVICE STORAGE
A1	F-5	GREENHOUSE QTRS A
A2	F-5	GREENHOUSE QTRS A
A3	F-5	GARDEN HOUSE QTRS A
A6	F-5	GARDEN HOUSE QTRS A
A7	F-5	TOOL HOUSE QTRS A
A9	G-4	GARAGE AND GREENHOUSE QTRS B
A10	G-4	UTILITY BUILDING QTRS C
A12	G-4	GARAGE QTRS D & E
A15	G-4	UTILITY BLDG QTRS F
A19	H-5	GARAGE QTRS O & P
A20	H-10	GARAGE AND GREENHOUSE QTRS N
A25	H-10	GARAGE QTRS 68
A38	H-9	GARAGE QTRS U
A39	H-8	GARAGE QTRS W
A44	I-2	GARAGE QTRS Y
A58	J-9	GARAGE QTRS Q
A74	H-10	GARAGE QTRS S
A75	I-10	GARAGE QTRS X
A76	H-8	GARAGE QTRS V
A83	H-4	FLAMMABLE STORAGE
BR1	E-3	BRIDGE #1
BR2	H-3	BRIDGE #2

NO.	LOC.	DESCRIPTION
DD#1	E-6	DRY DOCK 1
DD#2	G-6	DRY DOCK 2
DD#3	D-5	DRY DOCK 3
H1	K-7	US NAVAL CLINIC
H2	K-6	SPECIAL SERVICES STORAGE
H3	K-6	PUBLIC QTRS
H4	K-6	PUBLIC QTRS
H5	K-6	PUBLIC QTRS
H6	K-6	GARAGE QTRS H5
H10	K-7	MAINT.,GARAGE,ADMIN,HOBBY,DENTAL
H13	K-6	GARAGE QTRS H3 & H4
H21	K-6	UEP HOUSING
H23	J-6	UEP HOUSING,GUEST HOUSING
H25	K-8	SPECIAL SERVICES STORAGE
H26	L-5	CHIEF PETTY OFFICERS QTRS
H27	M-5	PUBLIC QTRS
H29	K-5	ADMIN OFFICES
H30	K-7	STORAGE
H31	K-7	FLAG POLE
M1	H-4	ADMIN BLDG
M2	H-4	COMMANDANT'S QUARTERS
M3	H-4	OFFICER'S QUARTERS
M4	H-4	ARMORY AND GYMNASIUM
M6	H-4	MAINT SHOP,SPECIAL SERVICES
M9	H-4	MAG. SMALL ARMS AMMUNITION
M10	H-4	COLD STORAGE
M11	H-4	STORAGE
M15	H-4	STORAGE
M16	H-4	GARBAGE HOUSE
M17	I-4	GARAGE
M18	H-4	SUPPLY OFFICE & STORAGE
M19	I-5	BASKETBALL COURT
L-120	N-8	RECREATION SHELTER
T1	H-10	FUEL OIL TANK
T2	H-9	FUEL OIL TANK
T3	H-9	DIESEL OIL TANK
T4	G-9	DIESEL OIL TANK (RECLAMATION)
T6	H-9	DIESEL OIL TANK
T8	H-6	WHEELER WASTE OIL STORAGE TANK
TB4	E-6	PRODUCTION SHOP
TB13	E-8	LATRINE
TB19	G-4	GARAGE AND STORAGE QTRS B
TB63	E-6	PRODUCTION STORAGE
TB65	E-7	TIDE GAUGE HOUSE
TB123	E-5	CLOCKING STATION
WH3	D-4	WELDING HOUSE NO.3

LEGEND

- LIMITS OF HISTORICAL DISTRICT
- HISTORICAL BUILDING
- BUILDINGS/AREAS CONTROLLED BY FACILITIES & MAINTENENCE DEPT.
- CONTROLLED INDUSTRIAL AREA FENCE
- MEAN HIGH WATER
- MEAN LOW WATER
- HISTORICAL SHORELINE COMPARE TO INTB (1985) (circa 1880)
- OUTLINE OF SWMU 8 (JILF)
- JW-12B LOW FLOW PILOT STUDY WELL
- MONITORING WELL
- SOIL BORING
- SEEP SAMPLE LOCATION
- OUT-FALL
- TIDAL GAUGE
- STAFF GAUGE
- SURFACE-SUBSURFACE SAMPLE LOCATION
- TEST PIT
- MINI-PIEZOMETER
- * INSTALLED BY STEARNS & WHELER, 1994

NOTES

1. THE 1880 SHORELINE OF JAMAICA ISLAND IS PROVIDED AS A GENERAL REFERENCE ONLY. IN THAT THE ISLAND WAS PRIVATE PROPERTY AT THAT TIME, THE 1880 SHORELINE CANNOT BE DETERMINED WITH A HIGH DEGREE OF PRECISION.
2. NUMEROUS SURFACE SOIL SAMPLES ARE NOT SHOWN.

SITE 5 - INDUSTRIAL WASTE OUTFALLS
SITE 6 - DRMO SALVAGE YARD
SITE 8 - JAMAICA ISLAND LANDFILL (JILF)
SITE 9 - MERCURY BURIAL SITES
SITE 10 - BLDG. 238 BATTERY ACID TANK (TANK No. 24)
SITE 11 - JAMAICA ISLAND WASTE OIL TANKS (TANKS Nos. 6 & 7) (PULLED)
SITE 12 - BLDG. 76 BOILER BLOW-DOWN TANK (TANK No. 25)
SITE 13 - BLDG. 76 RINSE WATER TANK (TANK No. 27)
SITE 16 - BLDG. 174 RINSE WATER TANK (TANK No. 34)
SITE 21 - BLDG. 75 RINSE WATER TANK (TANK No. 28)
SITE 23 - BLDG. 174 CHEMICAL CLEANING FACILITY FLOOR DRAIN TANK (TANK No. 26)
SITE 26 - OIL/WATER DUMPSTERS
SITE 27 - FUEL OIL SPILL BERTH No. 6

MAP A

PORTSMOUTH NAVAL SHIPYARD LOW FLOW PILOT STUDY WELLS KITTERY, MAINE

Brown & Root Environmental

ACAD: K:\CADD\8515\8515CM01.DWG 11/20/98 TAD

APPENDIX A

FIELD INVESTIGATION FORMS

GROUNDWATER
SAMPLE LOG SHEET

Page ____ of ____

Project Site Name: _____

Project No.: _____

☐ Domestic Well Data
☐ Monitoring Well Data
☐ Other Well Type: _____
☐ QA Sample Type: _____

Sample ID No.: _____

Sample Location: _____

Sampled By: _____

C.O.C. No.: _____

Sampling Data

Date: _____ Time: _____ Method: _____	pH	S.C.	Temp. (°C)	Turbidity	Color	TBD	TBD	TBD

Purge Data

Date: _____ Method: _____	Volume	pH	S.C.	Temp.(°C)	Turbidity	Color	TBD	TBD
	Initial							
Monitor Reading (ppm):	1							
Well Casing Dia. & Material Type:	2							
	3							
Total Well Depth (TD):	4							
Static Water Level (WL):	5							
TD-WL (ft.) =								
One Casing Volume: (gal/L)								
Start Purge (hrs.):								
End Purge (hrs.):								
Total Purge Time (min):								
Total Amount Purged (gal/L):								

Analysis	Preservative	Container Requirements	Collected (✓)

Observations/Notes:

Circle if Applicable:		Signature(s):
MS/MSD	Duplicate ID No:	

TBD: To Be Determined

LOW FLOW PURGE DATA SHEET

PROJECT SITE NAME: _____ WELL I.D.: _____

PROJECT NUMBER: _____ DATE: _____

Time (Hrs.)	Water Level (Ft. below TOC)	Flow (mL/Min.)	Temp. (Celcius)	pH (S.U.)	Cond.	DO (mg/L)	Sal. %	Turb. (NTU)	Comments

SIGNATURE(S) _____ PAGE __ of __

GROUNDWATER LEVEL MEASUREMENT SHEET

Page ___ of ___

PROJECT NAME: _____ LOCATION: _____
PROJECT NUMBER: _____ MEASURING DEVICE: _____
PERSONNEL: _____ ADJUSTMENT FACTOR: _____
DATE: _____ REMARKS: _____
WEATHER CONDITIONS: _____

Well or Piezometer Number	Time	Elevation of Reference Point (Feet)*	Water Level Indicator Reading (Feet)*	Groundwater Elevation (Feet)*	Comments

*Measurements to nearest 0.01 foot.

Signature(s): _____

Brown & Root Environmental

EQUIPMENT CALIBRATION LOG

INSTRUMENT NAME / MODEL : _____

JOB NAME : _____

MANUFACTURER : _____

JOB NUMBER : _____

CALIBRATION DATE	INITIAL SETTINGS	STANDARDS USED	PROCEDURE	ADJUSTMENTS MADE	FINAL SETTINGS	SIGNATURE	COMMENTS

CHAIN OF CUSTODY RECORD

PROJECT NO.:	SITE NAME:
SAMPLERS (SIGNATURE):	

STATION NO.	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CON-TAINERS							REMARKS

RELINQUISHED BY (SIGNATURE):	DATE / TIME:	RECEIVED BY(SIGNATURE):	RELINQUISHED BY (SIGNATURE):	DATE / TIME:	RECEIVED BY(SIGNATURE):
RELINQUISHED BY (SIGNATURE):	DATE / TIME:	RECEIVED BY (SIGNATURE):	RELINQUISHED BY (SIGNATURE):	DATE / TIME:	RECEIVED BY(SIGNATURE):
RELINQUISHED BY (SIGNATURE):	DATE / TIME:	RECEIVED FOR LABORATORY BY (SIGNATURE):	DATE / TIME:	REMARKS:	

Order No. 70440 (0693)

APPENDIX B

STANDARD OPERATING PROCEDURES (SOPS)

Sampling

SA-6.1, Section 5.0: Sample Identification and Chain of Custody

SA-6.2, Section 5.0: Sample Packaging and Shipping

SA-6.3, Section 5.0: Site Logbook

Support Field Methods

SF-1.2, Section 5.0: Sample Preservation

SF-2.3, Section 5.0: Decontamination of Chemical Sampling and Field Analytical Equipment

Hydrogeology

GH-2.5, Section 5.0: Water Level Measurement / Contour Mapping

Other

US EPA Region I - Low Flow Purging and Sampling Procedure

4.0 RESPONSIBILITIES

Field Operations Leader - Responsible for determining that chain-of-custody procedures are implemented up to and including release to the shipper.

Field Samplers - Responsible for initiating the Chain-of-Custody Record and maintaining custody of samples until they are relinquished to another custodian, to the shipper, or to the common carrier.

Remedial Investigation Leader - Responsible for determining that chain-of-custody procedures have been met by the sample shipper and analytical laboratory.

5.0 PROCEDURES

5.1 OVERVIEW

The term "chain-of-custody" refers to procedures which ensure that evidence presented in a court of law is what it is represented to be. The chain-of-custody procedures track the evidence from the time and place it is first obtained to the courtroom and, secondly, provide security for the evidence as it is moved and/or passes from the custody of one individual to another.

Chain-of-custody procedures, recordkeeping, and documentation are an important part of the management control of samples. Regulatory agencies must be able to provide the chain of possession and custody of any samples that are offered for evidence, or that form the basis of analytical test results introduced as evidence. Written procedures must be available and followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed.

5.2 SAMPLE IDENTIFICATION

The method of identification of a sample depends on the type of measurement or analysis performed. When in-situ measurements are made, the data are recorded directly in bound logbooks or other field data records, with identifying information.

5.2.1 Sample Label

Samples, other than in-situ measurements, are removed and transported from the sample location to a laboratory or other location for analysis. Before removal, however, a sample is often divided into portions, depending upon the analyses to be performed. Each portion is preserved in accordance with the Sampling Plan. Each sample container is identified by a sample label (see Attachment B). Sample labels are provided by the PMO. The information recorded on the sample label includes:

- **Project**: EPA Work Assignment Number (can be obtained from the Sampling Plan).
- **Station Location**: The unique sample number identifying this sample (can be obtained from the Sampling Plan).
- **Date**: A six-digit number indicating the day, month, and year of sample collection; e.g., 12/21/85.
- **Time**: A four-digit number indicating the 24-hour time of collection (for example: 0954 is 9:54 a.m., and 1629 is 4:29 p.m.).
- **Medium**: Water, soil, sediment, sludge, waste, etc.

- **Concentration**: The expected concentration (i.e., low, medium, high).
- **Sample Type**: Grab or composite.
- **Preservation**: Type of preservation added and pH levels.
- **Analysis**: VOA, BNAs, PCBs, pesticides, metals, cyanide, other.
- **Sampled By**: Printed name of the sampler.
- **Case Number**: Case number assigned by the Sample Management Office.
- **Traffic Report Number**: Number obtained from the traffic report labels.
- **Remarks**: Any pertinent additional information.

Using just the work assignment number of the sample label maintains the anonymity of sites. This may be necessary, even to the extent of preventing the laboratory performing analysis from knowing the identity of the site (e.g., if the laboratory is part of an organization that has performed previous work on the site).

5.2.2 Sample Identification Tag

A Sample Identification Tag (Attachment F) must also be used for samples collected for CLP (Contract Laboratory Program) analysis. The Sample Identification Tag is a white, waterproof paper label, approximately 3-by-6 inches, with a reinforced eyelet, and string or wire for attachment to the neck of the sample bottle. The Sample Tag is a controlled document, and is provided by the regional EPA office. Following sample analysis, the Sample Tag is retained by the laboratory as evidence of sample receipt and analysis.

The following information is recorded on the tag:

- **Project Code**: Work Assignment Number.
- **Station Number**: The middle portion of the Station Location Number, (between the hyphens).
- **Month/Day/Year**: Same as Date on Sample Label.
- **Time**: Same as Time on Sample Label.
- **Designate - Comp/Grab**: Composite or grab sample.
- **Station Location**: Same as Station Location on Sample Label.
- **Samplers**: Same as Sampled By on Sample Label.
- **Preservative**: Yes or No.
- **Analyses**: Check appropriate box(es).

- **Remarks**: Same as Remarks on Sample Label (make sure the Case Number and Traffic Report numbers are recorded).

- **Lab Sample Number**: For laboratory use only.

The tag is then tied around the neck of the sample bottle.

If the sample is to be split, it is aliquoted into similar sample containers. Identical information is completed on the label attached to each split.

Blank, duplicate, or field spike samples shall not be identified as such on the label, as they may compromise the quality control function. Sample blanks, duplicates, spikes, and splits are defined in Procedure SA-6.6.

5.3 CHAIN-OF-CUSTODY PROCEDURES

After collection, separation, identification, and preservation, the sample is maintained under chain-of-custody procedures until it is in the custody of the analytical laboratory and has been stored or disposed of.

5.3.1 Field Custody Procedures

- Samples are collected as described in the site-specific Sampling Plan. Care must be taken to record precisely the sample location and to ensure that the sample number on the label matches the sample log sheet and Chain-of-Custody Record exactly.

- The person undertaking the actual sampling in the field is responsible for the care and custody of the samples collected until they are properly transferred or dispatched.

- When photographs are taken of the sampling as part of the documentation procedure, the name of the photographer, date, time, site location, and site description are entered sequentially in the site logbook as photos are taken. Once developed, the photographic prints shall be serially numbered, corresponding to the logbook descriptions.

- Sample labels shall be completed for each sample, using waterproof ink unless prohibited by weather conditions, e.g., a logbook notation would explain that a pencil was used to fill out the sample label because a ballpoint pen would not function in freezing weather.

5.3.2 Transfer of Custody and Shipment

Samples are accompanied by a Chain-of-Custody Record Form. Chain-of-Custody Record Forms used in EPA Regions I-IV are shown in Attachments A through D. The appropriate form shall be obtained from the EPA Regional Office. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the Record. This Record documents sample custody transfer from the sampler, often through another person, to the analyst in the laboratory. The Chain-of-Custody Record is filled out as follows:

- Enter header information (project number, samplers, and project name -- project name can be obtained from the Sampling Plan).

- Sign, date, and enter the time under "Relinquished by" entry.

- Enter station number (the station number is the middle portion of the station location number, between the hyphens).
- Check composite or grab sample.
- Enter station location number (the same number as the station location on the tag and label).
- Enter the total number of containers per station number and the type of each bottle.
- Enter either the inorganic traffic report number, the organic traffic report number, or the SAS number for each station number in the remarks column.
- Enter the tag number from the bottom of the sample identification tag in the remarks column for each station location.
- Make sure that the person receiving the sample signs the "Received by" entry, or enter the name of the carrier (e.g., UPS, Federal Express) under "Received by." Receiving laboratory will sign "Received for Laboratory by" on the lower line and enter the date and time.
- Enter the bill-of-lading or Federal Express airbill number under "Remarks," in the bottom right corner, if appropriate.
- Place the original (top, signed copy) of the Chain-of-Custody Record Form in the appropriate sample shipping package. Retain the pink copy with field records.
- Sign and date the custody seal, a 1- by 3-inch white paper label with black lettering and an adhesive backing. Attachment G is an example of a custody seal. The custody seal is part of the chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field. Custody seals are provided by ZPMO on an as-needed basis.
- Place the seal across the shipping container opening so that it would be broken if the container is opened.
- Complete other carrier-required shipping papers.

The custody record is completed using black waterproof ink. Any corrections are made by drawing a line through and initialing and dating the change, then entering the correct information. Erasures are not permitted.

Common carriers will usually not accept responsibility for handling Chain-of-Custody Record Forms; this necessitates packing the record in the sample container (enclosed with other documentation in a plastic zip-lock bag). As long as custody forms are sealed inside the sample container and the custody seals are intact, commercial carriers are not required to sign off on the custody form.

If sent by mail, the package will be registered with return receipt requested. If sent by common carrier or air freight, proper documentation must be maintained.

The laboratory representative who accepts the incoming sample shipment signs and dates the Chain-of-Custody Record, completing the sample transfer process. It is then the laboratory's responsibility to maintain internal logbooks and custody records throughout sample preparation and analysis.

ATTACHMENT A
CHAIN-OF-CUSTODY RECORD FORM FOR USE IN REGION I
(Original is 8-1/2 by 11)

	PROJECT NAME					NO. OF CON-TAINERS	REMARKS
SAMPLERS: *(Signature)*							
STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION		

Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date / Time	Received for Laboratory by: *(Signature)*	Date / Time	Remarks:	

ATTACHMENT E
SAMPLE LABEL

NUS CORPORATION PROJECT: _____

STATION LOCATION: _____

DATE: ___/___/___ TIME: _____ hrs.

MEDIA: WATER ☐ SOIL ☐ SEDIMENT ☐ _____ ☐

CONCENTRATION: LOW ☐ MED ☐ HIGH ☐

TYPE: GRAB ☐ COMPOSITE ☐

ANALYSIS	PRESERVATION
VOA ☐ BNA's ☐	Cool to 4°C ☐
PCB's ☐ PESTICIDES ☐	HNO_3 to pH <2 ☐
METALS: TOTAL ☐ DISSOLVED ☐	NAOH to pH>12 ☐
CYANIDE ☐	_____ ☐
_____ ☐	

Sampled by: _____

Case No.: _____ Traffic Report No.: _____

Remarks:

ACFILE: FORMS\BOTLABL

ATTACHMENT G
CHAIN-OF-CUSTODY SEAL

CUSTODY SEAL

Date

Signature

NUS CORPORATION

NUS CORPORATION

CUSTODY SEAL

Date

Signature

5.3.3 Receipt for Samples Form

Whenever samples are split with a private party or government agency, a separate Receipt for Samples Record Form is prepared for those samples and marked to indicate with whom the samples are being split. The person relinquishing the samples to the party or agency shall require the signature of a representative of the appropriate party acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Received by" space. When appropriate, as in the case where the representative is unavailable, the custody record shall contain a statement that the samples were delivered to the designated location at the designated time. This form must be completed and a copy given to the owner, operator, or agent-in-charge even if the offer for split samples is declined. The original is retained by the Field Operations Leader.

6.0 REFERENCES

U.S. EPA, 1984. User's Guide to the Contract Laboratory Program, Office of Emergency and Remedial Response, Washington, D.C.

7.0 ATTACHMENTS

Attachment A - Chain-of-Custody Record Form for use in Region I
~~Attachment B - Chain-of-Custody Record Form for use in Region II~~
~~Attachment C - Chain-of-Custody Record Form for use in Region III~~
~~Attachment D - Chain-of-Custody Record Form for use in Region IV~~
Attachment E - Sample Label
~~Attachment F - Sample Identification Tag~~
Attachment G - Chain-of-Custody Seal

Reportable Quantity (RQ) - A parenthetical note of the form "(RQ-1000/454)" following an entry in the DOT Hazardous Materials table (49 CFR 172.101) indicates the reportable quantity of the substance in pounds and kilograms. If a spill of that amount or more of the substance occurs during transit or storage, a report must be filed with DOT according to ¥171.15-15 concerning hazardous materials incidents reports. If the material spilled is a hazardous waste, a report must always be filed, regardless of the amount, and must include a copy of the manifest. If the RQ notation appears, it must be shown either immediately before or after the proper shipping name on the shipping paper (or manifest). Most shipping papers and manifests will have a column designated "HM" which may be used for this purpose.

4.0 RESPONSIBILITIES

Field Operations Leader or Team Sampling Leader - responsible for determining that samples are properly packaged and shipped.

Sampling Personnel - responsible for implementing the packaging and shipping requirements.

5.0 PROCEDURES

5.1 INTRODUCTION

Samples collected for shipment from a site shall be classified as either environmental or hazardous material (or waste) samples. In general, environmental samples are collected off-site (for example from streams, ponds, or wells) and are not expected to be grossly contaminated with high levels of hazardous materials. On-site samples (for example, soil, water, and materials from drums or bulk storage tanks, obviously contaminated ponds, lagoons, pools, and leachates from hazardous waste sites) are considered hazardous. A distinction must be made between the two types of samples in order to:

- Determine appropriate procedures for transportation of samples. If there is any doubt, a sample shall be considered hazardous and shipped accordingly.
- Protect the health and safety of laboratory personnel receiving the samples. Special precautions are used at laboratories when samples other than environmental samples are received.

5.2 ENVIRONMENTAL SAMPLES

5.2.1 Packaging

Environmental samples may be packaged following the procedures outlined in Section 5.4 for samples classified as "flammable liquids" or "flammable solids." Requirements for marking, labeling, and shipping papers do not apply.

Environmental samples may also be packed without being placed inside metal cans as required for flammable liquids or solids.

- Place sample container, properly identified and with a sealed lid, in a polyethylene bag, and seal the bag.
- Place sample in a fiberboard container or metal picnic cooler which has been lined with a large polyethylene bag.
- Pack with enough noncombustible, absorbent, cushioning materials to minimize the possibility of the container breaking.
- Seal large bag.
- Seal or close outside container.

5.2.2 Marking Labeling

Sample containers must have a completed sample identification tag and the outside container must be marked "Environmental Sample." The appropriate side of the container must be marked "This End Up" and arrows placed appropriately. No DOT marking or labeling are required.

5.2.3 Shipping Papers

No DOT shipping papers are required. However, the appropriate chain-of-custody forms must be included with the shipment.

5.2.4 Transportation

There are no DOT restrictions on mode of transportation.

5.3 DETERMINATION OF SHIPPING CLASSIFICATION FOR HAZARDOUS MATERIAL SAMPLES

Samples not determined to be environmental samples, or samples known or expected to contain hazardous materials, must be considered hazardous material samples and transported according to the requirements listed below.

5.3.1 Known Substances

If the substance in the sample is known or can be identified, package, mark, label and ship according to the specific instructions for that material (if it is listed) in the DOT Hazardous Materials Table, 49 CFR 172.101.

Unz and Company have published the following steps to help in locating a proper shipping name from the Hazardous Materials Table, 49 CFR 172.101.

1. Look first for the chemical or technical name of the material, for example, ethyl alcohol. Note that many chemicals have more than one technical name, for example, perchloroethylene (not listed in 172.101) is also called tetrachloroethylene (listed 172.101). It may be useful to consult a chemist for all possible technical names a material can have. If your material is not listed by its technical name then. . . . . .

1.0 PURPOSE

This procedure describes the process for keeping a site logbook.

2.0 SCOPE

The site logbook is a controlled document which records all major on-site activities during a Remedial Investigation/Feasibility Study. At a minimum, the following activities/events shall be recorded in the site logbook:

- Arrival/departure of site visitors
- Arrival/departure of equipment
- Sample pickup (chain-of-custody form numbers, carrier, time)
- Sampling activities/sample logsheet numbers
- Start or completion of borehole/trench/monitoring well installation or sampling activities
- Health and Safety issues

The site logbook is initiated at the start of the first on-site activity (e.g., initial reconnaissance survey). Entries are made for every day that on-site activities take place which involve RI/FS contractor personnel. One current site logbook is maintained per site.

The site logbook becomes part of the permanent site file maintained in the RI contractor's office. Because information contained in the site logbook may be admitted as evidence in cost recovery or other legal proceedings, it is critical that this document be properly maintained.

3.0 GLOSSARY

Site Logbook - The logbook is a bound notebook with consecutively numbered pages that cannot be removed. Upon entry of data, the logbook requires signature by the responsible site leader (see Section 5.1).

4.0 RESPONSIBILITIES

The site logbook is issued by the Regional Manager (or his designee) to the Site Manager for the duration of the project. The Site Manager releases the site logbook to the Field Operations Leader or other person responsible for the direction of on-site activities (e.g., Reconnaissance Survey Team Leader, Sampling Team Leader). It is the responsibility of this person (or his designee) to keep the site logbook current while in his possession, and return it to the Site Manager or turn it over to another field team. Following the completion of all fieldwork, the site logbook is returned to the Site Manager for inclusion in the permanent site files.

5.0 PROCEDURES

5.1 GENERAL

The cover of each site logbook contains the following information:

- Project Name
- NUS Project Number
- RI/FS Contractor and Site Manager's Name
- Sequential Book Number

- Start Date
- End Date

Daily entries into the logbook may contain a variety of information. At the beginning of each day the following information must be recorded:

- Date
- Start time
- Weather
- All field personnel present
- Any visitors present

During the day, a summary of all site activities and level of personal protection shall be recorded in the logbook. The information need not duplicate that recorded in other field notebooks (e.g., sample logbook, Site Geologist's notebook, Health and Safety Officer's notebook, etc.), but shall summarize the contents of these other notebooks and refer to the page locations in these notebooks for detailed information. An example of a site logbook page is shown in Attachment A.

The sample logsheet for each sample collected (see Procedure SA-6.6) must be referenced. If measurements are made at any location, the measurements and equipment used must either be recorded in the site logbook or reference must be made to the notebook and page number(s) on which they are recorded (see Attachment A).

All entries shall be made in black pen. No erasures are permitted. If an incorrect entry is made, the data shall be crossed out with a single strike mark, and initialed and dated. At the completion of entries by any individual, the logbook must be signed. It must also be signed by the Field Operations Leader or responsible site leader at the end of each day.

5.2 PHOTOGRAPHS

When movies, slides, or photographs are taken of a site or any monitoring location, they are numbered to correspond to logbook entries. The name of the photographer, date, time, site location, site description, and weather conditions are entered in the logbook as the photographs are taken. A series entry may be used for rapid-sequence photographs. The photographer is not required to record the aperture settings and shutter speeds for photographs taken within the normal automatic exposure range. However, special lenses, films, filters, and other image-enhancement techniques must be noted in the logbook. If possible, such techniques shall be avoided, since they can adversely affect the admissibility of photographs as evidence. Chain-of-custody procedures depend upon the subject matter, type of film, and the processing it requires. Film used for aerial photography, confidential information, or criminal investigation require chain-of-custody procedures. Adequate logbook notation and receipts may be used to account for routine film processing. Once processed, the slides of photographic prints shall be serially numbered and labeled according to the logbook descriptions.

6.0 REFERENCES

None.

7.0 ATTACHMENTS

Attachment A - Typical Site Logbook Entry

ATTACHMENT A
TYPICAL SITE LOGBOOK ENTRY

START TIME: _____ DATE: _____

SITE LEADER: _____
PERSONNEL:

NUS	DRILLER	EPA
_____	_____	_____
_____	_____	_____
_____	_____	_____

WEATHER: Clear, 68°F, 2-5 mph wind from SE

ACTIVITIES:

1. Steam jenney and fire hoses were set up.

2. Drilling activities at well _____ resumes. Rig geologist was _____. See Geologist's Notebook, No. 1, page 29-30, for details of drilling activity. Sample No. 123-21-S4 collected; see sample logbook, page 42. Drilling activities completed at 11:50 and a 4 inch stainless steel well installed. See Geologist's Notebook, No. 1, page 31, and well construction details for well _____.

3. Drilling rig No. 2 steam-cleaned at decontamination pit. Then set up at location of well _____.

4. Well _____ drilled. Rig geologist was _____. See Geologist's Notebook, No. 2, page _____ for details of drilling activities. Sample numbers 123-22-S1, 123-22-S2, and 123-22-S3 collected; see sample logbook, pages 43, 44, and 45.

5. Well _____ was developed. Seven 55-gallon drums were filled in the flushing stage. The well was then pumped using the pitcher pump for 1 hour. At the end of the hour, water pumped from well was "sand free."

6. EPA remedial project manger arrives on-site at 14:25 hours.

7. Large dump truck arrives at 14:45 and is steam-cleaned. Backhoe and dump truck set up over test pit _____.

8. Test pit _____ dug with cuttings placed in dump truck. Rig geologist was _____. See Geologist's Notebook, No. 1, page 32, for details of test pit activities. Test pit subsequently filled. No samples taken for chemical analysis. Due to shallow groundwater table, filling in of test pit _____ resulted in a very soft and wet area. A mound was developed and the area roped off.

9. Express carrier picked up samples (see Sample Logbook, pages 42 through 45) at 17:50 hours. Site activities terminated at 18:22 hours. All personnel offsite, gate locked.

_____
Field Operations Leader

1.0 PURPOSE

This procedure describes the appropriate containers to be used for samples depending on the analyses to be performed, and the steps necessary to preserve the samples when shipped offsite for chemical analysis.

2.0 SCOPE

Different types of chemicals react differently with sample containers made of various materials. For example, trace metals adsorb more strongly to glass than to plastic, while many organic chemicals may dissolve various types of plastic containers. It is therefore critical to select the correct container in order to maintain the quality of the sample prior to analysis.

Many water and soil samples are unstable, and therefore require preservation when the time interval between field collection and laboratory analysis is long enough to produce changes in either the concentration or the physical condition of the constituent(s) requiring analysis. While complete and irreversible preservation of samples is not possible, preservation does retard the chemical and biological changes that inevitably take place after the sample is collected.

Preservation techniques are usually limited to pH control, chemical addition(s) and refrigeration/freezing. Their purpose is to (1) retard biological activity, (2) retard hydrolysis of chemical compounds/complexes, (3) reduce constituent volatility, and (4) reduce adsorption effects.

3.0 GLOSSARY

HCl - Hydrochloric Acid
H_2SO_4 - Sulfuric Acid
HNO_3 - Nitric Acid
NaOH - Sodium Hydroxide

Normality (N) - Concentration of a solution expressed as equivalent per liter, an equivalent being the amount of a substance containing one gram-atom of replaceable hydrogen or its equivalent. Thus, a one molar solution of HCl, containing one gram-atom of H, is "one-normal," while a one molar solution of H_2SO_4 containing two gram-atoms of H, is "two-normal."

4.0 RESPONSIBILITIES

Field Operations Leader - retains overall responsibility for the proper storage and preservation of samples. During the actual collection of samples, the sampling technician(s) will be directly responsible for the bottling, preservation, labeling, and custody of the samples they collect until released to another party for storage or transport to the analytical laboratory.

5.0 PROCEDURES

5.1 SAMPLE CONTAINERS

For most samples and analytical parameters either glass or plastic containers are satisfactory. In general, if the analyte(s) to be determined is organic in nature, the container shall be made of glass. If the analyte(s) is inorganic, then the container shall be plastic. Since container specification will depend on the analyte and sample matrix types (as indicated in Attachment A) duplicate samples shall be taken when both organic and inorganic analyses are required. Containers shall be kept in the

dark (to minimize biological or photooxidation/photolysis breakdown of constituent) until they reach the analytical laboratory. The sample container shall allow approximately 5-10 percent air space ("ullage") to allow for expansion/vaporization if the sample is heated during transport (1 liter of water at 4°C expands by 15 ml if heated to 130°F/55°C), however, head space for volatile organic analyses shall be omitted.

For CLP laboratories, containers will be obtained through the CLP Sample Management Office. For Responsible party actions or non-CLP laboratories, the laboratory shall provide containers that have been cleaned according to U.S. EPA procedures. Sufficient lead time shall be allowed. Shipping containers for samples, consisting of sturdy ice chests, are provided by the laboratory of the remedial investigation contractor.

Once opened, the container must be used at once for storage of a particular sample. Unused but opened containers are to be considered contaminated and must be discarded; because of the potential for introduction of contamination, they cannot be reclosed and saved for later use. Likewise, any unused containers which appear contaminated upon receipt, or which are found to have loose caps or missing Teflon liner (if required for the container) shall be discarded.

General sample container and sample volume requirements are listed in Attachment A. Specific container requirements are listed in Attachment B.

5.2 PRESERVATION TECHNIQUES

The preservation techniques to be used for various analytes are listed in Attachments A and B. Reagents required for sample preservation will either be added to the sample containers by the laboratory prior to their shipment to the Field or added in the Field. In general, aqueous samples of low concentration organics (or soil samples of low or medium concentration organics) are cooled to 4°C. Medium concentration aqueous samples and high hazard organics sample are not preserved. Low concentration aqueous samples for metals are acidified with HNO_3, while medium concentration and high hazard aqueous metal samples are not preserved. Low or medium concentration soil samples for metals are cooled to 4°C while high hazard samples are not preserved.

The following subsections describe the procedures for preparing and adding chemical preservatives. Attachments A and B indicate the specific analytes which require these preservatives.

5.2.1 Addition of Acid (H_2SO_4, HCl, or HNO_3) or Base

Addition of the following acids or bases may be specified for sample preservation; these reagents shall be analytical reagent (AR) grade and shall be diluted to the required concentration with double-distilled, deionized water in the laboratory, before Field sampling commences:

Acid Base	Concentration	Normality	Amount for Acidification*
HCl	1:1 dilution of concentrated HCl	6N	5-10 ml
H_2SO_4	1:1 dilution of concentrated H_2SO_4	18N	2-5 ml
HNO_3	Undiluted concentrated HNO_3	16N	2-5 ml
NaOH	400 grams solid NaOH in 870 ml water	10N	2 ml**

* Amount of acid to add (at the specified strength) per liter of water to reduce the sample pH to less than 2, assuming that the water is initially at pH 7, and is poorly buffered and does not contain particulate matter.

** To raise pH of 1 liter of water to 12.

The approximate volumes needed to acidify one liter of neutral water to a pH of less than 2 (or raise the pH to 12) are shown in the last column of the above table. These volumes are only approximate; if the water is more alkaline, contains inorganic or organic buffers, or contains suspended particles, more acid may be required. The final pH must be checked using narrow-range pH paper.

Sample acidification or base addition shall proceed as follows:

- Check initial pH of sample with wide range (0-14) pH paper.
- Fill sample bottle to within 5-10 ml of final desired volume and add about 1/2 of estimated acid or base required, stir gently and check pH with medium range pH paper (pH 0-6 or pH 7.5-14, respectively).
- Add acid or base a few drops at a time while stirring gently. Check for final pH using narrow range (0-2.5 or 11-13, respectively) pH paper; when desired pH is reached, cap sample bottle and seal.

  Never dip pH paper into the sample; apply a drop of sample to the pH paper using the stirring rod.

5.2.2 Cyanide Preservation

Pre-sample preservation is required if oxidizing agents such as chlorine are suspected to be present. To test for oxidizing agents, place a drop of the sample on KI-starch paper; a blue color indicates the need for treatment. Add ascorbic acid to the sample, a few crystals at a time, until a drop of sample produces no color on the KI-starch paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume. Add NaOH solution to raise pH to greater than 12 as described in 5.2.1. If oxidizing agents are not suspected, add NaOH as directed.

5.2.3 Sulfide Preservation

Samples for sulfide analysis must be preserved by addition of 4 drops (0.2 ml) of 2N zinc acetate solution per 100 ml sample. The sample pH is then raised to 9 using NaOH. The 2N zinc acetate solution is made by dissolving 220 g of zinc acetate in 870 ml of distilled water to make 1 liter of solution.

5.2.4 Preservation of Organic Samples Containing Residual Chlorine

Some organic samples containing residual chlorine must be treated to remove this chlorine upon collection (See Attachment A). Test the samples for residual chlorine using EPA methods 330.4 or 330.5 (Field Test Kits are available for this purpose). If residual chlorine is present, add 0.008% sodium thiosulfate (80 mg per liter of sample).

5.2.5 Field Filtration

When the objective is to determine concentration of dissolved inorganic constituents in a water system, the sample must be filtered through a non-metallic 0.45 micron membrane filter immediately after collection. A filtration system is recommended if large quantities of samples must be filtered in the field. The filtration system shall consist of a Büchner funnel inserted into a single-hole rubber stopper, sized to form a seal when inserted into the top of a vacuum filter flask equipped with a single side arm. Heavy-wall Tygon tubing shall be attached to the single side arm of the vacuum filter flask and the suction port of a vacuum pump. The stem of the Büchner funnel shall extend below the level of the side arm of the vacuum filter flask to prevent any solvent from entering the tubing leading to the vacuum pump. Before filtration, the filter paper, which shall be of a size to lay flat on the funnel plate, shall be wetted with the solvent in order to "seal" it to the funnel. Slowly pour the solvent into the funnel and monitor the amount of solvent entering the vacuum filter flask. When the rate of solvent entering the flask is reduced to intermittent dripping and the added aliquot of solvent in the funnel has passed through the filter, the used filter paper shall be replaced with new filter paper. If the solvent contains a high percentage of suspended solids, a coarser-sized nonmetallic membrane filter may be used prior to usage of the 0.45 micron membrane filter. This "prefiltering" step may be necessary to expedite the filtration procedure. Discard the first 20 to 50 ml of filtrate from each sample to rinse the filter and filtration apparatus to minimize the risk of altering the composition of the samples by the filtering operation. For analysis of dissolved metals, the filtrate is collected in a suitable bottle (see Section 5.1) and is immediately acidified to pH 2.0 or less with nitric acid whose purity is consistent with the measurement to be made. Inorganic anionic constituents may be determined using a portion of the filtrate that has not been acidified.

Samples used for determining temperature, dissolved oxygen, Eh, and pH should not be filtered. Do not use vacuum filtering prior to determining carbonate and bicarbonate concentration because it removes dissolved carbon dioxide and exposes the sample to the atmosphere. Pressure filtration can be done using water pressure from the well. If gas pressure is required, use an inert gas such as argon or nitrogen.

Do not filter samples for analysis of volatile organic compounds. If samples are to be filtered for analyzing other dissolved organic constituents, use a glass-fiber or metal-membrane filter and collect the samples in a suitable container (see Section 5.1). Because most organic analyses require extraction of the entire sample, do not discard any of it. After filtering, the membrane containing the suspended fraction can be sealed in a glass container and analyzed separately as soon as practicable. Total recoverable inorganic constituents may be determined using a second, unfiltered sample collected at the same time as the sample for dissolved constituents.

1.0 PURPOSE

The purpose of these procedures is to provide a general methodology, protocol, and reference information on the proper decontamination procedures to be used on chemical sampling and field analytical equipment.

2.0 SCOPE

This procedure addresses chemical sampling and field analytical equipment only, and should be consulted when equipment decontamination procedures are being developed as part of project-specific plans.

3.0 GLOSSARY

None.

4.0 RESPONSIBILITIES

Site Manager - responsible for ensuring that project-specific plans and the implementation of field investigations are in compliance with these guidelines.

Field Operations Leader - responsible for ensuring that decontamination procedures for all chemical sampling and field analytical equipment are programmed prior to the actual field effort and that personnel required to accomplish the task have been briefed and trained to execute the task.

5.0 PROCEDURES

In order to assure that chemical analysis results are reflective of the actual concentrations present at sampling locations, chemical sampling and field analysis equipment must be properly decontaminated prior to the field effort, during the sampling program (i.e., between sample points) and at the conclusion of the sampling program. This will minimize the potential for cross-contamination between sample points and the transfer of contamination offsite.

This procedure incorporates only those aspects of decontamination not addressed in other procedures. Specifically it incorporates those items involved in decontamination of chemical sampling and field analytical equipment.

5.1 ACCESS FOR SAMPLING

5.1.1 Bailers and Bailing Line

The potential for cross-contamination between sampling points via the use of common bailer, or its attached line, is high unless strict procedures for decontamination are followed. It is preferable, for the aforementioned reason, to dedicate an individual bailer and its line to each sample point, although this does not eliminate the need for decontamination of dedicated bailers. For non-dedicated sampling equipment, the following conditions and/or decontamination procedures should be followed.

Before the initial sampling and after each succeeding sampling point, the bailer must be decontaminated. The following steps should be followed if sampling for organic contaminants:

- Potable water rinse
- Alconox or Liquinox detergent wash
- Scrubbing of the line and bailer with a scrub brush may be required if the sample point if heavily contaminated with heavy or extremely viscous compounds
- Potable water rinse
- Rinse with 10 percent nitric acid solution*
- Deionized water rinse
- Acetone or methanol rinse
- Hexane rinse**
- Distilled/Deionized water rinse
- Air dry

If sampling for organics only, the nitric acid, acetone, methanol, and hexane rinses may be omitted. Contract-specific requirements may permit alternative procedures.

Braided nylon or polypropylene lines may be used with a bailer, however, the same line must not come in contact with the sample medium, otherwise, the line must be discarded in an approved receptacle and replaced. Prior to use, the bailer should be wrapped in aluminum foil or polyethylene sheeting.

5.1.2 Sampling Pumps

Most sampling pumps are normally low volume (less than 2 gpm) pumps. These include peristaltic, diaphragm, air-lift, pitcher and bladder pumps, to name a few. If these pumps are used for sampling from more than one sampling point, they must be decontaminated.

The procedures to be used for decontamination of sampling pumps compare to those used for a bailer except the 10 percent nitric acid solution is omitted. Each of the liquid factions is to be pumped through the system. The amount of pumping is dependent upon the size of the pump and the length of the intake and discharge hoses. Certain types of pumps are unacceptable for sampling purposes.

An additional problem is introduced when the pump relies on absorption of water via an inlet or outlet hose. For organic sampling, this hose should be Teflon. Other types of hoses leach organics into the water being sampled (especially the phthalate esters) or adsorb organics from the sampled water. For all other sampling, the hose should be Viton, polyethylene, or polyvinyl chloride (in order of preference). Whenever possible, dedicated hoses should be used.

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* Due to the leaching ability of nitric acid, on stainless steel, this step is to be omitted if a stainless steel sampling device is being used and metals analysis is required with detection limits less than approximately 50 ppb; or the sampling equipment is dedicated.

** If sampling for pesticides, PCBs, or fuels.

5.1.3 Filtering Equipment

Part of the sampling plan may incorporate the filtering of groundwater samples, and subsequent preservation. This should occur as soon after sample retrieval as possible; preferably in the field as soon as the sample is obtained. To this end, three basic filtration systems are most commonly used - the in-line disposable Teflon filter, the inert gas over-pressure filtration system, and the vacuum filtration system.

For the in-line filter, decontamination is not required since the filter cartridge is disposable, however, the cartridge must be disposed of in an approved receptacle and the intake and discharge lines must still be decontaminated.

For the over-pressure and the vacuum filtration systems, the portions of the apparatus which come in contact with the sample must be decontaminated as outlined in the paragraphs describing the decontamination of bailers. (Note: Varieties of both of these systems come equipped from the manufacturer with Teflon-lined surfaces for those that would come into contact with the sample. These filtration systems are preferred when decontamination procedures must be employed.)

5.2 FIELD ANALYTICAL EQUIPMENT

5.2.1 Water Level Indicators

Water level indicators that come into contact with groundwater must be decontaminated using the following steps:

- Rinse with potable water
- Rinse with deionized water
- Acetone or methanol rinse
- Rinse with deionized water

Water level indicators that do not come in contact with the groundwater but may encounter incidental contact during installation or retrieval need only undergo the first and last steps stated above.

5.2.2 Probes

Probes, e.g., pH or specific ion electrodes, geophysical probes, or thermometers which would come in direct contact with the sample, will be decontaminated using the procedures specified above unless manufacturer's instructions indicate otherwise; in those cases, the methods of decontamination must be clearly described in the FSAP. Probes that contact a volume of groundwater not used for laboratory analyses can be rinsed with deionized water. For probes which make no direct contact, e.g., OVA equipment, the probe will be wiped with clean paper-towels or cloth wetted with alcohol.

6.0 REFERENCES

None.

7.0 RECORDS

None.

5.0 PROCEDURES

5.1 GENERAL

Groundwater level measurements can be made in monitoring wells, private or public water wells, piezometers, open boreholes, or test pits (after stabilization). Groundwater measurements should generally not be made in boreholes with drilling rods or auger flights present. If groundwater sampling activities are to occur, groundwater level measurements shall take place prior to well evacuation or sampling.

All groundwater level measurements shall be made to the nearest 0.01 foot, and recorded in the geologist's field notebook or on the Groundwater Level Measurement Sheet (Attachment A), along with the date and time of the reading. The total depth of the well shall be measured and recorded, if not already known. Weather changes that occur over the period of time during which water levels are being taken, such as precipitation and bariometric pressure changes, should be noted.

In measuring groundwater levels, there shall be a clearly-established reference point of known elevation, which is normally identified by a mark on the upper edge of the inner well casing. The reference point shall be noted in the field notebook. To be useful, the reference point should be tied in with an established USGS benchmark or other properly surveyed elevation datum. An arbitrary datum could be used for an isolated group of wells if necessary.

Cascading water within a borehole or steel well casings can cause false readings with some types of sounding devices (chalked line, electrical). Oil layers may also cause problems in determining the true water level in a well. Special devices (interface probes) are available for measuring the thickness of oil layers and true depth to groundwater if required.

Water level readings shall be taken regularly, as required by the site hydrogeologist. Monitoring wells or open-cased boreholes that are subject to tidal fluctuations should be read in conjunction with a tidal chart (or preferably in conjunction with readings of a tide staff or tide level recorder installed in the adjacent water body); the frequency of such readings shall be established by the site hydrogeologist. All water level measurements at a site used to develop a groundwater contour map shall be made in the shortest practical time to minimize affects due weather changes, and at least during the same day.

5.2 WATER LEVEL MEASURING TECHNIQUES

There are several methods for determining standing or changing water levels in boreholes and monitoring wells. Certain methods have particular advantages and disadvantages depending upon well conditions. A general description of these methods is presented, along with a listing of various advantages and disadvantages of each technique. An effective technique shall be selected for the particular site conditions by the onsite hydrogeologist.

In most instances, preparation of accurate potentiometric surface requires that static water level measurements be obtained to a precision of 0.01 feet. To obtain such measurements in individual accessible wells, the Chalked Tape or Electrical Water Level Indicator methods have been found best, and thus are the most often utilized. Other, less precise methods, such as the Popper or Bell Sound or Bailer Line methods, may be appropriate for developing preliminary estimates of hydraulic conditions. When a large number of (or continuous) readings are required, time-consuming individual readings are not usually feasible. In such cases, it is best to use the Float Recorder or Pressure Transducer methods. When conditions in the well limit readings (i.e., turbulence in the

water surface or limited access through small diameter tubing), less precise, but appropriate, methods such as the Air Line or Capillary Tubing methods can be used.

5.2.1 Methods

Water levels can be measured by several different techniques, but the same steps shall be followed in each case. The proper sequence is as follows:

1. Check operation of recording equipment above ground. Prior to opening the well, don personal protective equipment as required.

2. Record all information specified below in the geologist's field notebook or on the Groundwater Level Measurement Sheet.

   a. Well number.
   b. Record water level to the nearest 0.01 foot (0.3 cm). Water levels shall be taken from the surveyed reference mark on the top edge of the inner well casing.
   c. Record the time and day of the measurement.

Water level measuring devices with permanently marked intervals shall be used when possible. If water level measuring devices marked by metal or plastic bands clamped at intervals along the measuring line are used, the spacing and accuracy of these bands shall be checked frequently as they may loosen and slide up or down the line, resulting in inaccurate reference points (see Section 5.2.3).

5.2.2 Water Level Measuring Devices

Chalked Steel Tape

The water level is measured by chalking a weighted steel tape and lowering it a known distance (to any convenient whole foot mark) into the well or borehole. The water level is determined by subtracting the wetted chalked mark from the total length lowered into the hole.

The tape shall be withdrawn quickly from the well because water has a tendency to rise up the chalk due to capillary action. A water finding paste may be used in place of chalk. The paste is spread on the tape the same way as the chalk, and turns red upon contacting water.

Disadvantages to this method include the following: depths are limited by the inconvenience of using heavier weights to properly tension longer tape lengths; ineffective if borehole/well wall is wet or inflow is occurring above the static water level; chalking the tape is time consuming; difficult to use during periods of precipitation.

Electric Water Level Indicators

These devices consist of a spool of small-diameter cable and a weighted probe attached to the end. When the probe comes in contact with the water, an electrical circuit is closed and a meter, light, and/or buzzer attached to the spool will signal the contact.

There are a number of commercial electric sounders available, none of which is entirely reliable under all conditions likely to occur in a contaminated monitoring well. In conditions where there is oil on the water, groundwater with high specific conductance, water cascading into the well, steel well casing, or a turbulent water surface in the well, measuring with an electric sounder may be difficult.

For accurate readings, the probe shall be lowered slowly into the well. The electric tape is marked at the measuring point where contact with the water surface was indicated. The distance from the mark to the nearest tape band is measured using an engineer's folding ruler or steel tape and added to the band reading to obtain the depth to water. If band is not a permanent marking band, spacing shall be checked periodically as described in Section 5.2.3.

Popper or Bell Sounder

A bell- or cup-shaped weight that is hollow on the bottom is attached to a measuring tape and lowered into the well. A "plopping" or "popping" sound is made when the weight strikes the surface of the water. An accurate reading can be determined by lifting and lowering the weight in short strokes, and reading the tape when the weight strikes the water. This method is not sufficiently accurate to obtain water levels to 0.01 feet, and thus is more appropriate for obtaining only approximate water levels quickly.

Float Recorder

A float or an electromechanically actuated water-seeking probe may be used to detect vertical changes of the water surface in the hole. A paper-covered recording chart drum is rotated by the up and down motion of the float via a pulley and reduction gear mechanism, while a clock drive moves a recording pen horizontally across the chart. To ensure continuous records, the recorder shall be inspected, maintained, and adjusted periodically. This type of device is useful for continuously measuring periodic water level fluctuations, such as tidal fluctuations or influences of pumping wells.

Air Line

An air line is especially useful in pumped wells where water turbulence may preclude the use of other devices. A small-diameter weighted tube of known length is installed from the surface to a depth below the lowest water level expected. Compressed air (from a compressor, bottled air, or air pump) is used to purge the water from the tube, until air begins to escape the lower end of the tube, and is seen (or heard) to be bubbling up through the water in the well. The pressure needed to purge the water from the air line multiplied by 2.307 (feet of water for 1 psi) equals the length in feet of submerged air line. The depth to water below the center of the pressure gauge can be calculated by subtracting the length of air line below the water surface from the total length of the air line.

The disadvantages to this method include the need for an air supply and lower level of accuracy (unless a very accurate air pressure gauge is used, this method cannot be used to obtain water level readings to the nearest 0.01 ft).

Capillary Tubing

In small diameter piezometer tubing, water levels are determined by using a capillary tube. Colored or clear water is placed in a small "U"-shaped loop in one end of the tube (the rest of the tube contains air). The other end of the capillary tube is lowered down the piezometer tubing until the water in the loop moves, indicating that the water level has been reached. The point is then measured from the bottom of the capillary tube or recorded if the capillary tube is calibrated. This is the best method for very small diameter tubing monitoring systems such as Barcad and other multilevel samples. Unless the capillary tube is calibrated, two people may be required to measure the length of capillary tubing used to reach the groundwater. Since the piezometer tubing and capillary tubing usually are somewhat coiled when installed, it is difficult to accurately measure absolute water level elevations using this method. However, the method is useful in accurately measuring differences or changes in water levels (i.e., during pumping tests).

Pressure Transducer

Pressure transducers can be lowered into a well or borehole to measure the pressure of water and therefore the water elevation above the transducer. The transducer is wired into a recorder at the surface to record changes in water level with time. The recorder digitizes the information and can provide a printout or transfer the information to a computer for evaluation (using a well drawdown/recovery model). The pressure transducer should be initially calibrated with another water level measurement technique to ensure accuracy. This technique is very useful for hydraulic conductivity testing in highly permeable material where repeated, accurate water level measurements are required in a very short period of time. A sensitive transducer element is required to measure water levels to 0.01 foot accuracy.

Borehole Geophysics

Approximate water levels can be determined during geophysical logging of the borehole (although this is not the primary purpose for geophysical logging and such logging is not cost-effective if used only for this purpose). Several logging techniques will indicate water level. Commonly-used logs which will indicate saturated/unsaturated conditions include the spontaneous potential (SP) log and the neutron log.

Bailer Line Method

Water levels can be measured during a bailing test of a well by marking and measuring the bailer line from the bottom of the bailer (where water is first encountered) to the point even with the top of the well casing. This is a useful technique during bailing tests (particularly if recovery is rapid) if the bailer is heard hitting the water. However, it is not recommended for measuring static water levels because it is not usually as accurate as some of the other methods described above.

5.2.3 Data Recording

Water level measurements, time, data, and weather conditions shall be recorded in the geologist's field notebook or on the Groundwater Level Measurement Sheet. All water level measurements shall be measured from a known reference point. The reference point is generally a marked point on the upper edge of the inner well casing that has been surveyed for an elevation. The exact reference point shall be marked with permanent ink on the casing since the top of the casing may not be entirely level. It is important to note changes in weather conditions because changes in the barometric pressure may affect the water level within the well.

5.2.4 Specific Quality Control Procedures for Water Level Measuring Devices

All groundwater level measurement devices must be cleaned before and after each use to prevent cross contamination of wells.

Some devices used to measure groundwater levels may need to be calibrated. These devices shall be calibrated to 0.01 foot accuracy periodically. A water level indicator calibration sheet shall be completed each time the measuring device is checked. A water level indicator calibration form is shown in Attachment A. The "actual reading" column on the sheet is the actual length of the interval from the end of the indicator to the appropriate marked depth interval. In many cases, these measurements are different because the water level measuring device is connected to the end of the measuring tape or line, and may extend beyond "0" feet on the measuring line.

5.3 POTENTIOMETRIC SURFACE MAPPING

5.3.1 Selection of Wells

All wells used to prepare a flow net in a plan or map view should represent the same hydrogeologic unit, be it aquifer or aquitard. All water level measurements used shall be collected on the same day.

Before mapping, review the recorded water levels and monitoring-well construction data, site geology and topographic setting to ascertain that the wells are completed in the same hydrogeologic unit and to determine if strong vertical hydraulic gradients may be present. Such conditions will be manifested by a pronounced correlation between well depth and water level, or by a difference in water level between two wells located near each other but set to different depths or having different screen lengths. Professional judgment of the hydrogeologist is important in this decision. If vertical gradients are significant, the data to be used must be limited vertically, and only wells finished in a chosen vertical zone of the hydrogeologic unit can be used.

At least three wells must be used to provide an estimation of the direction of groundwater flow, and many more wells will be needed to provide an accurate contour map. Generally, shallow systems require more wells than deep systems for accurate contour mapping.

5.3.2 Construction of Equipotential Lines

Plot the water elevations in the chosen wells on a site map. Other hydrogeologic features associated with the zone of interest -- such as seeps, wetlands, and surface-water bodies -- should also be plotted along with their elevations.

The data should then be contoured, using mathematically valid and generally accepted techniques. Linear interpolation is most commonly used, as it is the simplest technique. However, quadratic interpolation or any technique of trend-surface analysis or data smoothing is acceptable. Computer-generated contour maps may be useful for large data sets. Contour lines shall be drawn as smooth, continuous lines which never cross one another.

Inspect the contour map, noting known features, such as pumping wells and site topography. The contour lines must be adjusted in accordance with these, utilizing the professional judgment of the hydrogeologist. Closed contours should be avoided unless a known sink exists. Groundwater mounding is common under landfills and lagoons; if the data imply this, the feature must show in the contour plot.

5.3.3 Determination of Groundwater-Flow Direction

Flow lines shall be drawn so that they are perpendicular to equipotential lines. Flow lines will begin at high head elevations and end at low head elevations. Closed highs will be the source of additional flow lines. Closed depressions will be the termination of some flow lines. Care must be used in areas with significant vertical gradients to avoid erroneous conclusions concerning gradients and flow directions.

5.4 HEALTH AND SAFETY CONSIDERATIONS

Groundwater contaminated by volatile organic compounds may release toxic vapors into the air space inside the well pipe. The release of this air when the well is initially opened is a Health/Safety hazard which must be considered. Initial monitoring of the well headspace and breathing zone

concentrations using a PID (HNU) or FID (OVA) and combustible gas meters shall be performed to determine required levels of protection.

6.0 REFERENCES

Freeze, R. A. and J. A. Cherry, 1979. Groundwater. Prentice-Hall, Englewood Cliffs, New Jersey, 604 pp.

Cedergren, H. R., 1977. Seepage, Drainage and Flow Nets (2nd edition). John Wiley and Sons, New York.

Fetter, C. W., 1980. Applied Hydrogeology. Merrill, Columbus, Ohio, 488 pp.

7.0 ATTACHMENTS

Attachment A - Groundwater Level Measurement Sheet

~~Attachment B - Water Level Indicator Calibration Sheet.~~

ATTACHMENT A

GROUNDWATER LEVEL MEASUREMENT SHEET

Project Name: _____
Project No.: _____
Personnel: _____
Date: _____

LOCATION

Municipality: _____
County: _____
State: _____
Street or Map Location (If Off-Site) _____

WEATHER CONDITIONS

Temperature Range: _____
Precipitation: _____
Barometric Pressure: _____

Equipment No.: _____
Equipment Name: _____
Latest Calibration Date: _____

Tidally-Influenced: [ ] Yes [ ] No

Well or Piezometer Number	Date/Time	Elevation of Reference Point (Feet)*	Water Level Indicator Reading (Feet)*	Adjusted Depth (Feet)*	Groundwater Elevation (Feet)*

* All elevations to nearest 0.01 foot.

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION I

Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells

Revision Number 2
July 30, 1996

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION I

LOW STRESS (low flow) PURGING AND SAMPLING PROCEDURE FOR THE COLLECTION OF GROUND WATER SAMPLES FROM MONITORING WELLS

I. SCOPE & APPLICATION

This standard operating procedure (SOP) provides a general framework for collecting ground water samples that are indicative of mobile organic and inorganic loads at ambient flow conditions (both the dissolved fraction and the fraction associated with mobile particulates). The SOP emphasizes the need to minimize stress by low water-level drawdowns, and low pumping rates (usually less than 1 liter/min) in order to collect samples with minimal alterations to water chemistry. This SOP is aimed primarily at sampling monitoring wells that can accept a submersible pump and have a screen, or open interval length of 10 feet or less (this is the most common situation). However, this procedure is flexible and can be used in a variety of well construction and ground-water yield situations. Samples thus obtained are suitable for analyses of ground water contaminants (volatile and semi-volatile organic analytes, pesticides, PCBs, metals and other inorganics), or other naturally occurring analytes.

This procedure does not address the collection of samples from wells containing light or dense non-aqueous phase liquids (LNAPLs and DNAPLs). For this the reader may wish to check: Cohen, R.M. and J.W. Mercer, 1993, DNAPL Site Evaluation; C.K. Smoley (CRC Press), Boca Raton, Florida and U.S. Environmental Protection Agency, 1992, RCRA Ground-Water Monitoring: Draft Technical Guidance; Washington, DC (EPA/530-R-93-001).

The screen, or open interval of the monitoring well should be optimally located (both laterally and vertically) to intercept existing contaminant plume(s) or along flowpaths of potential contaminant releases. It is presumed that the analytes of interest move (or potentially move) primarily through the more permeable zones within the screen, or open interval.

Use of trademark names does not imply endorsement by U.S.EPA but is intended only to assist in identification of a specific type of device.

Proper well construction and development cannot be overemphasized, since the use of installation techniques that are appropriate to the hydrogeologic setting often prevents "problem well" situations from occurring. It is also recommended that as part of development or redevelopment the well should be tested to determine the appropriate pumping rate to obtain stabilization of field indicator parameters with minimal drawdown in shortest amount of time. With this information field crews can then conduct purging and sampling in a more expeditious manner.

The mid-point of the saturated screen length (which should not exceed 10 feet) is used by convention as the location of the pump intake. However, significant chemical or permeability contrast(s) within the screen may require additional field work to determine the optimum vertical location(s) for the intake, and appropriate pumping rate(s) for purging and sampling more localized target zone(s). Primary flow zones (high(er) permealability and/or high(er) chemical concentrations) should be identified in wells with screen lengths longer than 10 feet, or in wells with open boreholes in bedrock. Targeting these zones for water sampling will help insure that the low stress procedure will not underestimate contaminant concentrations. The Sampling and Analysis Plan must provide clear instructions on how the pump intake depth(s) will be selected, and reason(s) for the depth(s) selected.

Stabilization of indicator field parameters is used to indicate that conditions are suitable for sampling to begin. Achievement of turbidity levels of less than 5 NTU and stable drawdowns of less than 0.3 feet, while desirable, are not mandatory. Sample collection may still take place provided the remaining criteria in this procedure are met. If after 4 hours of purging indicator field parameters have not stabilized, one of 3 optional courses of action may be taken: a) continue purging until stabilization is achieved, b) discontinue purging, do not collect any samples, and record in log book that stabilization could not be achieved (documentation must describe attempts to achieve stabilization) c) discontinue purging, collect samples and provide full explanation of attempts to achieve stabilization (note: there is a risk that the analytical data obtained, especially metals and strongly hydrophobic organic analytes, may not meet the sampling objectives).

Changes to this SOP should be proposed and discussed when the site Sampling and Analysis Plan is submitted for approval. Subsequent requests for modifications of an approved plan must include adequate technical justification for proposed changes. All changes and modifications must be approved before implementation in field.

II. EQUIPMENT

A. Extraction device

Adjustable rate, submersible pumps are preferred (for example, centrifugal or bladder pump constructed of stainless steel or Teflon).

Adjustable rate, peristaltic pumps (suction) may be used with caution. Note that EPA guidance states: "Suction pumps are not recommended because they may cause degassing, pH modification, and loss of volatile compounds" (EPA/540/P-87/001, 1987, page 8.5-11).

The use of inertial pumps is discouraged. These devices frequently cause greater disturbance during purging and sampling and are less easily controlled than the pumps listed above. This can lead to sampling results that are adversely affected by purging and sampling operations, and a higher degree of data variability.

B. Tubing

Teflon or Teflon lined polyethylene tubing are preferred when sampling is to include VOCs, SVOCs, pesticides, PCBs and inorganics.

PVC, polypropylene or polyethylene tubing may be used when collecting samples for inorganics analyses. However, these materials should be used with caution when sampling for organics. If these materials are used, the equipment blank (which includes the tubing) data must show that these materials do not add contaminants to the sample.

Stainless steel tubing may be used when sampling for VOCs, SVOCs, pesticides, and PCBs. However, it should be used with caution when sampling for metals.

The use of 1/4 inch or 3/8 inch (inner diameter) tubing is preferred. This will help ensure the tubing remains liquid filled when operating at very low pumping rates.

Pharmaceutical grade (Pharmed) tubing should be used for the section around the rotor head of a peristaltic pump, to minimize gaseous diffusion.

C. Water level measuring device(s), capable of measuring to 0.01 foot accuracy (electronic "tape", pressure transducer). Recording pressure transducers, mounted above the pump, are especially helpful in tracking water levels during pumping operations, but their use

must include check measurements with a water level "tape" at the start and end of each record.

D. Flow measurement supplies (e.g., graduated cylinder and stop watch).

E. Interface probe, if needed.

F. Power source (generator, nitrogen tank, etc.). If a gasoline generator is used, it must be located downwind and at least 30 feet from the well so that the exhaust fumes do not contaminate the samples.

G. Indicator field parameter monitoring instruments - pH, Eh, dissolved oxygen (DO), turbidity, specific conductance, and temperature. Use of a flow-through-cell is required when measuring all listed parameters, except turbidity. Standards to perform field calibration of instruments. Analytical methods are listed in 40 CFR 136, 40 CFR 141, and SW-846. For Eh measurements, follow manufacturer's instructions.

H. Decontamination supplies (for example, non-phosphate detergent, distilled/deionized water, isopropyl alcohol, etc.).

I. Logbook(s), and other forms (for example, well purging forms).

J. Sample Bottles.

K. Sample preservation supplies (as required by the analytical methods).

L. Sample tags or labels.

M. Well construction data, location map, field data from last sampling event.

N. Well keys.

O. Site specific Sample and Analysis Plan/Quality Assurance Project Plan.

P. PID or FID instrument (if appropriate) to detect VOCs for health and safety purposes, and provide qualitative field evaluations.

III. PRELIMINARY SITE ACTIVITIES

Check well for security damage or evidence of tampering, record pertinent observations.

Lay out sheet of clean polyethylene for monitoring and sampling equipment.

Remove well cap and immediately measure VOCs at the rim of the well with a PID or FID instrument and record the reading in the field logbook.

If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Describe its location and record the date of the mark in the logbook.

A synoptic water level measurement round should be performed (in the shortest possible time) before any purging and sampling activities begin. It is recommended that water level depth (to 0.01 ft.) and total well depth (to 0.1 ft.) be measured the day before, in order to allow for re-settlement of any particulates in the water column. If measurement of total well depth is not made the day before, it should not be measured until after sampling of the well is complete. All measurements must be taken from the established referenced point. Care should be taken to minimize water column disturbance.

Check newly constructed wells for the presence of LNAPLs or DNAPLs before the initial sampling round. If none are encountered, subsequent check measurements with an interface probe are usually not needed unless analytical data or field head space information signal a worsening situation. Note: procedures for collection of LNAPL and DNAPL samples are not addressed in this SOP.

IV. PURGING AND SAMPLING PROCEDURE

Sampling wells in order of increasing chemical concentrations (known or anticipated) is preferred.

1. Install Pump

Lower pump, safety cable, tubing and electrical lines slowly (to minimize disturbance) into the well to the midpoint of the zone to be sampled. The Sampling and Analysis Plan should specify the sampling depth, or provide criteria for selection of intake depth for each well (see Section I). If possible keep the pump intake at least two

feet above the bottom of the well, to minimize mobilization of particulates present in the bottom of the well. Collection of turbi free water samples may be especially difficult if there is two feet or less of standing water in the well.

2. Measure Water Level

Before starting pump, measure water level. If recording pressure transducer is used-initialize starting condition.

3. Purge Well

3a. Initial Low Stress Sampling Event

Start the pump at its lowest speed setting and slowly increase the speed until discharge occurs. Check water level. Adjust pump speed until there is little or no water level drawdown (less than 0.3 feet). If the minimal drawdown that can be achieved exceeds 0.3 feet but remains stable, continue purging until indicator field parameter stabilize.

Monitor and record water level and pumping rate every three to five minutes (or as appropriate) during purging. Record any pumping rate adjustments (both time and flow rate). Pumping rates should, as needed, be reduced to the minimum capabilities of the pump (for example, 0.1 - 0.4 l/min) to ensure stabilization of indicator parameters. Adjustments are best made in the first fifteen minutes of pumping in order to help minimize purging time. During pump start-up, drawdown may exceed the 0.3 feet target and then "recover" as pump flow adjustments are made. Purge volume calculations should utilize stabilized drawdown value, not the initial drawdown. Do not allow the water level to fall to the intake level (if the static water level is above the well screen, avoid lowering the water level into the screen). The final purge volume must be greater than the stabilized drawdown volume plus the extraction tubing volume.

Wells with low recharge rates may require the use of special pumps capable of attaining very low pumping rates (bladder, peristaltic), and/or the use of dedicated equipment. If the recharge rate of the well is lower than extraction rate capabilities of currently manufactured pumps and the well is essentially dewatered during purging, then the well should be sampled as soon as the water level has recovered sufficiently to collect the appropriate volume needed for all anticipated samples (ideally the intake should not be moved during this recovery period). Samples may then be collected even though the indicator field parameters have not stabilized.

3b. Subsequent Low Stress Sampling Events

After synoptic water level measurement round, check intake depth and drawdown information from previous sampling event(s) for each well. Duplicate, to the extent practicable, the intake depth and extraction rate (use final pump dial setting information) from previous event(s). Perform purging operations as above.

4. Monitor Indicator Field Parameters

During well purging, monitor indicator field parameters (turbidity, temperature, specific conductance, pH, Eh, DO) every three to five minutes (or less frequently, if appropriate). Note: during the early phase of purging emphasis should be put on minimizing and stabilizing pumping stress, and recording those adjustments. Purging is considered complete and sampling may begin when all the above indicator field parameters have stabilized. Stabilization is considered to be achieved when three consecutive readings, taken at three (3) to five (5) minute intervals, are within the following limits:

turbidity (10% for values greater than 1 NTU),
DO (10%),
specific conductance (3%),
temperature (3%),
pH (± 0.1 unit),
ORP/Eh (± 10 millivolts).

All measurements, except turbidity, must be obtained using a flow-through-cell. Transparent flow-through-cells are preferred, because they allow field personnel to watch for particulate build-up within the cell. This build-up may affect indicator field parameter values measured within the cell and may also cause an underestimation of turbidity values measured after the cell. If the cell needs to be cleaned during purging operations, continue pumping and disconnect cell for cleaning, then reconnect after cleaning and continue monitoring activities.

The flow-through-cell must be designed in a way that prevents air bubble entrapment in the cell. When the pump is turned off or cycling on/off (when using a bladder pump), water in the cell must not drain out. Monitoring probes must be submerged in water at all times. If two flow-through-cells are used in series, the one containing the dissolved oxygen probe should come first (this parameter is most susceptible to error if air leaks into the system).

5. Collect Water Samples

Water samples for laboratory analyses must be collected before water has passed through the flow-through-cell (use a by-pass assembly or disconnect cell to obtain sample).

VOC samples should be collected first and directly into pre-preserved sample containers. Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

During purging and sampling, the tubing should remain filled with water so as to minimize possible changes in water chemistry upon contact with the atmosphere. It is recommended that 1/4 inch or 3/8 inch (inside diameter) tubing be used to help insure that the sample tubing remains water filled. If the pump tubing is not completely filled to the sampling point, use one of the following procedures to collect samples: (1) add clamp, connector (Teflon or stainless steel) or valve to constrict sampling end of tubing; (2) insert small diameter Teflon tubing into water filled portion of pump tubing allowing the end to protrude beyond the end of the pump tubing, collect sample from small diameter tubing; (3) collect non-VOC samples first, then increase flow rate slightly until the water completely fills the tubing, collect sample and record new drawdown, flow rate and new indicator field parameter values.

Add preservative, as required by analytical methods, to samples immediately after they are collected if the sample containers are not pre-preserved. Check analytical methods (e.g. EPA SW-846, water supply, etc.) for additional information on preservation. Check pH for all samples requiring pH adjustment to assure proper pH value. For VOC samples, this will require that a test sample be collected during purging to determine the amount of preservative that needs to be added to the sample containers prior to sampling.

If determination of filtered metal concentrations is a sampling objective, collect filtered water samples using the same low flow procedures. The use of an in-line filter is required, and the filter size (0.45 um is commonly used) should be based on the sampling objective. Pre-rinse the filter with approximately 25 - 50 ml of ground water prior to sample collection. Preserve filtered water sample immediately. Note: filtered water samples are not an acceptable substitute for unfiltered samples when the monitoring objective is to obtain chemical concentrations of total mobile contaminants in ground water for human health risk calculations.

Label each sample as collected. Samples requiring cooling (volatile organics, cyanide, etc.) will be placed into a cooler with ice or refrigerant for delivery to the laboratory. Metal samples after acidification to a pH less than 2 do not need to be cooled.

6. Post Sampling Activities

If recording pressure transducer is used, remeasure water level with tape.

After collection of the samples, the pump tubing may either be dedicated to the well for resampling (by hanging the tubing inside the well), decontaminated, or properly discarded.

Before securing the well, measure and record the well depth (to 0.1 ft.), if not measured the day before purging began. Note: measurement of total well depth is optional after the initial low stress sampling event. However, it is recommended if the well has a "silting" problem or if confirmation of well identity is needed.

Secure the well.

V. DECONTAMINATION

Decontaminate sampling equipment prior to use in the first well and following sampling of each subsequent well. Pumps will not be removed between purging and sampling operations. The pump and tubing (including support cable and electrical wires which are in contact with the well) will be decontaminated by one of the procedures listed below.

Procedure 1

The decontaminating solutions can be pumped from either buckets or short PVC casing sections through the pump or the pump can be disassembled and flushed with the decontaminating solutions. It is recommended that detergent and isopropyl alcohol be used sparingly in the decontamination process and water flushing steps be extended to ensure that any sediment trapped in the pump is removed. The pump exterior and electrical wires must be rinsed with the decontaminating solutions, as well. The procedure is as follows:

Flush the equipment/pump with potable water.

Flush with non-phosphate detergent solution. If the solution is

recycled, the solution must be changed periodically.

Flush with potable or distilled/deionized water to remove all of the detergent solution. If the water is recycled, the water must be changed periodically.

Flush with isopropyl alcohol (pesticide grade). If equipment blank data from the previous sampling event show that the level of contaminants is insignificant, then this step may be skipped.

Flush with distilled/deionized water. The final water rinse must not be recycled.

Procedure 2

Steam clean the outside of the submersible pump.

Pump hot potable water from the steam cleaner through the inside of the pump. This can be accomplished by placing the pump inside a three or four inch diameter PVC pipe with end cap. Hot water from the steam cleaner jet will be directed inside the PVC pipe and the pump exterior will be cleaned. The hot water from the steam cleaner will then be pumped from the PVC pipe through the pump and collected into another container. Note: additives or solutions should not be added to the steam cleaner.

Pump non-phosphate detergent solution through the inside of the pump. If the solution is recycled, the solution must be changed periodically.

Pump potable water through the inside of the pump to remove all of the detergent solution. If the solution is recycled, the solution must be changed periodically.

Pump distilled/deionized water through the pump. The final water rinse must not be recycled.

VI. FIELD QUALITY CONTROL

Quality control samples are required to verify that the sample collection and handling process has not compromised the quality of the ground water samples. All field quality control samples must be prepared the same as regular investigation samples with regard to sample volume, containers, and preservation. The following quality control samples shall be collected for each batch of samples (a batch

may not exceed 20 samples). Trip blanks are required for the VOC samples at a frequency of one set per VOC sample cooler.

Field duplicate.

Matrix spike.

Matrix spike duplicate.

Equipment blank.

Trip blank (VOCs).

Temperature blank (one per sample cooler).

Equipment blank shall include the pump and the pump's tubing. If tubing is dedicated to the well, the equipment blank will only include the pump in subsequent sampling rounds.

Collect samples in order from wells with lowest contaminant concentration to highest concentration. Collect equipment blanks after sampling from contaminated wells and not after background wells.

Field duplicates are collected to determine precision of sampling procedure. For this procedure, collect duplicate for each analyte group in consecutive order (VOC original, VOC duplicate, SVOC original, SVOC duplicate, etc.).

If split samples are to be collected, collect split for each analyte group in consecutive order (VOC original, VOC split, etc.). Split sample should be as identical as possible to original sample.

All monitoring instrumentation shall be operated in accordance with EPA analytical methods and manufacturer's operating instructions. EPA analytical methods are listed in 40 CFR 136, 40 CFR 141, and SW-846 with exception of Eh, for which the manufacturer's instructions are to be followed. Instruments shall be calibrated at the beginning of each day. If a measurement falls outside the calibration range, the instrument should be re-calibrated so that all measurements fall within the calibration range. At the end of each day, check calibration to verify that instruments remained in calibration. Temperature measuring equipment, thermometers and thermistors, need not be calibrated to the above frequency. They should be checked for accuracy prior to field use according to EPA Methods and the manufacturer's instructions.

VII. FIELD LOGBOOK

A field log shall be kept to document all ground water field monitoring activities (see attached example matrix), and record all of the following:

- Well identification.
- Well depth, and measurement technique.
- Static water level depth, date, time and measurement technique.
- Presence and thickness of immiscible liquid (NAPL) layers and detection method.
- Pumping rate, drawdown, indicator parameters values, and clock time, at the appropriate time intervals; calculated or measured total volume pumped.
- Well sampling sequence and time of each sample collection.
- Types of sample bottles used and sample identification numbers.
- Preservatives used.
- Parameters requested for analysis.
- Field observations during sampling event.
- Name of sample collector(s).
- Weather conditions.
- QA/QC data for field instruments.
- Any problems encountered should be highlighted.
- Description of all sampling equipment used, including trade names, model number, diameters, material composition, etc.

VIII. DATA REPORT

Data reports are to include laboratory analytical results, QA/QC information, and whatever field logbook information is needed to allow for a full evaluation of data useability.

EXAMPLE (Minimum Requirements)

Page____of____

Well PURGING-FIELD WATER QUALITY MEASUREMENTS FORM

Location (Site/Facility Name)_____

Well Number_____ Date_____

Field Personnel_____

Sampling Organization_____

Identify MP_____

Depth to _____/_____ of screen (below MP) top bottom

Pump Intake at (ft. below MP)_____

Purging Device; (pump type)_____

Clock Time 24 HR	Water Depth below MP ft	Pump Dial[1]	Purge Rate ml/min	Cum. Volume Purged liters	Temp. °C	Spec. Cond.[2] µS/cm	pH	ORP/ Eh[3] mv	DO mg/L	Turb-idity NTU	Comments

1. Pump dial setting (for example: hertz, cycles/min, etc).
2. µSiemens per cm(same as µmhos/cm)at 25°C.
3. Oxidation reduction potential (stand in for Eh).

APPENDIX C

ANALYTICAL LABORATORY STANDARD OPERATING PROCEDURES (SOPs)
KATAHDIN

Katahdin
ANALYTICAL SERVICES

MEMO TO FILE

DATE: September 23, 1996
RE: Status of Katahdin Analytical Services SOPs

Katahdin Analytical Services, Inc. (Katahdin) has developed a new Standard Operating Procedure (SOP) format. SOPs that were in use at the Westbrook, ME facility (formerly PACE, Inc., Maine Lab) and the Hampton, NH facility (formerly PACE, Inc., New Hampshire Lab) are actively being converted to the new format which bears the Katahdin name. Controlled copies of any SOP previously in place at either facility are approved for use by Katahdin Analytical personnel until the SOP is converted and finalized in the new Katahdin Analytical format, at which time the previous version will be removed from use and archived. These SOPs may bear the names of the laboratories as they were designated prior to becoming Katahdin Analytical Services, Inc., including PACE, Inc., Coast-to-Coast Analytical Services (CCAS-Northeast), Resource Analysts Incorporated (RAI), or ABB Environmental Services, Inc. (ABB-ES). The QA department will maintain and periodically distribute an inventory of SOPs and their current status of conversion to the Katahdin SOP format.

340 County Road No. 5
P.O. Box 720, Westbrook, ME 04098
Tel: (207) 874-2400 Fax: (207) 775-4029

210 West Road No. 5, Portsmouth, NH 03801
Tel: (603) 431-5777 Fax: (603) 436-3356

Katahdin
ANALYTICAL SERVICES

October 23, 1996

Ms. Kelly A. Johnson
Brown and Root Environmental
661 Andersen Drive, Foster Plaza 7
Pittsburgh, PA 15201

Dear Ms. Johnson:

Per your request, enclosed please find copies of Katahdin Analytical Services, Inc., standard operating procedures (SOPs) as listed on the attached inventory. Please note the wet chemistry method references included with this SOP submittal are those that Katahdin would propose to use for groundwater monitoring. SOPs submitted for gasoline and diesel include the Maine DEP methods (SOPs CA-087-01 and CA-088-01) as well as procedures that would typically be used for samples originating in New Hampshire (SOPs QA-5501 and QA-5308). Katahdin would use the appropriate SOPs as directed by Brown and Root Environmental relative to the State having jurisdiction over the analytical program.

For preparation of saline water samples for metals analysis, two modifications to the CLP method will be required. For sample preparation, a 20 mL sample aliquot will be digested then brought to 100 mL final volume. For the digestion, 1 mL concentrated nitric acid and 5 mL concentrated hydrochloric acid will be used in place of the 2 mL 1:1 nitric acid and 10 mL 1:1 hydrochloric acid specified in the method. We also note the enclosed SOP for trace metals by ICP (CA-609) is applicable to the TJA 61 ICAP; the SOP applicable to the TJA Trace 61E is currently under final revision. The QC requirements for the Trace 61E will be the same as those presented in Table 1 of SOP CA-609. The procedure for the Trace 61E will differ slightly from the 61 ICAP in order to incorporate the use of internal standards, and to describe maintenance procedures and calibration standard concentrations appropriate to the Trace 61E.

If you have any questions, please contact Deborah McGrath or me at 207/874-2400.

Sincerely,

Katahdin Analytical Services, Inc.

Julie Ricardi

Julie Ricardi
Quality Assurance Officer

Enclosures

c C. Kelleher
D. McGrath
L. Pepin

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KATAHDIN ANALYTICAL SERVICES, INC.
LIST OF STANDARD OPERATING PROCEDURES
submitted to Brown and Root Environmental

TITLE	OLD SOP NO.	NEW SOP NO.	REV.	DATE
CHEMICAL ANALYSIS - GC/MS				
Analysis of VOAs by Purge and Trap GC/MS: SW-846 Method 8260	CA-107	CA-202	0	Final
* Analysis of VOAs by Purge and Trap GC/MS: USEPA CLP, Document Number OLM01.0 (including revisions OLM01.1 through OLM01.6)	CA-068	CA-203	0	
Analysis of SVOAs by Capillary Column GC/MS: SW-846 Method 8270 and 40 CFR Method 625 (to become Method 8270 SOP)	CA-006	CA-204	0	
* Analysis of SVOAs by Capillary Column GC/MS: USEPA CLP, Doc. No.OLM01.0 (including rev. OLM01.1 - OLM01.6 and OLM01.8)	CA-067	CA-206	0	
CHEMICAL ANALYSIS - GC				
Analysis of Pesticides/PCBs by GC/ECD, Method 8081	CA-108	CA-302	0	Final
* Analysis of Pesticides/ PCBs by GC/ECD USEPA CLP June, 1990, SOW OLM01.6	CA-035	CA-304	0	
* Analysis of Gasoline in Water by Purge and Trap GC/FID (Note: applicable to samples originating in Maine)	CA-087	CA-307	0	
* Analysis of Water and Soil Samples for Semivolatile Petroleum Products (Fuel Oil) (Note: applicable to samples originating in Maine)	CA-088	CA-308	0	
Analysis of Petroleum Hydrocarbons in Extracts of Water and Soil (Note: applicable to samples originating in NH)	QA-5308		0	
CHEMICAL ANALYSIS - ORGANICS EXTRACTIONS				
Preparation of Aqueous Samples for Extractable SVOA Analysis	CA-093	CA-502	0	Final
* CLP Sample Preparation for Pesticides/PCBs in Water or Soil/Sediment	CA-033	CA-508	0	
* CLP Sample Preparation and Clean-up for Extractable SVOAs in Water or Soil/Sediment	CA-034	CA-509	0	
Preparation of Aqueous Samples for Pesticides/PCBs Analysis	CA-008	CA-515	0	Final
Separatory Funnel Extraction of Aqueous Samples for Petroleum Hydrocarbon Analysis by GC-FID (Note: applicable to samples originating in NH)	QA-5501		0	

Revision No.: 1
Date: 10/24/96

KATAHDIN ANALYTICAL SERVICES, INC.
LIST OF STANDARD OPERATING PROCEDURES
submitted to Brown and Root Environmental

TITLE	OLD SOP NO.	NEW SOP NO.	REV.	DATE
CHEMICAL ANALYSIS - METALS DIGESTS AND INSTRUMENTATION				
* Acid Digestion of Water Samples for Analysis of Total or Dissolved Metals by ICP	CA-013	CA-604	0	
* Trace Metals Analysis Using the TJA 61 ICAP	CA-109	CA-609	0	Final
* Total Mercury Analysis in Water and Wastewater by Manual CVAA	CA-106	CA-610	0	Final
CHEMICAL ANALYSIS - WET CHEMISTRY				
* Spectrophotometric Determination of Cyanide in Domestic and Industrial Wastewater, Drinking, Surface, and Saline Waters and Sediment/Soil Samples (Note: applicable to distillation procedure only)	CA-020	CA-704	2	
* Alkalinity - Potentiometric, Titration pH 4.5	CA-040	CA-700	0	
* BOD in Aqueous Samples	CA-019	CA-701	0	Draft
* Analysis of TOC, DOC, TIC in Aqueous Samples Using the Dohrman Carbon Analyzer	CA-030	CA-702	0	
* pH Measurement in Aqueous Samples and Solutions	CA-055	CA-708	0	
* Spectrophotometric Determination of Total Recoverable Phenolics	CA-026	CA-714	0	
* Turbidimetric Determination of Sulfate	CA-051	CA-721	0	
* Analysis of Chloride by Flow Injection Analysis	QA-5860		0	Draft
* Total Nitrate/Nitrite Cadmium Reduction and Flow Injection Analysis	QA-5854		0	Draft
* Analysis of Cyanide Extracts by Flow Injection Analysis	QA-5855		0	Draft
* Anions by IC (Bromide)	QA-5802		2	Draft

* Included herein in the order shown.

STANDARD OPERATING PROCEDURE

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TITLE: Analysis of Volatile Organic Compounds by Purge and Trap GC/MS: USEPA Contract Laboratory Program, Document Number OLM01.0 (including revisions OLM01.1, OLM01.2, OLM01.3, OLM01.4, OLM01.5 and OLM01.6)

PURPOSE: To describe the procedures utilized by the Analytical Laboratory Services Division (ALSD) to prepare and analyze aqueous and solid matrix samples for purgeable organics, according to USEPA CLP protocol.

SCOPE: The general methodology involves purging samples with helium, an inert gas, for a set period of time to efficiently transfer purgeable organics to the gaseous phase. These volatile organics are then retained on a cooled trap (tenax/silica gel medium) before heating causes desorption into a gas chromatograph for compound separation. Detection occurs with an electron impact ionization mass spectrometer. This standard operating procedures (SOP) addresses all aspects of the preparation and analysis of aqueous and solid matrix samples for volatile organics as mandated by the USEPA CLP Statement-of-Work (SOW) referenced above (OLM01.6 - SOW). This SOP will consolidate all aspects of the analyses in one working document, to be revised as necessary, for the purpose of consistency in data quality.

REQUIREMENTS: Before beginning analysis of any samples under the USEPA CLP, the analyst is required to fulfill the minimum education/experience, as follows:

- bachelors degree in chemistry/science/engineering plus one year GC/MS/DS experience, or
- three years GC/MS/DS experience and GC/MS interpretation

A certificate of training (ABB-ES issued; see SOP AD-002) must be issued, signed by the appropriate Supervisor, indicating that the analyst is qualified to work with USEPA CLP samples before work can proceed.

GC/MS Spectral Interpretation Specialist requirements, as follows, must be fulfilled before an analyst can review and interpret mass spectral data, including tentatively-identified compound (TIC) determinations:

- bachelors degree in chemistry/science/engineering plus a training course in mass spectral interpretation plus two years experience

Once again, a completed ABB-ES certificate of training must be issued before interpretation can proceed.

Prior to analysis of any samples under the OLM01.6 SOW, the analyst is required to review in detail and become familiar with all aspects of the SOW. This review should include, but not be limited to: screening, standards preparation and traceability, sample preparation and analysis, data review, and instrument calibration protocols and criteria.

To aid in organization and recordkeeping in the GC/MS volatiles (VOA) section, strict naming and coding conventions are required for analytical standards, data files, quantitation output files, identification (ID) files and calibration files, archive tapes, and file header information. The required naming conventions are as follows:

- Analytical Standards - only standards received with vendor-supplied QC documentation packages are to be used for CLP work. Before use, upon receipt, all standards must be logged into the organics standard receipt logbook with the date of receipt, source (supplier), lot number, and expiration date. A copy of a page from this logbook is attached as Attachment A. All standard preparation must be recorded in the standards preparation notebook. A copy of a page from the volatile standards preparation notebook is appended as Attachment B. The GC/MS laboratory's convention for coding all VOA standards is as follows:

VOA: XXXXXX:N_1:N_2
CC ug/ml
Exp. date: YYYYYY
Analyst:

where:
VOA = volatile organics section (GC/MS)
XXXXXX = date of preparation (e.g. 120991)
N_1 = page number of VOA standards preparation notebook where prep details can be found
N_2 = preparation logbook number
CC = concentration of solution contained in vial (either single component or multi-component, single concentration)
YYYYYY = date of expiration

On all vials in storage, this information must appear, along with a description of the contents (e.g. BFB, Purgeable A Mix, etc.)

Vials stored without the above information are subject to being discarded during periodic (unannounced) supervisory/QC Coordinator inspections.

All injection log entries of BFB, standards, etc. must be notated with this standard code, i.e. VOA:XXXXXX:N_1:N_2. Should it become necessary, the injection log entry can then be traced back to the standards preparation log and, ultimately, to the standard receipt log.

Fresh standards must be prepared every two months for gases and for reactive compounds such as styrene. All other stock standards must be replaced after six months, or sooner if indications are present of either degradation or evaporation. All standards must be stored in the VOA standards freezer (separate from samples and other standards) at -10 to -20 degrees C. All working calibration standard solutions must be prepared weekly.

Computer (data system) conventions - Two GC/MS units are employed for VOA analysis, a HP5970B (unit 700104, equipped with a capillary column) and a HP5995C (unit 960202, equipped with a packed column). Both units are interfaced to and directly controlled by a HP1000 RTE-A computer with Aquarius software.

Conventions for the HP5970B are as follows:

Cartridges for data acquisition and storage: D4, D5, D1, D2
Cartridge for quantitation output files: D3
Tune file: MT4000

Method files:	M_YH (all CLP samples and standards) M_YBFB (BFB tuning acquisition) - all acquisition parameters must be identical for M_YH and M_YBFB. M_YCON (use for new column conditioning only)
Data files:	>Y_ _ _ _, where _ _ _ _ is a number in chronological order from 0000 to 9999
Data files for BFB:	>YB_ _ _ where _ _ _ is a number in chronological order from 000 to 999
Quantitation output files:	^Y_ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999 corresponding to the data file
Identification (ID) files:	I_YCW: Aqueous samples I_YCLS: Low-level soil samples I_YCMS: Medium-level soil samples Note: ID files are not to be edited without supervisor approval

Calibration Files: C_YCLW: aqueous and medium-level soil samples
C_YCLS: low-level soil samples
Note: Calibration files are not to be edited without supervisor approval.

Conventions for the HP5995C are as follows:

Cartridge for data acquisition and storage: D5, D4, D1, D2
Cartridge for Quantitation output files: D3
Tune file: MT2000
Method files: M_CH (all CLP samples and standards)
M_CBFB (BFB tuning acquisition) - all acquisition parameters must be identical for M_YH and M_YBFB.
M_CCON (use for new column conditioning only)
Data files: >C_ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999
Data files for BFB: >CB_ _ _ where _ _ _ is a number in chronological order from 000 to 999
Quantitation output files: ^C_ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999 corresponding to the data file
Identification (ID) files: I_CCW: aqueous samples
I_CCMS: medium-level soil samples
I_CCLS: low-level soil samples
Note: ID files are not to be edited without supervisor approval.
Calibration files: C_CCLW: aqueous and medium-level soil samples
C_CCLS: low-level soil samples
Note: Calibration files are not to be edited without supervisor approval.

Sample header information must be structured exactly as follows in the "BEDIT" program under Aquarius:

Name: Sample Management Office (SMO)/EPA Sample ID
Misc: Instrument ID; Case No; SDG No; Contract No.

No deviations from the above nomenclature are allowed.

PROCEDURE: The standard procedures utilized for analysis of volatile organics by GC/MS according to CLP SOW OLM01.6 will be described in separation sections.

Immediately after starting a run, the injection logbook must be filled out completely according to SOP SD-003, "Records of Sample Preparation and Analysis for Samples Requiring CLP Protocols." Standard receipt and preparation logbooks must also be filled out immediately after a pertinent activity by the person performing that activity. ABB-ES internal codes must accompany each standard entry. For further information, consult the GC/MS Supervisor.

1.0 INSTRUMENT TUNING

Prior to analysis of any calibration standards, blanks, or samples, the GC/MS system must be shown to meet the mass spectral ion abundance criteria for 4-Bromofluorobenzene (BFB), tabulated below:

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

The analysis of BFB is accomplished as a direct injection of the standard into the GC/MS. Refer to the standards preparation section of this SO (10.0) for instructions concerning preparation of this solution.

The following are the GC/MS operating conditions for injection of BFB on the HP5995C:

Column temperature: 200°C isothermal
Injection port temperature: 170°C
Transfer line/source temperature: 170°C
Scan start time: 10.0 min.
Run time: 16.0 min.
Sample volume: 2.0 ul of 25 ng/ul solution
Carrier gas: helium at approx. 30 mL/min
Mass range: 35 to 300 amu

The following are the GC/MS operating conditions for injection of BFB on the HP5970B:

Column temperature: 100°C isothermal
Injection port temperature: 170°C
Transfer line/source temperature: 170°C
Scan start time: 3.00 min.
Run time: 12.00 min.
Sample volume: 2.0 uL of 25 ng/uL solution
Carrier gas: helium at approx. 10 mL/min.
Make up gas: 30 mL/min.
Mass range: 35 to 300 amu

The above are set up in the method files M_CBFB and M_YBFB respectively, and must not be changed without Supervisor approval.

It is assumed here that the analyst is proficient with the HP RTE-A/Aquarius software package prior to analysis since at least one year of GC/MS/DS experience must be gained before analysis of CLP samples. The aquarius program "BEDIT" should be used to set up and start the run. Consult the Aquarius software manual in the laboratory or ask the GC/MS Supervisor if there are questions on how to proceed.

Once the BFB run is completed, the mass spectrum of this tuning compound must be evaluated to determine if calibration and sample analysis can proceed. The mass spectrum must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged (ENH,-1:1). Background subtraction is required, and must be accomplished using a single scan prior to the elution of BFB.

The mass spectra can be compared to CLP criteria by typing in: TUNER, = VOLM. If the mass spectrum of BFB does not meet the specified criteria, the instrument must be manually tuned (MTUNE) and the BFB reinjected. If the BFB spectrum is still not in criteria, notify the GC/MS Supervisor for corrective action instructions.

The BFB solution must be analyzed once at the beginning of each twelve hour period during which samples or standards are analyzed.

The twelve hour period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve hours have elapsed according to the system clock. The last injection must be accomplished prior to expiration of the twelve hour; conceivably, the run time may end after the twelve hours have elapsed.

After tuning criteria have been met, a hardcopy report must be generated and filed.

The first page of the hardcopy must contain an injection header (MSH) and a copy of the bargraph spectrum. The second page must contain a full mass listing, with all masses normalized to m/z 95 at 100 percent. The third and final page of the BFB hardcopy must contain a copy of the reconstructed total ion chromatogram, labeled with the date and time of injection.

2.0 ANALYSIS OF AQUEOUS SAMPLES

2.0.1 Tekmar LSC 2000/2016 Autosampler

Analysis of volatile samples utilizes a purge and trap apparatus to concentrate volatiles prior to introduction into

the GC/MS system. Our laboratory uses two Tekmar LSC 2000 purge and trap units in conjunction with two model 2016 autosamplers.

Successful analysis of calibration standards, blanks, and samples is contingent upon correct and consistent Tekmar methods and purge gas flow through the purge and trap unit; therefore, daily measurement of purge flow is required, and must be recorded in the maintenance log of each instrument.

The parameters for the Tekmar (stored in method 1) are listed below:

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ± 0.1 min.
Purge Flow Rate:	approx. 24-40 mL/min.
Purge Temperature:	Ambient (water or medium level soil), 40°C (low level soil)

Desorb Conditions:

Desorb Temperature:	180° C
Desorb Flow Rate:	15mL/min.
Desorb Time:	5.0 ± 0.1 min.
Bake Time:	5.00 min.
Bake Temperature:	225° C

2.0.2 Instrument Calibration

2.0.2.1 Prior to the analysis of samples and required method blanks, and after the instrument performance check solution criteria (BFB) have been met, the GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and linearity of GC/MS response for the volatile target compounds.

Calibration standards containing all volatile target compounds and system monitoring compounds must be prepared at 10, 20, 50, 100, and 200 ug/L. Also each calibration standard must contain three internal standards (bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5) at 50 ug/L. Consult the standards preparation section of this SOP for detailed instructions concerning preparation and documentation of stock solutions. Aqueous calibration standards may be prepared directly in a syringe used to inject the standard into the sparger.

After preparation of the standards as described in the prep section of this SOP (6.0), a sequence containing these five standards is set up under the program

"BEDIT". Ensure that both the data file and quantitation output file are achieved automatically to magnetic tape after each run; this is an absolute necessity!

After analysis of the five points, they must be quantitated and evaluated for adherence to QC criteria, as follows. Quantitation must occur using I_CCW for the HP5995C and I_YCW for the HP5970B.

The ID files are not to be edited without written approval of the Supervisor. Minimum requirements of ID files are use of specific quantitation ions and quantitating a specific set of targets and system monitoring compounds with a specific internal standard. These requirements are as follows:

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon Tetrachloride	4-Methyl-2-Pentanone
Vinyl Chloride	Bromodichloromethane	Tetrachloroethene
Chloroethane	1,2-Dichloropropane	1,1,2,2-Tetrachloroethane
Methylene Chloride	trans-1,3-Dichloropropene	Toluene
Acetone	Trichloroethene	Chlorobenzene
Carbon Disulfide	Dibromochloromethane	Ethylbenzene
1,1-Dichloroethene	1,1,2-Trichloroethane	Styrene
1,1-Dichloroethane	Benzene	Xylene (total)
1,2-Dichloroethene (totl.)	cis-1,3-Dichloropropene	Bromofluorobenzene (smc)
Chloroform	Bromoform	Toluene-d_8 (smc)
1,2-Dichloroethane		
2-Butanone		
1,2-Dichloroethane-d_4 (smc)		

(smc) - system monitoring compound

A second requirement of the ID file used for CLP analysis are set and defined primary (quantitation) ions, as well as recommended secondary ions. These ions are as follows for each target and system monitoring compounds:

Analyte	Primary Ion*	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	**43	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	--
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2 Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	91	92
Chlorobenzene	112	114
Ethylbenzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91

* The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

** m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Relative response factors (RRFs) must be calculated and evaluated for each of the target compounds and system monitoring compounds.

The Hewlett-Packard program "CBUPD" should be used to generate a calibration curve and "CBRPT" to print out the curve. The printout will contain a RRF for each compound, as well as an average RRF and average relative retention time (RRT). The percent RSD over the five points is also automatically calculated. If information is needed concerning the use of these programs, consult the GC/MS Supervisor. To reiterate, no changes can be made to the calibration files without supervisory approval.

Response factor criteria have been established for the calibration of volatile target and system monitoring compounds. For the initial calibration to be considered valid, the response factors of the compounds listed below must meet the minimum RRF criteria at each concentration level and maximum %RSD criteria, with allowance made for up to two volatile compounds. The RRFs of the two compounds that do not meet criteria must be greater than or equal to 0.010, and the percent differences for the two outliers must be less than or equal to 40.0% for the initial calibration to be acceptable.

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Bromomethane	0.100	20.5	25.0
Vinyl chloride	0.100	20.5	25.0
1,1-Dichloroethene	0.100	20.5	25.0
1,1-Dichloroethane	0.200	20.5	25.0
Chloroform	0.200	20.5	25.0
1,2-Dichloroethane	0.100	20.5	25.0
1,1,1-Trichloroethane	0.100	20.5	25.0
Carbon tetrachloride	0.100	20.5	25.0
Bromodichloromethane	0.200	20.5	25.0
cis-1,3-Dichloropropene	0.200	20.5	25.0
Trichloroethene	0.300	20.5	25.0
Dibromochloromethane	0.100	20.5	25.0
1,1,2-Trichloroethane	0.100	20.5	25.0
Benzene	0.500	20.5	25.0
trans-1,3-Dichloropropene	0.100	20.5	25.0
Bromoform	0.100	20.5	25.0
Tetrachloroethene	0.200	20.5	25.0
1,1,2,2-Tetrachloroethane	0.500	20.5	25.0
Toluene	0.400	20.5	25.0
Chlorobenzene	0.500	20.5	25.0
Ethylbenzene	0.100	20.5	25.0
Styrene	0.300	20.5	25.0
Xylenes (total)	0.300	20.5	25.0
Bromofluorobenzene	0.200	20.5	25.0

The following compounds have no maximum %RSD, or maximum % difference criteria; however, these compounds must meet a minimum RRF criterion of 0.010:

Acetone	1,2-Dichloropropane
2-Butanone	2-hexanone
Carbon disulfide	Methylene chloride
Chloroethane	4-Methyl-2-Pentanone
Chloromethane	Toluene-d8
1,2-Dichloroethene (tot)	1,2-Dichloroethane-d4

Internal standard responses and retention times in all standards must be evaluated immediately after data acquisition; if the RT for any internal standard changes by more than 0.50 minutes from the latest daily calibration standard, corrections must be made to the chromatographic system. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of 2 (-50% to +100%), corrective action should be undertaken, and the GC/MS system recalibrated.

Each GC/MS system must be calibrated upon award of the contract and following system corrective action, including ion source cleaning or repair and column removal or replacement.

If time remains in the twelve hour clock (timed from the injection of the system performance check) after meeting the initial calibration acceptance criteria, samples may be analyzed. The VSTD050 in the curve may be used as the continuing calibration standard as long as it meets the continuing calibration acceptance criteria. All samples must be quantitated using the response factors from the VSTD050; this is accomplished by using the "QCAL" command instead of the "CBCAL" command.

Medium quantitation reports and a copy of the "CBRPT" should be filed in the appropriate notebook in the GC/MS laboratory. Older calibration information (greater than 1 month) is removed from the notebooks and is filed in manilla folders in the file cabinet in the GC/MS laboratory. Ensure that each page of the medium quantitation report contains the date and time of injection as well as the pertinent EPA case and SDG number.

2.0.2 Continuing Calibration

A check of the calibration curves must be performed once every twelve hours, immediately following analysis of the system performance check compound (BFB). This check is accomplished by analysis of a 50 ppb standard containing all target and system monitoring compounds.

After quantitation of this continuing calibration standard, response factors must be calculated and compared to the mean response factors in the initial calibration. This is accomplished using the program "CBCHK". This program calculates response factors and compares them to the mean RF by calculating percent differences. The continuing calibration criteria for both minimum RRF and maximum percent

difference must be met before method blank and/or samples analysis can proceed. Refer to Table 2 on page 10 of this SOP for maximum percent difference and minimum RRF criteria for a continuing calibration check.

If the continuing calibration standard does not meet criteria (with allowance for 2 deviations), corrective action must be undertaken.

2.0.3 Method Blank Analysis

A method blank must be analyzed in every twelve hour time period, immediately following an initial or continuing calibration, and prior to analysis of any samples.

For water samples, a volatile method blank consists of a 5 mL volume of reagent water (Poland spring) spiked with system monitoring compounds and internal standards at a concentration of 50 ug/L.

An acceptable volatile method blank for water samples must contain less than or equal to five times the contract required quantitation level (CRQL) of methylene chloride, acetone, and/or 2-butanone, and less than or equal to the CRQL of any other volatile compound.

2.0.4 Sample Analysis

All water samples must be allowed to warm to ambient temperature prior to analysis.

Samples may be analyzed only after the GC/MS system has met tuning criteria, initial calibration, and continuing calibration requirements. Ensure that the same instrument conditions were used for tuning, calibration, and sample analysis by reviewing the GC parameters using the Hewlett-Packard program "LMETH".

The sample is poured into the barrel of a 5 mL gas tight syringe and the volume adjusted to 5 mL, taking care to remove any residual air. Once sample aliquots have been taken for the VOA vial, the pH of the water sample must be determined. The purpose of this determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper; do not immerse the pH paper in the VOA sample. The pH at each sample must be recorded in the appropriate GC/MS notebook and a copy of this notebook page given to the GC/MS Supervisor for inclusion into the SDG narrative. No pH adjustments are to be made by the analyst.

The system monitoring compounds and internal standard mix should be added to the 5 mL syringe containing the sample, and the mixture transferred to an autosampler sparger without delay. Refer to section 6.0 of this SOP for guidance in the preparation of the system monitoring/internal standards mix.

The Tekmar LSC2000 and 2016 autosampler should be set to run the entire batch of samples without delay. For a detailed description of the operation and conditions of the Tekmar autosampler refer to section 2.0.1 of this SOP.

Each analytical run must be checked also for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial calibration requires that the system should not be saturated for high response compounds at 200 ug/L for VOA target compounds. In addition, the system must not be saturated by the two xylene isomers that coelute on the GC column used for analysis when the coeluting peak represents 400 ug/L, or for the two 1,2-dichloroethene isomers that may coelute when the coeluting peak represents 400 ug/L.

After analysis of a sample that contains a target compound at a level exceeding the initial calibration, measures must be taken to demonstrate that subsequent analyses are free from carryover. The analyst should analyze a method blank immediately after the contaminated sample, and a method blank in the same sparger position during its next use. Both of these blanks must not contain the target compound in question at a level greater than the contract required quantitation level (CRQL) for that compound. Alternatively, the analyst, in conjunction with the Section Supervisor, may elect to monitor both the sample immediately after the contaminated sample and the sample next run in the same sparger position for the target compound in question. Both of these samples must not contain the target compound in question at a level greater than the CRQL for that compound. If these criteria are not met, the sample in question of being contaminated by carryover must be reanalyzed.

3.0 ANALYSIS OF LOW-LEVEL SOIL SAMPLES

3.0.1 Set Up and Operation of Tekmar LSC2000/2016 Autosampler

The low-level soil method is based upon a heated purge of a 5g soil/sediment sample mixed with 5 mL of reagent water containing the system monitoring compounds and internal standards. Prior to analysis of an initial or continuing calibration, the Tekmar LSC2000 must be edited to include the

heated purge. The preheat time and sample heater temperature should be set as follows:

- Preheat Time: 1.00 min.
- Sample Heater Temperature: 40°C

All other Tekmar LSC2000/2016 parameters are identical to those used of aqueous samples, and are listed below:

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ± 0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	Ambient (water or medium level soil); 40°C (low level soil) required

Desorb Conditions:

Desorb Temperature:	180° C
Desorb Flow Rate:	15 mL/min.
Desorb Time:	4.0 ± 0.1 min.
Bake time:	5.00 min.

3.0.2 Instrument Calibration

3.0.2.1 Initial Calibration Low-Level Soil/Sediment

Prior to use, perform the daily balance calibration check and record the results in the appropriate logbook.

A five point calibration containing 5 g of muffled blank sand, all target and system monitoring compounds is analyzed at the following levels: 10, 20, 50, 100, 200 ug/kg. Also each calibration standard must contain internal standards (bromochloromethane, 1,4,-difluorobenzene, and chlorobenzene-d5) at 50 ug/kg. Consult the standards preparation section of this SOP for detailed instructions concerning preparation and documentation of stock solutions.

5g of muffled blank sand should be weighed into a clean tared sparge vessel, and connected to the 2016 autosampler. Introduction of 5 mL reagent water containing all target and system monitoring compound and internal standards is identical to that of the aqueous initial calibration curve. A detailed discussion of the aqueous initial calibration requirements can be found in section 2.0.2.1 of this SOP.

After analysis of the five points, they must be quantitated and evaluated for adherence to QC criteria,

as follows. Quantitation must occur using I_CCLS for the HP5995C and I_YCLS for the HP5970B. The ID files are not to be edited without written approval of the GC/MS Section Supervisor. Minimum requirements of these ID files are the same as outlined for the water ID files in section 2.0 of this SOP.

Initial calibration curve evaluation criteria are discussed in Section 2.0.2.1 of this SOP. No changes are to be made to calibration or ID files without written approval of the GC/MS Section Supervisor. Separate initial calibration curves must be maintained for water and low-level soil analyses.

If time remains in the twelve hour clock (timed from injection of the system performance check) after meeting the initial calibration acceptance criteria, samples may be analyzed. The VSTD050 in the curve may be used as the continuing calibration standard as long as it meets the continuing calibration acceptance criteria. All samples must be quantitated using the response factors from the VSTD050; this is accomplished by using the "QCAL" command instead of the "CBCAL" command.

3.0.3 Method Blank Analysis

A method blank must be analyzed in every twelve hour time period, immediately following an initial or continuing calibration, and prior to analysis of any samples.

For low level soil samples, a method blank consists of 5g muffled blank sand, 5 ml of reagent water (Poland Spring; non-carbonated) spiked with system monitoring compounds and internal standards at a concentration of 50 ug/kg. An acceptable volatile low level soil method blank must contain less than or equal to 5 (five)times the CRQL of methylene chloride, acetone, and/or 2-butanone, and less than or equal to the CRQL of any other volatile target compound.

3.0.4 Sample Analysis Low Level Soil

All soil samples must be allowed to warm to ambient temperature before analysis.

The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 5g into a tared purging device. Note and record the actual weight to the nearest 0.1g.

Connect the purge device to the 2016 autosampler without delay to avoid less of volatile organics.

After a sample that contains a target compound at a level exceeding the initial calibration range, measures must be taken to demonstrate that subsequent analyses are free from carryover.

The analyst should analyze a method blank immediately after the contaminated sample, and a method blank in the same sparger position during its next use. Both of these blanks must not contain the target compounds in question at a level greater than the CRQL for that compound.

Alternatively, the analyst, in conjunction with the Section Supervisor, may elect to monitor both the sample immediately after the contaminated sample and the sample run in the same sparger position for the target compound in question. Both samples must not contain the target compound in question at a level greater than the CRQL for that compound.

To prepare the contract required matrix spike and matrix spike duplicate, weigh out 5g portions of the sample chosen for spiking. Add 5 mL of reagent water (Poland Spring; non-carbonated) containing the matrix spike mix and system monitoring compounds for a final concentration of 50 ug/kg.

A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, or the following, whichever is more frequent:

- Each case of field samples received, or
- Each 20 field samples in a case, or
- Each group of field samples of a similar concentration level (soils only), or
- Each 14 calendar day period during which field samples in a case were received.

If a question arises about frequency of matrix spikes, consult the Section Supervisor.

4.0 ANALYSIS OF MEDIUM-LEVEL SOIL SAMPLES

4.0.1 Extraction

The medium-level soil method is based on extracting the soil sample with methanol. An aliquot of the methanol extract is added to reagent water containing the system monitoring compounds and the internal standards. The reagent water containing the methanol extract is purged at ambient temperature.

The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 4 g (wet weight) into a tared vial. Add 9 mL of methanol to the vial and 1.0 ml of smc solution. Cap and shake for two minutes. Centrifuge to assist in phase separation. Using a disposable pipet, transfer approximately 1 mL of extract into a 1 mL vial for storage. Clearly label the extract with sample number, date of extraction, case number, and analyst initials. The remainder of extract may be discarded. Transfer approximately 1 mL of methanol to a labeled 1 mL vial for use as a method blank for each case, SDG, or day on which medium level extractions are performed. The extracts should be stored in the dark at 4°C (± 2°C) prior to analysis.

To prepare a matrix spike and matrix spike duplicate for medium-level soil samples, add 8.0 mL of methanol, 1.0 mL of matrix spike solution, and 1.0 mL of smc. solution to two 4 g portions of sample. This results in a 6200 ug/kg concentration of each matrix spike compound.

4.0.2 Tekmar LCS2000/2016 Setup and Operation

Analysis of medium-level soil extracts requires a purge at ambient temperature; therefore, the autosampler set up and operation is identical to that of aqueous samples.

4.0.3 Instrument Calibration Medium-Level Soil

4.0.3.1/ 4.0.3.2 Initial and Continuing Calibration

Because the methanol extract and reagent water mixture is purged at ambient temperature, the instrument performance check (BFB), initial calibration, and continuing calibration for water samples may be used for analysis of medium level soil extracts.

4.0.4 Medium-Level Soil Method Blank Analysis

A method blank must be analyzed in every twelve hour time period, immediately following an initial or continuing calibration, and prior to analysis of any samples.

For medium-level soils, a method blank consists of 4g of purified sand spiked with the smc. solution and carried throughout the analytical process.

An acceptable volatile method blank for medium-level soil samples must contain less than or equal to five (5) times the CRQL of methylene chloride, acetone, and 2-butanone, and less than or equal to the CRQL of any other volatile compound.

4.0.5 Sample Analysis -- Medium-Level Soil

Since the medium-level soil extract is quantitated under aqueous calibrations, the 100 uL aliquot of methanol extract is spiked into 5 mL of reagent water containing internal standards.

To analyze a medium-level soil matrix spike and matrix spike duplicate, add 100 uL of methanol extract to 5 mL of reagent water containing internal standards.

5.0 DATA REVIEW

5.0.1 Initial Data Review (IDR)

The initial data review is accomplished by the analyst who is assigned to process paperwork for that week. The review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed.

The requirement of the GC/MS laboratory is that this initial data review be completed within twelve hours of batch completion. In the majority of instances, the initial data review should be accomplished at the beginning of a work shift for the previous set of analyses. After the analyst has completed his or her IDR, the IDR packet (defined below) should immediately be forwarded to the GC/MS Section Supervisor.

The initial data review is accomplished with the use of the IDR sheet (template following on next page) and full quantitation reports from each sample. This data review examines six key criteria that directly impact whether or not the sample needs to be reanalyzed.

- system monitoring compound (SMC) recoveries
- stability of internal standard responses
- method blank acceptance
- chromatography
- target compound detection/quantitation
- matrix spike/matrix spike duplicate recoveries

ABB Environmental GC/MS Laboratory

VOA INITIAL DATA REVIEW SHEET FOR CLP-OLM01.8

(To be filled out within 12 hours of batch completion)

Date: _____

Primary Analyst: _____

Supervisor: _____

Data was collected under BFB Tune File: _____ Inj. Time: _____

Data was collected under Calibration Check File: _____ apex scan: _____

Data was collected under Method Blank File: _____ ENH,-1:1

SUB scan: _____

clock ends: _____

Curve Date: _____ Files: _____ Matrix: _____

CASE NO.	SDG NO.	EPA CLP sample no.	Data File	Internal Standard Area			System Monitoring Compounds			Chromatography Acceptable (Y or N)	Target Compounds in Working Range (Y or N)	Preliminary Data Acceptable (Y or RERUN)
				-50%:			76-114	Water 88-110	86-115			
				+100%:				Soil				
				BCM	1,4-DFB	CB-d5	70-121 1,2DCA-d4	84-138 TOL-d8	59-113 BFB			
Cal Check Std							NA	NA	NA			
Method Blank												

File: VCLPIDR

Comments: _____

5.0.1.1 System Monitoring Compounds

Recoveries for each system monitoring compound (SMC) are calculated as follows:

$$\% \text{ Recovery} = \frac{\text{concentration (or amount) found}}{\text{concentration (or amount) spiked}} \times 100$$

If the recovery of any one SMC is not within limits, the following is required:

- Check calculations and instrument performance.
- Reanalyze the sample if none of the above reveals a problem
- If an undiluted analysis with acceptable SMC recoveries must be diluted and reanalyzed, the SMC recoveries for the diluted reanalysis may be outside the limits.
- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD SMC recoveries are within limits. If the sample and associated MS/MSD show the sample pattern (outside limits), then the sample does not require reanalysis.

5.0.1.2 Method Blank Criteria

An acceptable method blank must contain less than or equal to five times the CRQL of methylene chloride, acetone, and/or 2-butanone, and less than or equal to the CRQL of any other volatile target compound.

For detailed descriptions of set up and analysis of method blanks, refer to the following sections of this document:

2.0.3 Aqueous Samples
3.0.3 Low-Level Soil Samples
4.0.4 Medium-Level Soil Samples

5.0.1.3 Stability of Internal Standard Responses

Internal standard responses and retention times in all samples and blanks must be evaluated as part of the IDR. The ID files have been set up to only detect compounds that fall within a set retention time (RT) window of ± 0.50 minutes or less; therefore, only the internal standard areas and not RTs need be recorded on the IDR sheet. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor

of two (-50% to + 100%) as compared to the daily continuing calibration standard, reanalysis must occur. If the reanalysis meets criteria, only the in-criteria run should be reported. If the reanalysis is out of criteria, both analyses should be included in the data package.

MS/MSD samples that do not meet the EICP area criteria do not have to be reanalyzed.

5.0.1.4 Chromatography

The chromatography should be examined for the presence of any "ghost" peaks and can also be useful in evaluating the influence of matrix interference on SMC recoveries and internal standard responses. Whether or not the chromatography is acceptable is a judgement call on the part of the analyst and should be used in conjunction with other monitored QC to determine the necessity of reanalysis. For further guidance, consult the GC/MS Section Supervisor.

5.0.1.5 Target Compound Detection/Quantitation

The ID files have been set up to err on the side of false positives; that is they identify and quantitate peaks as target compounds that may not necessarily be valid hits.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- all ions found in the standard mass spectra at a relative intensity >10% must be present in the sample spectrum

- the relative intensities of primary and secondary ions must agree within ± 20% between the standard and sample spectra

- ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst

If a compound cannot be verified by all three criteria above, but, in the technical judgement of the mass spectral interpretation specialist the identification is correct, then the laboratory shall report that compound on form I as a valid hit.

Review the quantitation report and mass spectra and cross out any non-valid hits (with a ruler, single line, dated and initialed). In order for the analysis to be valid, all concentrations must fall within the upper limits of the calibration curve, defined as follows:

upper limit = 200 ng(highest curve point) x DF

If any target concentration exceeds the upper limit, a dilution must be made and analyzed. The dilution chosen should keep the response of the largest target compound hit in the upper half of the initial calibration range. MS/MSD samples need not be diluted to get either spiked or non-spiked analytes within the calibration range. If a dilution is required, keep in mind the "carryover criteria" for subsequent samples; this criteria was explained in a previous section of this SOP.

5.0.1.6 Matrix Spike/Matrix Spike Duplicate Recoveries

A matrix spike and matrix spike duplicate (MS/MSD) must be analyzed for each group of samples of a similar matrix, or the following, whichever is more frequent:

- each case, or
- each 20 samples in a case, or
- each group of samples of a similar concentration level, or
- each 14 day calendar period during which samples are received

Matrix spike compound recovery and relative percent difference (RPD) of the recoveries must be calculated. The limits, outlined below, are advisory and should not be used to determine the necessity of reanalysis; however, should there be any deviations, a CCAS corrective action report (CAR) should be filed.

	% Recovery		% Recovery	
Compound	Water	RPD	Soil	RPD
1,1-Dichloroethane	61-145	14	59-172	22
Trichloroethene	71-120	14	62-137	24
Benzene	76-127	11	66-142	21
Toluene	76-125	13	59-139	21
Chlorobenzene	75-130	13	60-133	21

5.0.2 IDR Packet Review by Supervisor

After the IDR sheet has been completely filled out, the analyst needs to assemble the following information in a

packet and provide it to the GC/MS Supervisor for review and signature.

- IDR sheet
- Tuning hardcopy
- Continuing calibration report with medium quantitation report (no spectra)
- Initial Calibration report with medium quantitation reports if analyzed as part of that batch
- Full Quantitation reports (including mass spectra) of blanks, samples, and MS/MSDs

This information needs to be assembled and passed in to the Supervisor for his review within twelve hours after batch completion. In reality, the packet should be prepared as soon as possible following the start of the next work shift.

The Supervisor needs to carefully review the entire packet for QC compliance and to ensure that no dilutions and/or reanalyses were missed during the initial review process.

The GC/MS section will then decide, depending on workload, who is to perform the next step, preparation of data for transfer to a personal computer (PC).

5.0.3 Preparation of Data for Transfer to PC

It is the policy of the GC/MS group that a complete sample delivery group (SDG) be analyzed prior to any data transfer. This allows for greater organization and permits the data management staff more efficient time management.

Only qualified mass spectral interpretation specialists (see qualification guidelines in the beginning of this SOP) are permitted to perform this step.

The following needs to be accomplished prior to data transfer:

- o Prepare a tracking sheet for data management staff that shows each data file that is to be used (ie. a sequence showing each days runs with only those files that are to be included)

- o Using each reviewed IDR packet, gather all tuning hardcopies, calibration standard medium quantitation reports, and full quantitation reports (omitting spectra for internal standards and system monitoring compounds) for samples, blanks, and MS/MSDs

- o Rip apart the computer paper into single sheets and paperclip together each sample's information

- Review the decisions made by the initial analyst concerning the validity of mass spectral hits. Ensure that all non-valid hits have been crossed out on the quantitation reports with a ruled, single line, dated and initialed.

- Using the Hewlett-Packard program "QDEL", delete from each output file all non-valid mass spectral hits.

- Write the case and SDG numbers on all pages where it is not present (ie. standard medium quantitation reports, tuning hardcopies, etc.). Write the date and time of injection on all tuning hardcopy pages.

- Using the Hewlett-Packard program, *FTICV, and the GC/MS library search procedure file "LIBSEA" as a template, run library searches on all samples and blanks. Library searches need not be run on matrix spike/matrix spike duplicate samples.

- Review the library search hardcopies. Double check that the correction factor used for calculations of estimated concentrations (on the bottom of the first page) is the same as the CF on the quantitation report. If any tentatively-identified compound (TIC) has an area less than ten percent of the corresponding internal standard area, it should not be reported. This is accomplished by crossing it out on the first page. Write the analysis date and time of injection on each page and either circle the correct identification of each TIC or characterize it as much as possible (eg. unknown hydrocarbon, unknown aromatic, etc.).

- Generate reduced results files (RR files) from BFBs, calibration standards, matrix spikes, and matrix spike duplicates by editing the GC/MS template, RR_JIM.

- After RR files have been generated, set up a file of all pertinent RR files to dump (transfer) to the PC by editing the GC/MS template dump file, DU_JIM.

- Provide the GC/MS Supervisor with a copy of the dump file, any notes which might be pertinent, to the SDG narrative and a package in the following order:

    - sample quantitation reports in order by EPA-SMO sample ID
    - sample library searches

- initial calibration curves in chronological order (medium)
- continuing calibration reports (medium)
- tuning hardcopies
- method blank quantitation reports
- matrix spike quantitation reports
- GPC chromatograms
- information for the complete SDG file, to include: original IDR sheets, copies of logbook pages (injection, maintenance, standards receipt, and preparation, traceability), GC/FID chromatograms, any hand-written notes (including tracking sheet prepared in step 1), and any other case specific documents.

The GC/MS Supervisor will then review the package for completeness, accuracy, and contract compliance and coordinate the transfer of the SDG to the PC and data management staff.

SDG preparation and review will then be accomplished following the guidelines in the CCAS SOP "CLP Data Package Assembly and Review".

6.0 STANDARDS PREPARATION

Volatile stock standards are purchased from RESTEK, Inc. and include USEPA required quality control documentation. Because these standards are procured with a QC documentation package, ABB-ES standards traceability protocol may be waived. In the event that a standard without the vendor-supplied data package is used, ABB-ES internal traceability procedures must be adhered to. For a detailed explanation of traceability requirements, refer to SOP No. ALSQA-004. In no instance should a standard without a vendor-supplied data package be used before a traceability study has been completed. If there are any questions about the suitability of a standard, consult the GC/MS Section Supervisor.

Each standard has a specific expiration date that <u>must</u> be followed. Commercially obtained stock standards should be transferred into multiple teflon lined screw-cap amber vials when the ampul is cracked open. These screw-cap amber vials must be stored with no headspace at -10°C to -20°C. When one of these screw-cap amber vials has been opened, the label must be notated with an expiration date of one week. Fresh working standards must be prepared every two months for gases and styrene, and every six months for all other volatile standards. It is mandatory to label all vials and to record each preparation in the VOA standard and prep logbook. Refer to pages 2-3 of the introduction in this SOP for a detailed discussion of required labeling conventions of all standards and stocks.

6.0.1 General Procedures for Standard Preparation

When preparing standards in water or spiking samples with internal standards/system monitoring compounds or matrix spike solution, be sure to rinse all syringes a minimum of three times with purge and trap grade methanol between uses, and once with the solution you are about to measure. Failure to do this will result in cross-contamination of samples and standards.

6.0.2 Instrument Performance Check Solution p-Bromofluorobenzene

A 25 ug/mL solution of 4-bromofluorobenzene (BFB) is prepared in purge and trap grade methanol in the following manner:

- Crack open the BFB ampul received from RESTEK (5000 ug/mL in methanol - catalog no. 30003-500).
- Transfer contents to an amber teflon-lined screw-cap vial and label appropriately.
- Add 0.75 ul of this 5000 ug/mL stock to 1.5 ml of purge and trap methanol in a 1.0 mL vessel sealed with a mini-inert valve. The conicals used for storage of this solution hold approximately 1.5 ml even though they are calibrated to only 1.0 ml.

6.0.3 Initial/Continuing Calibration Standards

A total of five stock standard mixes are obtained from RESTEK, Inc.; these five mixes are combined in a 1.0 mL vessel with a mini-inert valve for a working standard at 200 ug/mL concentration as follows:

6.0.3.1 VOA Calibration Mix No. 1 (catalog No. 30006-500)

This mixture contains the following analytes at a concentration of 5000 ug/mL:

Acetone	4-Methyl-2-Pentanone
2-butanone	2-hexanone

Procedure:

- Crack open an ampul of Calibration Mix No. 1.
- Add 60 uL of Calibration Mix No. 1 to 840 uL of purge and trap grade methanol in a vessel sealed with a mini-inert valve.

6.0.3.2 VOA Calibration Mix No. 2 (catalog No. 30007-500)

This mixture contains the following analytes at a concentration of 2000 ug/mL:

carbon disulfide	Ethylbenzene
benzene	p-xylene
toluene	o-xylene

Procedure:

- o Crack open an ampul of Calibration Mix No. 2.
- o Add 150 uL of Calibration Mix No. 2 to the standard mix vessel.

6.0.3.3 VOA Calibration Mix No. 3 (Catalog No. 30008-500)

This mixture contains the following analytes at a concentration of 2000 ug/mL:

1,1-Dichloroethene	Trichloroethene
Methylene chloride	1,2-Dichloropropane
1,1-Dichloroethane	1,1,2-Trichloroethane
Chloroform	Chlorobenzene
Carbon Tetrachloride	m-Xylene

Procedure:

- o Crack open an ampul of Calibration Mix No. 3.
- o Add 150 uL of Calibration Mix No. 3 to the vessel containing the standard mix.

6.0.3.4 VOA Calibration Mix No. 4 (Catalog 30004-500)

This mixture contains the following analytes at a concentration of 2000 ug/mL:

trans-1,2-dichloroethene	trans-1,3-dichloropropene*
cis-1,2-dichloroethene	tetrachloroethene
1,1,1-trichloroethane	Dibromochloromethane
1,2-dichloroethane	Styrene
Bromodichloromethane	Bromoform
cis-1,3-dichloropropene*	1,1,2,2,-tetrachloroethane

* The proportion of these isomers varies with each lot. It is imperative that the proportions be identified when a new standard mix is prepared, and the GC/MS Section Supervisor notified so the ID and calibration files may be amended prior to analysis of any samples.

Procedure:

- o Crack open an ampul of Calibration Mix No. 4.
- o Add 150 uL of Calibration Mix No. 4 to the vessel containing the standard mix.

6.0.3.5 VOA Calibration Mix No. 5 (Catalog No. 30010-500)

This mixture contains the following analytes at a concentration of 2000 ug/mL:

chloromethane	Bromomethane
Vinyl chloride	chloroethane

Due to the extreme volatility of these compounds, this stock mix should always be added last to the standard mix.

Procedure:

- Due to the extreme volatility of these compounds, transfer should be performed as rapidly as possible using the cold ampul directly from the VOA standards freezer.
- Crack open ampul of Calibration Mix No. 5.
- Rapidly remove 150 uL and add to the vessel containing the standard mix.
- The expiration date for this calibration mix is one week from the initial date of preparation.

6.0.4 VOA System Monitoring Compound Mix (Catalog No. 30004-500)

This mixture contains the following compounds at a concentration of 2500 ug/mL:

1,2-dichloroethane-d4
Toluene-d8
4-Bromofluorobenzene

Procedures for system monitoring compound mix only:

- Crack open ampul of stock mix.
- Add 150 uL of system monitoring stock mix to 1350 uL of purge and trap grade methanol in a vessel sealed with a mini-inert valve.

6.0.5 Internal Standard Mix (Catalog No. 30011-500)

This mix contains each of the following compounds at a concentration of 2500 ug/L:

bromochloromethane
chlorobenzene-d5
1,4-difluorobenzene

Two different mixes must be prepared using this internal standard mix stock solution, one working internal standard-only solution at 50 ug/mL for initial calibration curves, and a combined internal standard/system monitoring compound mix at 50 ug/mL.

Procedure for internal standard-only solution:

- Crack open ampul of Internal Standard stock mix.
- Add 30 uL of stock to 1470 uL of purge and trap grade methanol in a vessel sealed with a mini-inert valve.

Procedure for combined internal standard/system monitoring compound solution:

- Add 30 uL of internal standard stock mix to 1440 uL of purge and trap grade methanol.
- Add 30 uL of system monitoring compound mix stock to the methanol internal standard solution just described.
- Seal the vessel with a mini-inert valve.

6.0.6 Matrix spike Mix (Catalog No. 30005-500)

This mix contains each of the following compounds at a concentration of 2500 ug/mL:

1,1-dichloroethene	Toluene
Benzene	Chlorobenzene
Trichloroethene	

Procedure:

- Crack open ampul of matrix spike mix stock.
- Add 30 uL of matrix spike mix stock to 1470 uL of purge and trap grade methanol in a vessel sealed with a mini-inert valve.

REFERENCES:

USEPA CLP Statement of Work for Organics Analysis, Document No. OLM01.0, including revisions OLM01.1, OLM91.2, OLM01.3, OLM01.4, OLM01.5, and OLM01.6.

ATTACHMENTS:

Attachment A: Standards Receipt Logbook page
Attachment B: Standards Preparation Notebook page

ABB-EI

Attachment A

Notebook No. 2

PROJECT ORGANIC STD. RECEIPT LOG

Continued From Page

Supplier	Standard		date rec'd	Lot #	data pkg rec'd on file	date opened	date disarded
Restek	Surrogate standard	#1	03/10/92	A001097	yes		
		#2					
		#3					
		#4					
		#5					
Restek	VOA CAL Mix 4	#1	03/10/92	A 000921	yes		
		#2					
		#3					
		#4					
		#5					
Restek	VOA CAL Mix 3	#1	03/10/92	A000883	yes		
		#2					
		#3					
		#4					
		#5					
Restek	VOA CAL Mix 2	#1	03/10/92	A 000885	yes		
		#2					
		#3					
		#4					
		#5					
Restek	VOA CAL Mix 1	#1	03/10/92	A 000934	yes		
		#2					
		#3					
		#4					
		#5					
Restek	VOA CAL Mix 5	#1	03/10/92	A 001057	yes		
		#2					
		#3					
		#4					
		#5					
		#6					
		#7					
		#8					

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Read and Understood By

Date | Signed | Date | Signed | Date

PROJECT ABBES VOA STANDARD PREP LOG

Notebook No. 5 Attachment 13

Continued From Page

Prep of Surrogate mix 030492 JK

VOA LM Surrogate Spike Mix
2500ug/ml ea. in methanol
Cat.# 30004 Lot # A 000648
Restek Corporation • 110 Benner Circle • Bellefonte, P

Surrogate stock 2500ug/ml lot A000648 80uL in 920uL of MeOH
conc 200ug/ml
code VOA030492P24:5
exp 9/92

Prep of Internal standard Mix 030492 JK

VOA LM Internal Standard Mix
2500µg/ml ea. in methanol
Cat.# 30011 Lot # A 000599
Restek Corporation • 110 Benner Circle • Bellefonte, F

20uL of Internal standard stock lot A000599 (2500ug/ml)
980uL of MeOH

conc 50ug/ml
Code VOA030492P24:5
exp 9/92

Prep of Matrix spike Mix 030492 JK

VOA LM Matrix Spike Mix
2500ug/ml ea. in methanol
Cat.# 30005 Lot # A 000596
Restek Corporation • 110 Benner Circle • Bellefonte, PA

~~80uL~~ 20 JK 030492 of matrix spike stock lot A000596 (2500ug/ml)
JK 030492 ~~920ug~~ ~~920uL of MeOH~~ JK 030492 980 uL MeOH
~~conc 5~~ JK 030492
conc = 50ug/ml code = VOA030492P24:5 exp 9/92

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Read and Understood By

Signed Date Signed Date

STANDARD OPERATING PROCEDURE

Author: J.F. Galasyn, Ph.D/J.J. Casarin
Approved By:

Willard C. Warren, III
President, Northeastern Division

Issuing Unit: CCAS-Northeast
SOP No.: CA-067-00
Date: February 1993

TITLE: Analysis of Semivolatile Organic Compounds by Capillary Column GC/MS: USEPA Contract Laboratory Program, Document Number OLM01.0 (including revisions OLM01.1, OLM01.2, OLM01.3, OLM01.4, OLM01.5, OLM01.6 and OLM01.8).

PURPOSE: To describe the procedures utilized by the CCAS-NE laboratory to prepare and analyze sample extracts for semivolatile organics in accordance with US EPA CLP protocols.

SCOPE: This standard operating procedure (SOP) addresses analysis of aqueous and soil extracts for semivolatile (base/neutral and acid fractions) organics according to the most current SOW (referred to as OLM01.8 in this document). Soil samples are first screened using GC/FID to determine proper dilution levels and extraction technique. After the extraction and screening process (defined in the current revisions of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Cleanup for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment," and SOP No. CA-098, "Screening of Semivolatile Organic Extracts by Gas Chromatography/Flame Ionization Detector by USEPA CLP (August, 1991, OLM01.8 Revision)," identification and quantitation is performed by capillary column GC/MS.

To summarize, the technique begins with extraction of semivolatiles from the sample using an appropriate solvent, followed by clean-up steps, and concentration of the extract. An aliquot of the extract is then injected into the gas chromatograph for compound separation, followed by the electron impact mass spectrometer for identification and quantitation.

This SOP will consolidate all aspects of the analyses in one working document, to be revised as necessary, for the purposes of consistency in data quality.

REQUIREMENTS:

Before beginning analysis of any samples under the USEPA CLP protocol, the analyst is required to fulfill the minimum education/experience, as follows:

- bachelors degree in chemistry/science/engineering plus one year GC/MS/DS experience, or:
- three years GC/MS/DS experience and GC/MS interpretation

A certificate of training (see the current revision of CCAS-NE SOP No. AD-002, "Personnel Training") must be issued, signed by the appropriate supervisor, indicating that the analyst is qualified to perform sample analyses following this SOP.

GC/MS Spectral Interpretation Specialist requirements, as follows, must be fulfilled before an analyst can review and interpret mass spectral data, including tentatively-identified compound (TIC) determinations:

- bachelors degree in chemistry/science/engineering plus a training course in mass spectral interpretation plus two years experience

Once again, a completed CCAS-NE certificate of training must be issued before interpretation can proceed.

Prior to analysis of any samples under the OLM01.8 SOW, the analyst is required to review in detail and become familiar with all aspects of the SOW. This review should include, but not be limited to: screening, standards preparation and traceability, sample preparation and analysis, data review, and instrument calibration protocols and criteria.

To aid in organization and record keeping in the GC/MS semivolatiles section, strict naming and coding conventions are required for analytical standards, data files, quantitation output files, identification (ID) files and calibration files, archive tapes, and file header information. The required naming conventions are as follows:

SV: XXXXXX : N_1 : N_2 : Z
CC ug/ml
Exp. date: YYYYYY
Analyst:

where:
SV= semivolatile organics section (GC/MS)
XXXXXX = date of preparation (e.g. 121891)
N_1 = page number of SVOA standards preparation log where prep details can be found
N_2 = preparation logbook number
Z = standard entry on page (e.g., A,B,C,D, etc.)
CC = concentration of solution contained in vial (either single component or multi-component, single concentration)
YYYYYY: date of expiration

On all vials in storage, this information must appear, along with a description of the contents (e.g. DFTPP, internal standard mix, etc.)

Vials stored without the above information are subject to being discarded during periodic (unannounced) supervisory/QC coordinator inspections/audits.

Fresh standards must be prepared every twelve months at a minimum, and stored in a freezer at -10°C to -20°C. The continuing calibration standard (50 ng) must be prepared weekly and stored at 4°C (± 2°C).

Standard preparation procedures are described in detail in section 10.0 of this SOP. An audit of the coding system, as well as the storage conditions and standard preparation logbook(s) is performed by the GC/MS supervisor on a monthly basis. Should any deviations be detected, a corrective action report (CAR) is filed with the QA/QC coordinator. The QA/QC coordinator also audits for the above items on a semiannual basis; copies of the internal audit reports, as well as corrective action reports, are filed in the QA/QC office.

All BNA standards, except for the SSTD050 continuing calibration check, are stored in the white cube freezer in the GC/MS laboratory, labelled "GC/MS BNA Standards Freezer." The continuing calibration standard is stored in a white cube refrigerator in the GC laboratory, labelled "Org. Extractables Continuing Calibration Stds Refrigerator." All extracts are stored in the white refrigerator in the extractions laboratory, labelled "Refrigerator: Organic Extracts."

- Computer (data system) conventions - two GC/MS units are employed for BNA analysis, both Hewlett-Packard model 5970B, designated as MS1 and MS2. Both units are interfaced to and directly controlled by a HP1000 RTE-VI computer with Aquarius software.

Conventions for the MS1 are as follows:

Cartridges for data acquisition and storage: D5, D4, D3, D2, D1, A2, A0, and A1
Cartridge for quantitation output files:
A1 (default); SC (backup if QT temporarily full)
Tune file: MT1000
Method files: M_XCLP (all CLP samples and standards)
M_XDFC (DFTPP tuning acquisition)
Note: all acquisition parameters must be identical in M_XDFC and M_XCLP.

Data files: >X_ _ _ _, where _ _ _ _ is a number in chronological order from 0000 to 9999. Data files for DFTPP: >XD_ _ _ where _ _ _ is a number in chronological order from 000 to 999. Quantitation output files: ^X _ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999 corresponding to the data file.

Identification (ID) files:

I_XCLW: aqueous samples (TCL)
I_XCLS: soil/sediment samples (TCL)
I_XPES: pesticide/PCBs (for confirmation of GC results when needed)
Note: ID files are not to be edited without supervisor approval

Calibration files:
C_XCLP (all samples-BNA TCL list)
C_XPES (pesticides/PCBs)

Note: calibration files are not to be edited without supervisor approval

Conventions for the MS2 are as follows:

Cartridges for data acquisition and storage: A0, A2, D1, D2, D3, D4, D5, and A1
Cartridge for quantitation output file storage: A1 (default); SC (backup if QT temporarily full)
Tune File: MT2000

Method files: M_BCLP (all CLP samples and standards)
M_BDFC (DFTPP tuning acquisition)
Note: all acquisition parameters must be identical in M_BCLP and M_BDFC.
Data files: >B_ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999.
Data files for DFTPP: >BD_ _ _ where _ _ _ is a number in chronological order for 000 to 999.
Quantitation output files: ^B_ _ _ _ where _ _ _ _ is a number in chronological order from 0000 to 9999 corresponding to the data file

Identification (ID) files:

I_BCLW: aqueous samples (TCL)
I_BCLS: soil/sediment samples (TCL)
I_BPES: pesticides/PCBs (for confirmation of GC results when required)

Note: ID files are not to be edited without supervisor approval.
Calibration files:
C_BCLP: all samples-BNA TCL list
C_BPES: pesticides/PCBs
Note: ID files are not to be edited without supervisor approval.

Sample header information must be structured exactly as follows in the batch edit ("BEDIT") program under Aquarius:

Name: EPA Sample ID/Sample ID
Misc: Instrument ID;Case No.;SDG No.; Contract No. (if applicable)

No deviations from the above nomenclature are allowed.

PROCEDURE: The standard procedures utilized for analysis of semivolatile Organics in extracts by GC/MS according to CLP SOW OLM01.8 will be described in separate sections.

Documentation of all activities associated with the sample analysis is a necessity; all information must be entered into pertinent logbooks by the analyst performing the activity at the time the activity is performed. Analytical run/injection logbooks are maintained for each instrument, and must be completely and accurately completed while analyzing any standard, blank, or sample. Information to be entered includes the client, job (Case/SDG No.), description of the sample, assigned data file number, dilution factor, no. of ul injected, auto sampler position number, and analyst initials. In addition, the top of each page must contain the logbook title. Each page must be numbered sequentially, with the date of analysis appearing. Each standard must have a code assigned to it and the code must be written under the sample description (for an explanation of the standard coding system, see page 2 of this SOP). Reasons for reruns/dilutions must be entered. Refer to the current revision of CCAS-NE SOP No. SD-003, "Records of Sample Preparation and Analysis for Samples Requiring CLP Protocols," for more information. Logbooks are reviewed and signed off on a monthly basis by the GC/MS supervisor. If further information is required, consult the GC/MS supervisor.

1.0 INSTRUMENT TUNING

Prior to the analysis of any calibration standards, blanks, or samples, the GC/MS system must be shown to meet the mass spectral ion abundance criteria for decafluorotriphenylphosphine (DFTPP), tabulated below:

DFTPP Key Ions and Ion Abundance Criteria

Mass	Criteria
51	30.0-80.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	present
70	less than 2.0 percent of mass 69
127	25.0-75.0 percent of mass 198

Mass	Criteria
197	less than 1.0 percent of mass 198
198	base peak, 100 percent of mass 198
199	5.0-9.0 percent of mass 198
275	10.0-30.0 percent of mass 198
365	greater than 0.75 percent of mass 198
441	present, but less than mass 443
442	40.0-110.0 percent of mass 198
443	15.0-24.0 percent of mass 442

* All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

The analysis of DFTPP is accomplished as a direct injection of the standard into the GC/MS. Refer to the standards preparation part of this SOP (section 10.0) for instructions concerning preparation of this solution.

The following are the GC/MS operating conditions for injection of DFTPP:

Initial column temperature hold - 40°C for 3 minutes
Column temperature program - 40-260°C at 10 degrees/min.
Final column temperature hold - 260°C
Injection port temperature - 285°C
Transfer line/source temperature - 250°C
Injector - splitless, valve time 0.18 minutes
Scan start time - 18.0 minutes
Sample volume - 2.0 ul of 25 ng/ul solution
Carrier gas - helium at approx. 30 ml/min
Mass range - 35 to 500 amu
Capillary column: J&W Scientific DB-5, 30m x 0.25 mm ID

All of the above are set up in the method files M_XDFC (and M_BDFC) and must not be changed without supervisor approval.

It is assumed here that the analyst is proficient with the HP-RTE VI/Aquarius Software package prior to analysis since at least one year of GC/MS/DS experience must be gained before analysis of CLP samples. The Aquarius program "BEDIT" should be used to set up and start the run. Consult the Aquarius software manual in the laboratory or ask the GC/MS supervisor if there are questions on how to proceed.

Once the DFTPP run is completed, the mass spectrum of this tuning compound must be evaluated to determine if calibration and sample analysis can proceed. The mass spectrum must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and

averaged (ENH,-1:1). Background subtraction is required, and must be accomplished using a single scan prior to the elution of DFTPP.

If the mass spectrum of DFTPP does not meet the specified criteria, the instrument must be manually tuned and DFTPP reinjected. If the DFTPP spectrum is still not in criteria, notify the GC/MS supervisor for corrective action instructions.

The DFTPP solution must be analyzed once at the beginning of each twelve hour period during which samples or standards are analyzed.

The twelve hour time period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve hours have elapsed according to the system clock. The last injection must be accomplished prior to expiration of the twelve hours; conceivably, the run-time could end after the twelve hours have elapsed.

After tuning criteria have been met, a hardcopy report must be generated and filed.

The first page of the hardcopy must contain an injection header ("MSH") and a copy of the bar graph spectrum. The second page must contain a full mass listing, with all masses normalized to m/z 198 at 100 percent. The third and final page of the DFTPP hardcopy must contain a copy of the reconstructed total ion chromatogram, labelled with the date and time of injection.

2.0 INSTRUMENT CALIBRATION

2.0.1 Initial Calibration

Prior to the analysis of samples and required method blanks, and after the instrument performance check solution criteria (DFTPP tuning) have been met, the GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target compounds.

Calibration standards containing all semivolatile targets and surrogates must be prepared at 20, 50, 80, 120, and 160 total ng per 2ul. 2ul injections are required for all analyses done according to this SOP. Accordingly, the initial calibration standards must be prepared at concentrations of 10, 25, 40, 60, and 80 ng/ul, with the internal standards [1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12] being held constant at 40ng per 2ul injection. Consult the standards

preparation section (Section 10.0) of this SOP for detailed instructions concerning preparation of these solutions.

Eight target compounds, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, and pentachlorophenol require only a four point calibration at 50, 80, 120, and 160 total ng, since detection at less than 50 ng per injection is difficult. If these eight compounds are detected in the 20ng injection, they should be deleted from the quantitation output file using the program "QDEL".

Great care must obviously be used in preparation and storage of these standards. They must be prepared every twelve months at a minimum, and stored in a freezer at -10°C to -20°C in screw-cap amber bottles with teflon liners.

After preparation of the standards as described in the prep section of this SOP, a sequence containing these five injections is set up under the program "BEDIT". Ensure that both the data file and quantitation output file are archived automatically to magnetic tape after each run; this is an absolute necessity!

After analysis of the five points, they must be quantitated and evaluated for adherence to QC criteria, as follows. Quantitation must occur by both of the CLP ID files, I_XCLW and I_XCLS, to ensure that both ID files are working properly. The ID files are not to be edited without written approval of the supervisor. Minimum requirement of ID files are use of specific quantitation ions and quantitating a specific set of targets and surrogates with a set internal standard. These requirements are as follows:

<u>Internal Standard: 1,4-dichlorobenzene-d4</u>

Targets and surrogates:

- Phenol
- bis(2-chloroethyl)ether
- 2-chlorophenol
- 1,3-dichlorobenzene
- 1,4-dichlorobenzene
- 1,2-dichlorobenzene
- 2-methylphenol
- 2,2'-oxybis(1-chloropropane)
- 4-methylphenol
- N-nitroso-di-n-propylamine
- hexachloroethane
- 2-fluorophenol (surr.)
- phenol-d5 (surr.)
- 2-chlorophenol-d4 (surr.)
- 1,2-dichlorobenzene-d4 (surr.)

Internal Standard: Naphthalene-d8

Targets and Surrogates:
- Nitrobenzene
- Isophorone
- 2-nitrophenol
- 2,4-dimethylphenol
- bis (2-chloroethoxy) methane
- 2,4-dichlorophenol
- 1,2,4-trichlorobenzene
- Naphthalene
- 4-chloroaniline
- Hexachlorobutadiene
- 4-chloro-3-methylphenol
- 2-methylnaphthalene
- nitrobenzene-d5 (surr.)

Internal Standard: Acenaphthene-d10

Targets and surrogates:
- hexachlorocyclopentadiene
- 2,4,6-trichlorophenol
- 2,4,5-trichlorophenol
- 2-chloronaphthalene
- 2-nitroaniline
- dimethyl phthalate
- acenaphthylene
- 3-nitroaniline
- acenaphthene
- 2,4-dinitrotoluene
- 2,6-dinitrotoluene
- diethylphthalate
- 4-chlorophenylphenyl ether
- fluorene
- 4-nitroaniline
- 2-fluorobiphenyl (surr.)
- 2,4,6-tribromophenol (surr.)

Internal Standard: Phenanthrene-d10

Targets and surrogates:
- 4,6-dinitro-2-methylphenol
- N-nitrosodiphenylamine
- 4-bromophenyl phenyl ether
- hexachlorobenzene
- pentachlorophenol
- phenanthrene
- carbazole
- anthracene
- di-n-butyl phthalate
- fluoranthene

Internal Standard: Chrysene-d12

Targets and surrogates:
- pyrene
- butylbenzylphthalate
- 3,3'-dichlorobenzidine
- benzo(a)anthracene
- bis(2-ethylhexyl)phthalate
- chrysene
- terphenyl-d14 (surr.)

Internal Standard: Perylene-d12

Targets and surrogates:
- di-n-octyl phthalate
- benzo(b) fluoranthene
- benzo(k) fluoranthene
- benzo(a) pyrene
- indeno(1,2,3-cd)pyrene
- dibenz(a,h)anthracene
- benzo(g,h,i)perylene

A second requirement of the ID files used for CLP analysis are set and defined primary (quantitation) ions, as well as recommended secondary ions. These ions are as follows for each target compound and surrogate:

COMPOUND	Primary Ion	Secondary Ion(s)
Phenol	94	65,66
bis(2-chloroethyl)ether	93	63,95
2-chlorophenol	128	64,130
1,3-dichlorobenzene	146	148,113
1,4-dichlorobenzene	146	148,113
1,2-dichlorobenzene	146	148,113
2-methylphenol	108	107
2,2'oxybis (1-chloropropane)	45	77,79
4-methylphenol	108	107
N-nitroso-di-n-propylamine	70	42,101,130
hexachloroethane	117	201,199
nitrobenzene	77	123,65
isophorone	82	95,138
2-nitrophenol	139	65,109
2,4-dimethylphenol	107	121,122
bis(2-chloroethoxy)methane	93	95,123
2,4-dichlorophenol	162	164,98
1,2,4-trichlorobenzene	180	182,145

Compound (con't.)	Primary Ion	Secondary Ion(s)
naphthalene	128	129,127
4-chloroaniline	127	129
hexachlorobutadiene	225	223,227
4-chloro-3-methylphenol	107	144,142
2-methylnaphthalene	142	141
hexachlorocyclopentadiene	237	235,272
2,4,6-trichlorophenol	196	198,200
2,4,5-trichlorophenol	196	198,200
2-chloronaphthalene	162	164,127
2-nitroaniline	65	92,138
dimethyl phthalate	163	194,164
acenaphthylene	152	151,153
3-nitroaniline	138	108,92
acenaphthene	153	152,154
2,4-dinitrophenol	184	63,154
4-nitrophenol	109	139,65
dibenzofuran	168	139
2,4-dinitrotoluene	165	63,182
2,6-dinitrotoluene	165	89,121
diethylphthalate	149	177,150
4-chlorophenyl-phenylether	204	206,141
fluorene	166	165,167
4-nitroaniline	138	92,108
4,6-dinitro-2-methylphenol	198	182,77
N-nitrosodiphenylamine	169	168,167
4-bromophenyl-phenylether	248	250,141
hexachlorobenzene	284	142,249
pentachlorophenol	266	264,268
phenanthrene	178	179,176
anthracene	178	179,176
carbazole	167	166,139
di-n-butylphthalate	149	150,104
fluoranthene	202	101,000
pyrene	202	101,000
butylbenzylphthalate	149	91,206
3,3'-dichlorobenzidine	252	254,126
benzo(a)anthracene	228	229,226
bis(2-ethylhexyl)phthalate	149	169,279
chrysene	228	226,229
di-n-octyl phthalate	149	--
benzo(b) fluoranthene	252	253,125
benzo(k) fluoranthene	252	253,125
benzo(a) pyrene	252	253,125
indeno(1,2,3-cd) pyrene	276	138,227
dibenz(a,h)anthracene	278	139,279
benzo(g,h,i)perylene	276	138,277
phenol-d5 (surr.)	99	42,71
2-fluorophenol (surr.)	112	64

Compound (con't.)	Primary Ion	Secondary Ion(s)
2,4,6-tribromophenol (surr.)	330	332,141
nitrobenzene-d5 (surr.)	82	128,54
2-fluorobiphenyl (surr.)	172	171
terphenyl-d14 (surr.)	244	122,212
2-chlorophenol-d4 (surr.)	132	68,134
1,2-dichlorobenzene-d4 (surr.)	152	115,150
1,4-dichlorobenzene-d4 (istd)	152	115
naphthalene-d8 (istd)	136	68
acenaphthene-d10 (istd)	164	162,160
phenanthrene-d10 (istd)	188	94,80
chrysene-d12 (istd)	240	120,236
perylene-d12 (istd)	264	260,265

Relative response factors (RRFs) must be calculated and evaluated for each of the target compounds and surrogates. To reiterate, a 2 ul injection is mandatory. The RRF is defined as follows:

$$RRF = \frac{Ax}{AIS} \times \frac{CIS}{Cx} \quad \text{where}$$

Ax = area of the primary ion for the target compound
AIS = area of the primary ion for the corresponding istd.
CIS = concentration of the istd (ng/ul)
Cx = concentration of the target compound (ng/ul)

The Hewlett-Packard program "CBUPD" should be used to generate a calibration curve and "CBRPT" used to print out the curve. The printout will contain a RRF for each compound, as well as an average RRF and average relative retention time (RRT). The percent RSD over the five points is also automatically calculated. If information is needed concerning the use of these programs, consult the GC/MS supervisor. To reiterate, no changes can be made to the calibration files without supervisory approval.

Response factor criteria have been established for the calibration of the semivolatile target and surrogate compounds. For the initial calibration curve to be considered valid, the response factors of the compounds listed below must meet the minimum RRF criteria <u>at each</u> concentration level and maximum % RSD criteria, with allowance made for up to four semivolatile targets and surrogates. However, the RRFs for these four outliers must be greater than 0.010, and the % RSD of those four must be less than or equal to 40.0% for the curve to be acceptable.

INITIAL and CONTINUING CALIBRATION CRITERIA

COMPOUND	MINIMUM RRF	MAXIMUM % RSD (Initial)	MAXIMUM % DIFFERENCE (Continuing)
Phenol	0.800	20.5	25.0
bis(2-chloroethyl)ether	0.700	20.5	25.0
2-chlorophenol	0.800	20.5	25.0
1,3-dichlorobenzene	0.600	20.5	25.0
1,4-dichlorobenzene	0.500	20.5	25.0
1,2-dichlorobenzene	0.400	20.5	25.0
2-methylphenol	0.700	20.5	25.0
4-methylphenol	0.600	20.5	25.0
n-nitroso-di-n-propylamine	0.500	20.5	25.0
hexachloroethane	0.300	20.5	25.0
nitrobenzene	0.200	20.5	25.0
isophorone	0.400	20.5	25.0
2-nitrophenol	0.100	20.5	25.0
2,4-dimethylphenol	0.200	20.5	25.0
bis(2-chloroethoxy)methane	0.300	20.5	25.0
2,4-dichlorophenol	0.200	20.5	25.0
1,2,4-trichlorobenzene	0.200	20.5	25.0
naphthalene	0.700	20.5	25.0
4-chloro-3-methylphenol	0.200	20.5	25.0
2-methylnaphthalene	0.400	20.5	25.0
2,4,6-trichlorophenol	0.200	20.5	25.0
2,4,5-trichlorophenol	0.200	20.5	25.0
2-chloronaphthalene	0.800	20.5	25.0
acenaphthylene	1.300	20.5	25.0
2,6-dinitrotoluene	0.200	20.5	25.0
acenaphthene	0.800	20.5	25.0
dibenzofuran	0.800	20.5	25.0
2,4-dinitrotoluene	0.200	20.5	25.0
4-chlorophenyl-phenylether	0.400	20.5	25.0
fluorene	0.900	20.5	25.0
4-bromophenyl-phenylether	0.100	20.5	25.0
hexachlorobenzene	0.100	20.5	25.0
pentachlorophenol	0.050	20.5	25.0
phenanthrene	0.700	20.5	25.0
anthracene	0.700	20.5	25.0
fluoranthene	0.600	20.5	25.0
pyrene	0.600	20.5	25.0
benzo(a)anthracene	0.800	20.5	25.0
chrysene	0.700	20.5	25.0
benzo(b)fluoranthene	0.700	20.5	25.0
benzo(k)fluoranthene	0.700	20.5	25.0
benzo(a)pyrene	0.700	20.5	25.0
indeno(1,2,3-cd)pyrene	0.500	20.5	25.0
dibenzo(a,h)anthracene	0.400	20.5	25.0
benzo(ghi)perylene	0.500	20.5	25.0

COMPOUND (con't.)	MINIMUM RRF	MAXIMUM % RSD (Initial)	MAXIMUM % DIFFERENCE (Continuing)
nitrobenzene-d5	0.200	20.5	25.0
2-fluorobiphenyl	0.700	20.5	25.0
terphenyl-d14	0.500	20.5	25.0
phenol-d5	0.800	20.5	25.0
2-fluorophenol	0.600	20.5	25.0
2-chlorophenol-d4	0.800	20.5	25.0
1,2-dichlorobenzene-d4	0.400	20.5	25.0

The following compounds have no maximum % RSD or maximum % Difference criteria (for continuing calibrations); however, these compounds must, with no exceptions, meet a minimum RRF criterion of 0.010:

2,2'oxybis(1-chloropropane)	4-nitroaniline
4-chloroaniline	4,6-dinitro-2-methylphenol
hexachlorobutadiene	n-nitrosodiphenylamine
hexachlorocyclopentadiene	di-n-butylphthalate
2-nitroaniline	butylbenzylphthalate
dimethylphthalate	3,3'-dichlorobenzidine
3-nitroaniline	bis(2-ethylhexyl) phthalate
2,4-dinitrophenol	di-n-octylphthalate
4-nitrophenol	2,4,6-tribromophenol
diethylphthalate	carbazole

Internal standard responses and retention times in all standards must be evaluated immediately after data acquisition; if the RT for any istd changes by more than 0.50 minutes from the latest daily calibration standard, corrections must be made to the chromatographic system. If the extracted ion current profile (EICP) area for any istd changes by more than a factor of two (-50% to +100%), corrective action must be performed.

Each GC/MS system must be calibrated upon award of the contract and following system corrective action, including ion source cleaning or repair and column removal or replacement.

If time remains in the twelve hour clock after meeting the initial calibration acceptance criteria, samples may be analyzed. The SSTD050 in the curve may be used as the continuing calibration standard as long as it meets the continuing calibration acceptance criteria. All sample results must be quantitated using the SSTD050 response factors.

Medium quantitation reports and a copy of the "CBRPT" should be filed in the appropriate notebook in the GC/MS laboratory.

Ensure that each page of the medium quantitation report contains the date and time of analysis as well as the pertinent EPA case and SDG number.

2.0.2 Continuing Calibration

A check of the calibration curve must be performed once every twelve hours, immediately following analysis of the tuning compound DFTPP. This check is accomplished by analysis of a 50 ng standard (2 ul injection of a 25 ng/ul standard) containing all target compounds and surrogates.

After quantitation of this continuing calibration standard, response factors must be calculated and compared to the mean response factors in the initial calibration. This is accomplished using the Hewlett-Packard software program, "CBCHK." This program calculates response factors and compares them to the mean RF by calculating percent differences. The continuing calibration criteria for both minimum RRF and maximum percent difference outlined on pages 12 and 13 of this SOP must be met before method blank and/or sample analysis can proceed.

If the continuing calibration standard does not meet criteria (again with allowance made for up to four compounds), corrective action must be taken. Depending on the situation, corrective action may be as follows:

- reanalyze the 50 ng continuing calibration standard
- change septum, install new/silanized quartz liner, cut off a small portion of the front end of the capillary column (this is most frequently done when acid RFs are low and/or chromatography is poor).
- initiate a new initial calibration curve

The last option, generation of a new initial calibration curve, is most often chosen when % differences are ≥ 30%, and there is little or no chance of a continuing calibration reanalysis meeting criteria. If you are in doubt concerning which corrective action to undertake, consult the GC/MS supervisor.

3.0 SAMPLE ANALYSIS

Sample extracts may be analyzed only after the GC/MS system has met tuning criteria, initial calibration, and continuing calibration requirements. Ensure that the same instrument conditions were used for tuning, calibration, and sample analysis by reviewing the GC parameters using the Hewlett-Packard program "LMETH".

Extracts are stored in the sole white refrigerator in the organics extraction laboratory at 4° C ± 2°C. After determination has been

made of the extracts to analyze (consult your supervisor for guidelines), remove those extracts from storage (remember to sign out the extracts on the chain-of-custody forms on the refrigerator) and place them in the GC/MS laboratory hood.

Internal standard solution, consisting of all six internal standards is added by the GC/MS analyst. This solution must contain all six internal standards at a concentration of 2000 ng/ul each. For instructions on preparation of this solution, consult the standards preparation section of this SOP.

Add 10 ul of internal standard solution to each accurately measured 1.0 ml of water sample extract. 5 ul of istd solution must be added to 0.5 ml of sample extract for those samples subjected to gel permeation chromatography (GPC) cleanup. This will result in a concentration of 20 ng/ul of each istd (or 40 ng total per injection).

The extracts to which internal standard has been added must be stored in an amber screw-top vial with a teflon-lined septa and must be clearly labelled with the following information:

- Sample identification
- date of extraction
- date istd solution added
- GC/MS analyst initials

These vials must be stored in the extract storage refrigerator in the organics extraction laboratory, not in the BNA standards freezer in the GC/MS laboratory to minimize any potential carryover from standards while in storage.

Immediately prior to analysis, transfer 100 ul of the istd-fortified extract to a clean conical vial (110 ul, clear-glass, crimp-top). For cleaning procedures of these vials, see Section 13.0 of this SOP.

After this has been accomplished, the auto sampler tray can be loaded and a sample batch written using the Hewlett-Packard program "BEDIT." If instructions are needed concerning the use of this program, consult the GC/MS supervisor. Ensure that the data file, quantitation output file, and id file are automatically archived for each sample by entering "Y" for the appropriate prompts under "BEDIT."

To reiterate, 2 ul injections must be used for each analysis.

The following compounds are part of the semivolatile target compound list and must be analyzed for in each analysis. Quantitation limits for waters, low soils and medium soils are also reported.

Target Compound	Water (ug/l)	Low Soil (ug/kg)	Med. Soil (ug/kg)
Phenol	10	330	10000
bis(2-chloroethyl)ether	10	330	10000
2-chlorophenol	10	330	10000
1,3-dichlorobenzene	10	330	10000
1,4-dichlorobenzene	10	330	10000
1,2-dichlorobenzene	10	330	10000
2-methylphenol	10	330	10000
2,2'oxybis(1-chloropropane)	10	330	10000
4-methylphenol	10	330	10000
N-nitrosodi-n-propylamine	10	330	10000
hexachloroethane	10	330	10000
nitrobenzene	10	330	10000
isophorone	10	330	10000
2-nitrophenol	10	330	10000
2,4-dimethylphenol	10	330	10000
1,2,4-trichlorobenzene	10	330	10000
naphthalene	10	330	10000
4-chloroaniline	10	330	10000
hexachlorobutadiene	10	330	10000
4-chloro-3-methylphenol	10	330	10000
2-methylnaphthalene	10	330	10000
hexachlorocyclopentadiene	10	330	10000
2,4,6-trichlorophenol	10	330	10000
2,4,5-trichlorophenol	25	800	25000
2-chloronaphthalene	10	330	10000
2-nitroaniline	25	800	25000
dimethylphthalate	10	330	10000
acenaphthylene	10	330	10000
2,6-dinitrotoluene	10	330	10000
3-nitroaniline	25	800	25000
acenaphthene	10	330	10000
2,4-dinitrophenol	25	800	25000
4-nitrophenol	25	800	25000
dibenzofuran	10	330	10000
2,4-dinitrotoluene	10	330	10000
diethylphthalate	10	330	10000
4-chlorophenyl-phenyl ether	10	330	10000
fluorene	10	330	10000
4-nitroaniline	25	800	25000
4,6-dinitro-2-methylphenol	25	800	25000
N-nitrosodiphenylamine	10	330	10000
4-bromophenyl-phenyl ether	10	330	10000
hexachlorobenzene	10	330	10000
pentachlorophenol	25	800	25000
phenanthrene	10	330	10000
anthracene	10	330	10000
carbazole	10	330	10000
di-n-butylphthalate	10	330	10000

TARGET COMPOUND	Water (ug/l)	Low Soil (ug/kg)	Med. Soil (ug/kg)
fluoranthene	10	330	10000
pyrene	10	330	10000
butylbenzylphthalate	10	330	10000
3,3'-dichlorobenzidine	10	330	10000
benzo(a)anthracene	10	330	10000
chrysene	10	330	10000
bis(2-ethylhexyl)phthalate	10	330	10000
di-n-octylphthalate	10	330	10000
benzo(b)fluoranthene	10	330	10000
benzo(K)fluoranthene	10	330	10000
benzo(a)pyrene	10	330	10000
Indeno(1,2,3-cd)pyrene	10	330	10000
Dibenz(a,h)anthracene	10	330	10000
benzo(g,h,i)perylene	10	330	10000

Two criteria must be satisfied to verify identification:

- elution of the sample component at the same GC relative retention time as the standard component
- correspondence of the sample component and standard component mass spectra

The ID files have been set up to only report hits for targets that fall within ± 0.20 minutes of the same component in the daily continuing calibration standard. The ID files also contain reference spectra previously acquired on the same instrument (e.g. for instrument MS1, the reference spectra in the ID file were acquired on MS1 at an earlier time under a valid tune).

4.0 INSTRUMENT SPECIFIC PROCEDURES

It is the policy of the GC/MS group that all data be acquired in the batch ("BAMON") mode rather than by use of single sample ("DATAC") acquisition. The following items must be checked prior to acquisitions of data in the batch mode:

- Ensure that the proper sequence and tune files are being used as described on pages 3 and 4 of this SOP.

- Ensure that the data cartridge being used for acquisition has sufficient space by executing the program "SHOSZ." If space is questionable (<20% availability), check with the supervisor.

- Check the autosampler syringe alignment and make sure the solvent-rinse vial is full

- Print a hardcopy of the batch to be analyzed and check the following:

  - o data files in numerical order with no duplication and quantitation output files corresponding to the data file

  - o sample name and misc. data filled out accurately and completely

  - o proper method file and tune file
    MS1: MT1000, M_XCLP
    MS2: MT2000, M_BCLP

  - o For MS1 and MS2, sample size = 2, bottle numbers are sequenced 1 through the number of bottles

  - o Use "F" for report option and subtract out internal standards and surrogates, so as not to print out spectra of these compounds (-I-S).

  - o <u>Always</u> archive data, ID, and quantitation output files

    - The GC/MS systems manager will purge data and quant output files as needed to ensure adequate computer space exists for further data acquisition; this occurs at a minimum of a biweekly basis. Before purging raw data files off the computer system, the systems manager rearchives all files to be purged to ensure no loss of raw data is possible.

      When an archive tape is full, a directory of all files on that tape is printed out and the hardcopy directory stored in a file cabinet in the GC/MS laboratory. Archive tapes are labelled RTE_ _ _, where _ _ _ is a three digit number in chronological order.

  - o Ensure that the number of the quantitation output file corresponds to the data file

Before leaving the laboratory at the conclusion of your shift, ensure that there is sufficient printer paper for reports and log off the report terminal to allow automatic dumping and printing of quantitation reports.

5.0 CALCULATIONS

5.0.1 Correction Factor Calculations

Correction factors need to take into account all preparation steps, including any gel permeation chromatography (GPC) cleanup, so that the concentration that appears on the quantitation report is the actual representation of what is present in the sample. Other factors that must be taken into account include total solids and any dilutions done at the instrument by the GC/MS analyst (e.g. as a result of GC/FID screening results or a previous undiluted GC/MS analysis).

For the purposes of this SOP, the correction faction (CF) is defined as the number that a target concentration must be multiplied by to obtain the actual sample concentration. This CF is entered in the appropriate field when setting up a batch under "BEDIT" to automatically obtain a correct printout. The dilution factor (DF) that is entered on the CLP forms does not take into account such entities as total solids.

In calculating correction factors, it is critical that all pertinent volume changes throughout the sample preparation and analysis sequence are taken into account. The following template equation should be used as a guideline:

$$CF = \frac{1}{\text{Initial Sample Wt. or Volume}} * \left[\text{All Intermediate Preparation Steps}\right] * \text{Final Sample Wt. or Volume} * \text{Instrument Dilutions} * \frac{1}{\text{T.S.}}$$

Each factor in the above equation is straightforward with the exception of the factor in brackets. This "intermediate preparation steps" can be thought of in the following way:

$$\text{Intermediate Preparation steps} = \frac{V1*V2*V3 \text{ etc.}}{V1'*V2'*V3' \text{ etc.,}}$$

where,

V1 = 1st intermediate volume that the initial wt. or vol is brought to
V1'= portion of V1 that is used in the next prep step
V2 = 2nd intermediate volume that V1' is brought to
V2'= portion of V2 that is used in the next prep step
V3 = 3rd intermediate volume that V2' is brought to
V3'= portion of V3 that is used in the next prep step
etc. = continue with the above steps until the final sample volume has been reached

An example calculation follows:

Soil matrix, initial wt. = 30.0 g, TS = 0.92
Final volume after extraction: 10 ml
Volume used for GPC cleanup: 5 ml
Volume out of GPC: 200 ml
GPC extract concentrated to: 10 ml
Extract split: 9.5 ml BNA, 0.5 ml pesticide/PCBs
Final volume: 0.95 ml

Note: this is an example only; for all CLP analyses performed under this SOP, no extract split is allowed and a final volume of 0.5 ml is used to offset the extract loss during GPC.

$$CF = \frac{1}{0.030\ kg} \times \frac{10\ ml}{5\ ml} \times \frac{200\ ml}{200\ ml} \times \frac{10\ ml}{9.5 ml} \times 0.95\ ml \times 1 \times \frac{1}{0.92}$$

$$CF = 72.464$$

For water samples analyzed under this SOW and SOP, where a 2 ul injection is mandatory:

$$CF = \frac{1}{1.00\ liter} \times 1.0\ ml(FV) \times \frac{1}{2.0\ ul}$$

$$CF = 0.500$$

Final concentration of compound = C_x

$$C_x = \frac{A_x\ C_{IS}}{RF\ A_{IS}}\ (CF), \text{ where}$$

C_{IS} = concentration of internal standard (40 ng/ul)
A_x = area of primary (quantitation) ion for compound X
RF = response factor (determined from SSTD050 analyzed in 12 hr clock)
A_{IS} = area of primary ion for corresponding internal standard
CF = correction factor, described above

5.0.2 Surrogate and Matrix Spike/Matrix Spike Duplicate

Recoveries:

The surrogate spiking solution contains the base-neutral compounds at 100 ug/ml [nitrobenzene-d5, 2-fluorobiphenyl, terphenyl-d14, and 1,2-dichlorobenzene-d4] and the acidic surrogates at 150 ug/ml [phenol-d5, 2,4,6-tribromophenol, 2-fluorophenol, and 2-chlorophenol-d4].

The matrix spiking solution consists of the following compounds at the specified levels:

Base/Neutrals : 100 ug/ml	Acids - 150 ug/ml
1,2,4-trichlorobenzene	pentachlorophenol
Acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
Pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

For aqueous samples and blanks, 0.5 ml of the surrogate mix is added by the extractions laboratory; for MS and MSD samples, both 0.5 ml of surrogate mix and 0.5 ml of matrix spike mix is added.

For soil matrices, the same amounts are spiked.

Percent recovery calculations for both surrogates and matrix spiking compounds need to be accomplished as follows:

Step 1: Calculate the actual concentration of the surrogate or spike (surr/spike) compound detected in the sample. This is done by treating the surr/spike compounds the same way as target compound concentrations are calculated (i.e., apply all correction factors-both prep and instrument - and use the same units as used for reporting target compound results [ug/L or ug/kg]).

Step 2: Calculate the theoretical or expected concentration of the surr/spike compound in the sample using the same units as employed for reporting target compound data as in Step 1.

$$\text{Theoretical recovery} = \frac{\text{(conc. surr/spike Mix) x (Volume surr/spike Added)}}{\text{(Initial Dry Wt. or volume of sample)}}$$

Example calculation:

Acid spike mix concentration = 150 ug/ml
Volume of spike added = 0.5 ml
Initial weight (wet): 30 g = 0.030 kg
Total solids = 87% = 0.87

$$\text{Theoretical recovery} = \frac{\text{(150 ug/ml) (0.5 ml)}}{\text{(0.030 kg) (0.87)}} = 2874 \text{ ug/kg}$$

Step 3: Calculate the percent recovery for the surr/spike compound by dividing the actual measured concentration (step 1) by the theoretical (or expected) concentration obtained in step 2. This result needs to be multiplied by 100 to obtain a percentage.

6.0 INITIAL REVIEW (IDR)

The initial data review is accomplished by the analyst who ran the samples and is a review of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed.

The requirement of the GC/MS laboratory is that this initial data review be completed within twelve hours of batch completion; in the majority of instances, the IDR should be accomplished at the beginning of a work shift for the previous set of analyses. After the analyst has completed his or her IDR, the IDR packet (defined below) should immediately be forwarded to the GC/MS supervisor.

The initial data review is accomplished with the use of the IDR sheet (copy follows on next page) and full quantitation reports from each sample. This data review examines six criteria that directly impact whether or not the sample needs to be reanalyzed:

- surrogate recoveries
- stability of internal standard responses
- method blank acceptance
- chromatography
- target compound detection/quantitation
- matrix spike/matrix spike duplicate recoveries

6.0.1 Method Blank Criteria

A method blank is defined as a volume of a clean reference material (deionized distilled water for water samples or a purified sodium sulfate matrix for soil/sediment matrices) that is carried through the entire analytical procedure. One method blank must be extracted with each group of samples of a similar matrix and must be analyzed on each GC/MS system used to analyze samples.

Method blank analysis must be performed once for the following, on each GC/MS system used to analyze samples, whichever is most frequent:

- each Case, or
- each 14 calendar day period during which samples in a Case are received, or
- each 20 samples in a Case that are of similar matrix or similar concentration, or
- whenever samples are extracted by the same procedure

An acceptable method blank must contain less than or equal to five times the Contract Required Quantitation Limit (CRQL) of the phthalate esters and less than or equal to the CRQL of any other target compound, and must meet <u>all</u> surrogate recovery criteria.

If the method blank exceeds these contamination levels, the analytical system is considered out-of-control and corrective action must be taken before sample analysis.

Reanalysis of the blank is the first step of the corrective action; if that does not solve the problem, reextraction of the blank and all associated samples must occur.

6.0.2 Surrogate Recoveries

Calculate surrogate recoveries on all samples, blanks and spikes using the procedures described in a previous section of this SOP, and fill out the pertinent section of the IDR sheet (see Attachment A).

The eight surrogates can be divided into three groups:
(B/N - nitrobenzene-d5, 2-fluorobiphenyl, and terphenyl-d14)
(acid - phenol-d5, 2 fluorophenol, and 2,4,6-tribromophenol)
(advisory - 2-chlorophenol-d4 and 1,2-dichlorobenzene-d4)

Specifications are defined as two B/N or two acid surrogates out-of-criteria or recovery of any one acid or B/N surrogate <10%. Criteria windows are noted on the IDR sheet.

If specifications are not met, the sample (or blank) should be reanalyzed. If specifications are met in the reanalysis, this reanalysis should only be submitted. If surrogate specifications are still not met, the sample must be reextracted and reanalyzed. If recoveries in a blank do not meet specifications after reanalysis, the blank and all associated samples must be reextracted. Any surrogate outliers must be noted in the SDG narrative.

For further information regarding the acceptance of surrogate recoveries, consult the GC/MS supervisor.

6.0.3 Chromatography

Internal standard responses and retention times in all samples and blanks must be evaluated as part of the IDR. The ID files have been set up to only detect compounds that fall within a set RT window; therefore, only the internal standard areas need be recorded on the IDR sheet. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to +100%) as compared to the daily continuing calibration standard, reanalysis must occur. If the reanalysis meets criteria, only the in-criteria run should be reported. If the reanalysis is still out-of-criteria, both analyses should be included in the data package.

MS/MSD samples that do not meet the EICP area criteria above do not have to be reanalyzed.

6.0.4 Chromatography

The chromatography should be examined for the presence or absence of any "ghost" peaks and can also be used as an indication of whether or not matrix interferences might be influencing surrogate recoveries and/or istd are recoveries. Whether or not the chromatography is acceptable is a judgement call on the part of the analyst and should be used in conjunction with other monitored QC (e.g., surrogate recoveries) to determine the necessity of reanalyses.

6.0.5 Target Compound Detection/Quantitation

The ID Files have been set up to err on the side of false positives, that is to identify and quantitate peaks as target compounds that may not necessarily be valid hits.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- all ions present in the standard mass spectra at a relative intensity > 10% must be present in the sample spectrum.
- the relative intensities of primary and secondary ions must agree within ±20% between the standard and sample spectra.
- ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst.

If a compound cannot be verified by all three criteria above, but, in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the laboratory shall report that compound on the Form I as a valid hit.

Review the quantitation report and mass spectra and cross-out any non-valid hits (with a ruler, single-line, dated and initialed). In order for the analysis to be valid, all concentrations must fall within the upper limits of the calibration curve, defined as follows:

upper limit = 160 ng (highest curve point) x CF

If any target concentration exceeds the upper limit, a dilution must be made and analyzed. The dilution chosen

should keep the response of the largest target compound hit in the upper half of the initial calibration range. MS/MSD samples need not be diluted to get either spike or non-spiked analytes within the calibration range.

6.0.6 Matrix Spike/Matrix Spike Duplicate Recoveries

A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, for the following, whichever is more frequent:

- each Case, or
- each 20 samples in a Case, or
- each group of samples or similar concentration level, or
- each 14 day calendar period during which samples are received

Matrix spike compound recovery and relative percent difference (RPD) of the recoveries must be calculated. The limits, outlined below, are advisory only and should not be used to determine the necessity of a reanalysis; however, any deviations should be noted in the SDG narrative.

Compound	% Rec Water	RPD Water	% Rec Soil	RPD Soil
Phenol	12-110	42	26-90	35
2-chlorophenol	27-123	40	25-102	50
1,4-dichlorobenzene	36-97	28	28-104	27'
n-nitro-di-n-propylamine	41-116	38	41-126	38
1,2,4-trichlorobenzene	39-98	28	38-107	23
4-chloro-3-methlyphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-nitrophenol	10-80	50	11-114	50
2,4-dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

7.0 IDR PACKET REVIEW BY SUPERVISOR

After the IDR sheet has been completely filled out, the analyst needs to assemble the following information in a packet and provide it to the GC/MS supervisor for his review and signature.

- IDR sheet
- Tuning hardcopy
- Continuing calibration report with medium quantitation report (no spectra)
- Initial calibration report with medium quantitation reports if analyzed as part of that batch
- Full quantitation reports (including mass spectra and instrument-specific reference spectra) of blanks and samples
- Medium quantitation reports (no mass spectra) for MS and MSDs

This information needs to be assembled and to the supervisor for his review within twelve hours after batch completion. In reality, the information should be prepared and the package submitted as soon as possible following the start of the next work shift.

The supervisor needs to carefully review the entire package for QC compliance and to ensure that no dilutions or reanalyses were missed by the analyst. Depending on workload, he will then make a decision on who is to perform the next step, preparation of the data for transfer to a PC.

8.0 PREPARATION OF DATA FOR TRANSFER TO PC

It is the policy of the GC/MS group that a complete sample delivery group (SDG) must be analyzed prior to any data transfer. This keeps better organization and allows the data management staff more efficient time management.

Only qualified mass spectral interpretation specialists (see the qualification guidelines in the beginning of this SOP) are permitted to perform this step.

The following needs to be accomplished prior to data transfer:

- Prepare a tracking sheet for data management staff that shows each data file that is to be used (i.e., a sequence showing each day's runs with only those files that are to be included).

- Using each reviewed IDR packet, gather all tuning hardcopies, standard medium quantitation reports, and full quantitation reports (not including mass spectra of istds or surrogates) for samples, blanks, and matrix spike/matrix spike duplicate samples.

- Rip apart the computer paper into single sheets and paperclip together each sample's information.

- Review the decisions made by the initial analyst concerning the validity of mass spectral hits. Ensure that all non-valid hits have been crossed-out on the quantitation report with a ruled single-line, dated and initialed.

- Ensure that samples were analyzed within holding times (defined as 40 days following the extraction date).

- Using the Hewlett-Package program "QDEL," delete from each output file all non-valid mass spectral hits.

- Write the Case and SDG numbers on all pages where it is not present (i.e., standard medium quantitation reports, tuning hardcopies, etc.). Write the date and time of injection on all tuning hardcopy pages.

- Using the Hewlett-Packard program, FITIC, and the GC/MS library search procedure file "LIBSEA" as a template, run library searches on all samples and blanks. Library searches need not be run on matrix spike/matrix spike duplicate samples.

- Up to twenty nonsurrogate organic compounds shall be identified via the library search. Substances with responses <10% of the nearest istd are not required to be searched. Peaks that are suspected as aldol-condensation reaction products shall be searched and reported, but not counted as part of the 20 most intense non-target semivolatile compounds.

- An estimated concentration is calculated using the following formula:

$$\text{Unknown concentration} = \frac{\text{Conc. Int.Std} * \text{Area unknown} * \text{CF}}{\text{Area Int. Std}}$$

  where, CF = correction factor defined above

  A response factor of 1.0 is assumed.

- Review the library search hardcopies. Double check that the correction factor used for calculations of estimated concentrations (on the bottom of the first page) is the same as the CF on the quantitation report. If any tentatively-identified compound (TIC) has an area <10% of the corresponding internal standard area, it need not be reported, but should be crossed off the first page. Write the analysis date and time of injection on each page, and either circle the correct identification of each TIC or characterize it in some other way (e.g., unknown, hydrocarbon).

- Generate reduced results files (RR files) for all DFTPPs, standards, matrix spikes, and matrix spike duplicates by editing the GC/MS template RR_JIM.

- After RR files have been generated, set up a file of all pertinent RR files to dump to the PC by editing the GC/MS template dump file, DU_JIM.

- Provide the GC/MS Supervisor with a copy of the dump file, any notes which might be pertinent to the SDG narrative, and a package in the following order.

  - sample quantitation reports in order by sample ID
  - sample library searches
  - initial calibration curves in chronological order

- continuing calibration stds. in chronological order
- Tuning hardcopies
- method blank quantitation reports
- matrix spike quantitation reports
- matrix spike duplicate quantitation reports
- GPC chromatograms
- Information for the complete SDG file, to include: original IDR sheets, copies of notebook pages (injection, maintenance, stds receipt, and preparation, traceability), GC/FID screening chromatograms, any handwritten notes (inc. tracking sheet prepared in step 1), and any other case-specific documents

The GC/MS supervisor will then review the package for completeness, accuracy, and compliance with the SOW and coordinate the transfer of the SDG to the PC and the data management staff.

Review and SDG preparation will then be accomplished following the guidelines in the current revision of CCAS-NE SOP No. SD-007, "CLP Data Package Assembly and Review."

9.0 STANDARD TRACEABILITY

A separate CCAS-NE SOP addressing this issue entitled "Traceability of Standards-Organics," SOP No. QA-004, has been prepared and must be adhered to prior to analysis of any samples by CLP protocols.

In addition, it is the policy of the GC/MS laboratory that all standards be procured with vendor-supplied QC data packages as when available. These data packages provided by the vendor should be stored in a file cabinet in the GC/MS laboratory.

10.0 STANDARDS PREPARATION

This part of the SOP addresses preparation of all standards used in conjunction with CLP sample analyses, including standards used in tuning, initial and continuing calibration, sample analysis, and pesticide/PCB confirmation.

10.1.0 Instrument Performance Check - Decafluorotriphenylphosphine (DFTPP)

The semivolatile tuning criteria are examined by injecting a total of 50 ng DFTPP into the GC/MS system. This is accomplished by preparing DFTPP at 25 ng/ul and injecting 2 ul of it. The preparation of DFTPP at 25 ng/ul is detailed in Table 1.0. The DFTPP standard is prepared a minimum of every 6 months.

10.2.0 Initial Calibration

In order for the initial calibration standards to meet requirements, as stated in section 2.0.1 of the SVOA SOP, a 100 ug/ml SVOA stock solution must first be prepared. Solutions supplied by Restek are combined as shown in Table 5.0.

The 100 ug/ml SVOA stock solution is then diluted to create initial calibration standards at concentrations of 10, 25, 40, 60 and 80 ng/ul. A 2000 ug/ml internal standard solution is added to these standards for a final internal standard concentration of 20 ng/ul (see Table 6.0). A 4000 ug/ml internal standard mix is supplied by Restek. The preparation for the 2000 ug/ml internal standard is shown in Table 2.0.

The working calibration standards and the DFTPP standard are prepared in clean 1.8 ml screw cap amber bottles. These bottles are topped with teflon lined caps and are stored in the SVOA standards freezer, which has the temperature set between -10°C and -20°C. Fresh calibration standards are prepared at a minimum of every 12 months. The continuing calibration standard (SSTD050) is stored in a refrigerator at 4°C ± 2°C.

Before injecting the initial calibration standards, they are transferred by pasteur pipet to clean 110 ul conical autosampler vials and are capped with teflon lined crimp top caps. The standards are then injected in 2 ul amounts for GC/MS analysis.

10.3.0 Continuing Calibration

The continuing calibration check is made exactly the same as the 25 ng/ul initial calibration standard. See Table 3.0. It is prepared weekly, at a minimum, and transferred by pasteur pipet to a clean 110 ul autosampler vial prior to instrument injection. The continuing calibration check must be stored separately from the other SVOA calibration standards in a refrigerator with a 4°C (±2°C) temperature setting.

10.4.0 Sample Preparation

2000 ng/ul internal standard solution is added to each sample and blank for a final concentration of 20 ng/ul of each internal standard. For each water sample 10 ul of 2000 ng/ul, internal standard is added to 1.0 ml of water sample extract. For soil and water samples that undergo GPC, 5 ul of 2000 ng/ul, internal standard is added to 0.5 ml of sample extract. If dilutions need to be made to a sample, additional additions of internal standard solution are made to maintain the 20 ng/ul internal standard concentration.

The aforementioned sample preparations are prepared in clean 1.8 ml screw top amber bottles with teflon lined caps. Prior to injection, the sample is transferred by pasteur pipet to a clean 100 ul autosampler vial.

10.5.0 Pesticide/PCB Confirmation

A 25 ng/ul pesticide/PCB standard is run prior to pesticide/PCB confirmation. Preparation is detailed in Table 4.0.

Table 1.0 Decafluorotriphenylphosphine (DFTPP)

Supplier	Standard	Initial Concen. (ng/ul)	Volume Added	Final Concen. (ng/ul)
RESTEK	DFTPP	2500	10	25
Baker	$MeCl_2$	—	990	—

FINAL VOLUME = 1.0 ml

Table 2.0 Internal Standard Solution

Supplier	Standard	Initial Concen. (ng/ul)	Volume Added	Final Concen. (ng/ul)
RESTEK	Internal Standard Mix	4000	500	2000
Baker	$MeCl_2$	—	500	—

FINAL VOLUME = 1.0 ml

Table 3.0 Internal Standard Solution

Final Concen. (ng/ul)	100 ng/ul SVOA Stock Solution Added (ul)	2000 ng/ul Internal Standard Solution Added (ul)	$MeCl_2$ Added (ul)	Final Volume (ul)
25	250	10	750	1010

Table 4.0 Internal Standard Solution

Final Concen. (ng/ul)	2000 ng/ul RESTEK Calibration Mix 6 Added (ul)	2000 ng/ul Internal Standard Solution Added (ul)	$MeCl_2$ Added (ul)	Final Volume (ul)
25	12.5	10	987.5	1010

Table 5.0 SVOA Stock Solution for Initial Calibration Preparation

Supplier	Standard	Initial Concen. (ng/ul)	Volume Added	Final Concen. (ng/ul)
RESTEK	SV Calibration Mix 1*	2000	150	100
RESTEK	SV Calibration Mix 2	2000	150	100
RESTEK	SV Calibration Mix 3	2000	150	100
RESTEK	SV Calibration Mix 4	2000	150	100

Supplier	Standard	Concen. (ng/ul)	Added	Concen. (ng/ul)
RESTEK	SV Calibration Mix 5	2000	150	100
RESTEK	SV Calibration Mix 7	2000	150	100
RESTEK	3,3-Dichlorobenzidine	2000	150	100
RESTEK	Acid Surrogate Standard Mix	7500	40	100
RESTEK	B/N Surrogate Standard Mix	5000	60	100
RESTEK	$MECl_2$	—	1850	—

FINAL VOLUME = 3 ml
FINAL CONCENTRATION = 100 ug/ml

* See RESTEK catalog for a list of analytes in each mix.

Table 6.0 Initial Calibration Preparation

Final Concen. (ng/ul)	100 ng/ul SVOA Stock Solution Added (ul)	2000 ng/ul Internal Standard Solution Added (ul)	$MeCl_2$ Added (ul)	Final Volume (ul)
10	100	10	900	1010
25	250	10	750	1010
40	400	10	600	1010
60	600	10	400	1010
80	800	10	200	1010

Table 7.0 Internal Standard Solution

Supplier	Standard	Initial Concen. (ng/ul)	Volume Added	Final Concen. (ng/ul)
RESTEK	Acid Surrogate Standard Mix	7500	5.0	150
RESTEK	B/N Surrogate Standard Mix	5000	5.0	100
EM Science	Methanol	—	240.0	—

FINAL VOLUME = 250 ml

Table 8.0 SVOA Matrix Spiking Solution

Supplier	Standard	Initial Concen. (ng/ul)	Volume Added	Final Concen. (ng/ul)
RESTEK	Acid Matrix Spike Mix	7500	5.0	150
RESTEK	B/N Matrix Spike Mix	5000	5.0	100
EM Science	Methanol	—	240.0	—

FINAL VOLUME = 250 ml

11.0 INSTRUMENT MAINTENANCE

11.1.0 Instrument Preventative Maintenance

Instrument preventative maintenance is performed on a semi-annual basis by Hewlett-Packard customer engineers. This maintenance includes a thorough inspection and cleaning of all parts, including changing rough and turbopump oils. Maintenance is performed on an as-needed basis by GC/MS analysts. Typically, routine maintenance involves clipping off the front end of the DB-5 column, replacing the injection port septum, and installing a freshly silanized quartz liner after sample analysis.

11.2.0 It is the responsibility of the analyst using a particular GC/MS to perform corrective maintenance when conditions warrant action. For instance, it is good practice to change the injection port liner after the analysis of viscous soil extracts prior to initiation of a new twelve hour clock. If an analyst is unsure of corrective maintenance needed, consult the GC/MS supervisor. Hewlett-Packard personnel perform preventative maintenance on a semiannual basis, which includes such items as changing pump oils and cleaning electronic boards.

All maintenance must be documented in the instrument-specific maintenance log, whether it is routine or not. Any maintenance over and above a routine source cleaning must be authorized by the GC/MS section supervisor.

12.0 GC/MS CONFIRMATION OF PESTICIDES AND AROCLORS

Any pesticide or Aroclor target compound for which a concentration is reported from a GC/ECD analysis must have the identification confirmed by GC/MS provided the concentration is sufficient for that purpose.

General guidelines for concentrations to be confirmed are 10 ug/L for aqueous samples and 330 ug/kg for soil samples. However, the detection of analytes and generation of reproducible mass spectra will routinely be possible at levels 3-10 times lower.

A reference standard containing the analyte(s) in question at 10 ng/ul (20 ng per injection) must be analyzed prior to analysis of the sample(s).

The GC/MS confirmation may be accomplished by one of three means:

- examination of the semivolatile GC/MS library search results
- a second analysis of the semivolatile extract
- analysis of the pesticide/Aroclor extract

Since the GC/MS laboratory does not routinely add pesticide/Aroclor standards to its initial and continuing calibration standards, a second analysis of the semivolatile extract is mandatory. This analysis must follow adherence to DFTPP criteria; the run sequence should be as follows:

DFTPP
10 ng/ul standard continuing analyte(s) to be confirmed
Corresponding method blank (SVOA extract)
Sample extract - SVOA

If the analyte cannot be confirmed by the above, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS. If the need for concentration of the extract is indicated by the GC/ECD determined level, it should be concentrated following standard techniques outlined in the current revision of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Cleanup for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment." The same run sequence should be used as that outlined above, with substitution of the method blank prepared for GC/ECD analysis.

For GC/MS confirmation of single component analytes, the required deliverables are copies of the analyte spectrum and the spectrum of the reference standard. For multicomponent analytes, spectra of three characteristic peaks are required for both the sample component and the reference standard.

The purpose of GC/MS analysis is for confirmation of identification, not quantitation. Concentrations will be based solely upon the GC/EDC results.

ID files to be used are I_XPES for instrument MS1 and IBPES for instrument MS2. Primary and secondary ions for each analyte are as follows:

Compound	Primary Ion	Secondary Ion(s)
alpha-BHC	183	181,109
beta-BHC	181	183,109
delta-BHC	183	181,109
gamma-BHC	183	181,109
heptachlor	100	272,274
aldrin	66	263,220
heptachlor epoxide	353	355,351
endosulfan I	195	339,341
dieldrin	79	263,220

Compound	Primary Ion	Secondary Ion(s)
4,4'-DDE	246	248,176
endrin	263	82,81
endrin ketone	317	37,319
endrin aldehyde	67	250,345
endosulfan II	337	339,341
4,4'-DDD	235	237,165
endosulfan-sulfate	272	387,422
4,4'-DDT	235	237,165
methoxychlor	227	228
chlordane	373	375,377
toxaphene	159	231,233
Aroclor-1016	222	260,292
Aroclor-1221	190	222,260
Aroclor 1232	190	222,260
Aroclor 1242	222	256,292
Aroclor 1248	292	362,326
Aroclor 1254	292	362,326
Aroclor 1260	360	362,394

Again, ID files are not to be edited without the approval of the GC/MS supervisor.

For information regarding operation of the GC/MS and data acceptance criteria, refer to sections 1.0 to 7.0 (inclusive) of this SOP.

13.0 AUTOSAMPLER VIAL CLEANING PROCEDURE

- In the hood, remove and dispose of the crimptop cap; pour any sample extract remaining into a labelled waste bottle.
- Place the vials open-end up in a large beaker and cover with methylene chloride.
- Place the beaker in an ultrasonic bath for 30 minutes.
- Decant the methylene chloride into the organics waste bottle.
- Repeat the above procedure for another 30 minute time period.
- Repeat the above procedure for a final time using purge and trap grade methanol.
- Bake in the muffle oven for a minimum of 2 hours prior to use.

REFERENCES: USEPA CLP Statement of Work for Organics Analysis Multi-Media, Multi-Concentration, Document No. OLM01.0, including revisions OLM01.1, OLM01.2, OLM01.3, OLM01.4, OLM01.5 OLM01.6 and OLM01.8, Revised August, 1991.

ATTACHMENTS: Attachment A - Initial Data Review Sheet for Semivolatile Organics

GLOSSARY: None.

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
GC/MS Laboratory

BNA INITIAL DATA REVIEW SHEET - CLP

(to be done within 12 hours of batch completion)

Date: _____
Primary Analyst: _____
Supervisor Review: _____

Data was collected under DFTPP Tune File: _____ Inj Time: _____
Apex scan: _____ (ENH,-1:1)
Scan SUB: _____
Data was collected under Calibration Check File: _____

Curve date: _____ Files: _____

Case No	EPA-SMO Sample #	Data File	Internal Standard Areas						Surrogate Recoveries Water: 16-110 12DCB*	35-114 NB	43-116 2-FBP	33-141 Ter	21-110 2FP	33-110 2CP*	10-110 Ph-d5	10-123 246TBP	Chroma-tography OK (Y or N)	Target Compound In Working Range (Y or N)	Pre-liminary Data Accept-able (Y or N)
			DCB	NAP	ACE	PHE	CHR	PER	Soil: 20-130 12DCB*	23-120 NB	30-115 2-FBP	18-137 Ter	25-121 2FP	20-130 2CP*	24-113 Ph-d5	19-122 246TBP			

File: CLPBIDR

Comments: * Surrogate recoveries are advisory only.

ATTACHMENT A

STANDARD OPERATING PROCEDURE

Author: Kelly Perkins
Approved by:

Issuing Unit: ABB-ES Portland
SOP No.: CA-035-00
Date: January 1992

Kyle T. Gross for
Willard C. Warren, III
President, Northeastern Division

TITLE: Analysis of Pesticides/PCBs by USEPA CLP June, 1990, Statement of Work (OLM01.6) utilizing Gas Chromatography/Electron Capture Detectors.

PURPOSE: This SOP consolidates all aspects of the Gas chromatographic analysis of pesticides/PCBs in water and soil/sediment by USEPA CLP June, 1991, SOW.

SCOPE: This document describes the analytical protocols for USEPA Contract Laboratory Program for the analysis pesticides/PCBs by gas chromatography/electron capture detector (GC/ECD). This SOP is specifically applicable to the USEPA CLP Statement of Work (SOW) OLM01.6.

REQUIREMENTS: Implementation of this SOP requires sufficiently trained analysts and properly functioning GC/ECD instrumentation. Samples must be properly extracted following Quality Assurance/Quality Control (QA/QC) guidelines of the USEPA Contract Laboratory Program or protocols.

1.0 INSTRUMENT PERFORMANCE SPECIFICATIONS

1.1 Gas Chromatograph

The gas chromatograph (GC) system must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases.

1.2 Gas Chromatographic Columns

1.2.1 Two wide-bore (0.53 mmID) fused silica GC columns are required. A separate detector is required for each column.

The columns employed are a DB-1701 30mx0.53 mm 1.00 um film thickness and DB-608 30 mx0.53 mm 0.83 um film thickness, or equivalent.

1.2.2 Columns are mounted in 0.25-inch injector ports by using a tee adapter. Use of this adapter allows simultaneous injection onto both columns. Columns are mounted in a split/splitless injection port using a methyl silicone deactivated injection liner, a deactivated silica guard column and a 0.53mm/0.53mm/0.53mm press tight tee. This tee also allows simultaneous injection onto both columns.

1.3 The carrier gas for routine applications is helium. All carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

1.4 Electron Capture Detector - The make-up gas must be P-5, P-10 (argon/methane) or nitrogen according to the instrument specification. The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector. The GC/EC system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants which may interfere with the analysis. The instrument must be vented to a trapping system which prevents the release of contaminants into the instrument room.

1.5 Data System - A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. The data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method. For system specifications, see Data Acquisition System Standard Operating Procedure.

The following list summarizes editing flag descriptions.

M	Begin manual integration
-M	End manual integration
+P	Enable peak detection
-P	Disable peak detection
+I	Peak end detection off
-I	Peak end detection on
+CB	Common baseline on
-CB	Common baseline off
E	End peak now
S	Start peak now
+X	Force exponential skin
-X	Prevent exponential skin
T	Force Tangential skim

All data editing must be reviewed by the Section Supervisor or designee before samples are reported.

2.0 CALIBRATION STANDARDS

2.1 Resolution Check Mixture - Prepare the mixture of pesticides in hexane or isooctane at the concentrations listed below. The mixture must be prepared every six months or sooner if the solution has degraded or concentrated.

gamma Chlordane	10.0 ng/ml	Endrin Ketone	20.0 ng/ml
Endosulfan I	10.0 ng/ml	Methoxychlor	100.0 ng/ml
p,p' - DDE	20.0 ng/ml	Tetrachloro-m-xylene	20.0 ng/ml
Dieldrin	20.0 ng/ml	Decachlorobiphenyl	20.0 ng/ml
Endosulfan sulfate	20.0 ng/ml		

2.2 Performance Evaluation Mixture (PEM) - Prepare the PEM in hexane or isooctane at the concentration levels listed below. The PEM must be prepared weekly, or more often if the solution has degraded or concentrated.

gamma - BHC	10.0 ng/ml	Endrin	50.0 ng/ml
alpha - BCH	10.0 ng/ml	Methoxychlor	250.0 ng/ml
4,4'-DDT	100.0 ng/ml	Tetrachloro-m-xylene	20.0 ng/ml
beta - BHC	10.0 ng/ml	Decachlorobiphenyl	20.0 ng/ml

2.3 Individual Standard Mixtures A and B - The single component pesticide standards must be prepared in hexane at three concentrations for each analyte, including the surrogates. Two separate calibration mixtures, A and B (listed below), are used to ensure that each peak is adequately resolved. The low point concentration corresponds to the CRQL for each analyte. The midpoint concentration must be 4 times the low point concentration. The high point concentration must be at least 16 times that of the low point. The high point concentration defines the upper end of the concentration range for which the concentration is valid. The solution must be prepared every six months, or sooner if the solution has degraded or concentrated.

Individual Standard Mixture A - Low Point Concentration.

alpha - BHC	5.0 ng/ml
Heptachlor	5.0 ng/ml
gamma - BHC	5.0 ng/ml
Endosulfan I	5.0 ng/ml
Dieldrin	10.0 ng/ml
Endrin	10.0 ng/ml
p,p' - DDD	10.0 ng/ml
p,p - DDT	10.0 ng/ml
Methoxychlor	50.0 ng/ml
Tetrachloro-m-xylene	5.0 ng/ml
Decachlorobiphenyl	10.0 ng/ml

Individual Standard Mixture B - Low Point Concentration.

beta - BHC	5.0 ng/ml
delta - BHC	5.0 ng/ml
Aldrin	5.0 ng/ml
Heptachlor Epoxide	5.0 ng/ml
alpha - Chlordane	5.0 ng/ml
gamma - Chlordane	5.0 ng/ml
p,p' - DDE	10.0 ng/ml
Endosulfan sulfate	10.0 ng/ml
Endrin Aldehyde	10.0 ng/ml
Endrin Ketone	10.0 ng/ml
Endosulfan II	10.0 ng/ml
Tetrachloro-m-xylene	5.0 ng/ml
Decachlorobiphenyl	10.0 ng/ml

2.4 Multicomponent standards - Toxaphene and Aroclor standards must be prepared individually except for Aroclor 1260 and Aroclor 1016, which may be combined in one standard mixture. The calibration standards for the Aroclors must be prepared at concentrations of 100 ng/ml, except for Aroclor 1221, which must be prepared at 200 ng/ml. Toxaphene must be prepared at 500 ng/ml. All multicomponent standards must contain surrogates at 200 ng/ml. The Aroclor and Toxaphene solutions must be prepared in hexane. Each solution must be prepared every six months, or sooner if the solution has degraded or evaporated.

3.0 GAS CHROMATOGRAPH OPERATING CONDITIONS

3.1 Initially, the injection port septum and liner should be changed and a conditioned column installed. After turning off the make-up gas, adjust the helium carrier gas flow to establish 4.0 ml/min through each column. Turn the make-up gas on; then adjust the make-up gas flow so that the total combined carrier/make-up gas flow is 60 ml/min through each detector. Set the gas chromatograph conditions as follows:

Column:	DB-1701 30m x 0.53mm or equivalent	DB-608 30m or 0.53mm or equivalent
Temperature:	300°C	300°C

Injector: 225°C
Injection: on column
Injection volume: 2 ul
Injector: splitless
Initial Temperature: 150°C
Initial Time: 0 min.
Rate 1: 5°C/min.
Temp 1: 275°C
Final Time: 15 min.

If the column is new, condition it by programming the oven at 40°C for 15 minutes, then heat at 2°C/minute to 220°C and hold overnight. After conditioning, prime the column by injecting a high concentration pesticide mix (i.e., 10 ng/ul). Record all maintenance activity in the GC logbook.

3.2 Instrument Maintenance

3.2.1 Daily Preventive Maintenance

Ensure gas tank pressures are adequate for helium and argon/methane.

Ensure autosampler rinse vials have an adequate volume of hexane and waste vials are not full.

Record all maintenance activity in the Instrument Maintenance Logbook.

3.2.2 Weekly Preventive Maintenance

Replace injector septum weekly or after 100 injections, whichever is sooner; cool oven and heated zones to less than 40° before replacing septum.

Replace autosampler rinse vials with new vials and hexane.

Record all maintenance activity in the Instrument Maintenance Logbook.

3.2.3 Monthly Preventive Maintenance

Replace injector inserts monthly, after five septa changes or whenever analyte breakdown is observed, whichever is sooner. New cleaned injection inserts should be deactivated according to laboratory procedures prior to use.

Check autosampler syringes for general condition, free motion and lack of deposits in the barrel and on the needle.

Replace GC effluent carbon traps on injectors and detectors with new carbon filters.

Consult with Section Supervisor if unsure of any procedure.

Record all maintenance activity in the Instrument Maintenance Logbook.

3.2.4 Non-routine Maintenance

When analyte breakdown is observed in the pesticide evaluation mixes, replace the septum, glass injector liner and cut off approximately 10 cm from the head of the column and reinstall according to the instrument manual.

Record all maintenance activity in the Instrument Maintenance Logbook.

Other non-routine problems (i.e. leaks, equipment malfunction or gross changes in the chromatography) should be recorded in the injection logbook and immediately reported to the Section Supervisor. If the repairs cannot be made by the in-house staff with the supplies on hand, the vendor's service department will be contacted to complete the repair.

4.0 ANALYSIS SEQUENCE FOR STANDARDS AND SAMPLES

4.1 The GC run log must be completed for all sequences run. Be sure to include the proper standard code for each standard entered. An example of the GC run log is attached. See Attachment A.

4.2 All acceptable samples must be analyzed within a valid analysis sequence as given below.

SEE FOLLOWING PAGE FOR ANALYSIS SEQUENCE

	Time	Injection #	Material Injected
		1 - 15	First 15 steps of the Initial Calibration
	0 hr	16	Instrument Blank at end of Initial Calibration
		17	PEM at end of Initial Calibration
		18	First Sample
		o	
		o	Subsequent Samples
		o	
	12 hr	o	Last Sample
		1st injection past 12:00 hr.	Instrument Blank
		2nd & 3rd injections past 12:00 hr.	Individual Standard Mixtures A & B
		o	Sample
		o	
		o	Subsequent Samples
		o	
Another 12 hr		o	Last Sample
		1st injection past 12:00 hr.	Instrument Blank
		2nd injection	Performance Evaluation Mixture
		o	Sample
		o	
		o	Subsequent Samples
		o	
		o	
Another 12 hr		1st injection past 12:00 hr.	Last Sample
		2nd & 3rd injections past 12:00 hr.	Individual Standard Mixtures A & B
		o	Sample
		o	
		o	Subsequent Samples
		etc	

Note: The first 12 hours are counted from the injection #16 (the Instrument Blank at the end of the initial calibration sequence), <u>not</u> from Injection #1. Samples may be <u>injected</u> until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic

run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the laboratory may run instrument blanks and standards more frequently.

4.3 Before any samples are analyzed, it is necessary to complete an acceptable initial calibration sequence.

4.4 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, performance evaluation mixtures, and individual standard mixtures A and B are analyzed at the required frequency.

4.5 An analysis sequence must also include all required matrix spike/matrix spike duplicate analyses and method blank.

4.6 A standard of any identified Arocolor must be run within 72 hours of its detection in a sample chromatogram.

5.0 INITIAL CALIBRATION

5.1 Initial Calibration Sequence

Before any samples are analyzed, it is necessary to complete the initial calibration sequence given below.

1. Resolution check
2. Performance Evaluation check
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Mid Point Standard A
13. Mid Point Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

5.2 Initial Calibration Acceptance

5.2.1 The resolution criterion is that the depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60% of the height of the shorter peak.

5.2.2 The breakdown of DDT and Endrin in both of the Performance Evaluation mixtures must be less than 20.0%, and the combined breakdown of DDT and Endrin must be less than 30.0% where

$$\% \text{ Breakdown DDT} = \frac{\text{Amount found in ng (DDD + DDE)} * 100}{\text{Amount in ng of DDT injected}}$$

$$\% \text{ Breakdown Endrin} = \frac{\text{Amount found in ng (Endrin aldehyde \& Endrin ketone)} * 100}{\text{Amount in ng of Endrin injected}}$$

Combined % Breakdown = % Breakdown DDT + % Breakdown Endrin

5.2.3 All peaks in the Performance Evaluation Mixture must be 100% resolved in both columns.

5.2.4 The absolute retention times of each analyte of the single component pesticides and surrogates in both of the PEMs must be within the retention time windows determined from the three-point initial calibration, in paragraph 7.

5.2.5 The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in both of the PEMs must be less than or equivalent to 25.0% where,

$$\text{Relative Percent Difference (RPD)} = \frac{\text{Cnom} - \text{Ccal}}{\text{Cnom}} \times 100$$

Cnom = True concentration of each analyte
Ccalc = Calculated concentration of each analyte from the analysis of the standard

5.2.6 At least one chromatogram from each of the two Individual Mixtures A and B, run during the initial calibration, must yield peaks that give recorder deflections of 50 to 100 percent of full scale.

5.2.7 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater or equal to 90 percent.

5.2.8 The % RSD of the calibration factors for each single component target compound must be less than or equal to 20.0%, except as noted below. The % RSD of the calibration factors for the two surrogates must be less than or equal to 30.0%. Up to two single component target compounds (but not surrogate) per column may exceed the 20.0% limit for % RSD, but those compounds must have a % RSD of less than or equal to 30.0%.

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

where,

$$\text{Standard Deviation} = \left| \frac{\sum_{i=1}^{n} (xi - x)^2}{n-1} \right|^{1/2}$$

where,

xi = each individual value used to calculate mean

x = the mean of the n values
n = the total number of values

5.3 Corrective Action

5.3.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake out the detector, clean the injection port, or take other corrective actions to achieve the acceptance criteria.

5.3.2 Initial calibration technical acceptance criteria must be met before any samples or required blanks are analyzed. Any samples analyzed after the initial calibration criteria have not been met will require reanalysis.

6.0 CALIBRATION VERIFICATION

6.1 The analyses of instrument blanks, Performance Evaluation Mixtures and the mid point concentration of Individual Standard Mixtures A and B constitute the continuing calibration. Sample data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEM, and both Individual Standard Mixtures A and B.

6.2 An instrument blank and the Performance Evaluation Mixture must bracket one end of a 12-hour period and a second instrument blank and the mid point concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

6.3 The injection of the instrument blank starts the beginning of that 12-hour period. The three injections immediately after that 12-hour period must be an instrument blank, Individual Standard Mixture A, and Individual Standard Mixture B. the Individual Standard Mixtures may be analyzed in either order (A,B or B,A).

6.4 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided they meet the acceptance criteria. The subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the acceptance criteria.

6.5 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.

6.6 If data collection is to be stopped before the entire 12-hour period, the sequence must be ended with either the instrument blank/PEM combination or the Instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of the 12-hour period.

6.7 The requirements for running the instrument blanks, PEM, and Individual Standard Mixtures A and B are waived when no samples, method blanks, or matrix spikes are run during that 12-hour period. After a break in analysis, the analysis of samples may resume and the initial calibration used for quantitation only after an acceptable PEM is run. If a successful PEM cannot be run, an acceptable initial calibration must be run before sample data may be collected.

6.8 Technical Acceptance Criteria for the calibration verification is the same as that for the initial calibration.

6.9 Corrective Action

6.9.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

6.9.2 Major corrective actions such as replacing the GC column or baking out the detector require that a new initial calibration be performed that meets the technical acceptance criteria.

6.9.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or Individual Mixture) that originally failed the criteria and an associated instrument blank immediately after the corrective action do meet all the acceptance criteria. If these analyses fail any of the technical acceptance criteria, a new initial calibration must be performed.

7.0 DETERMINATION OF ABSOLUTE RETENTION TIMES

7.1 During the initial calibration sequence, absolute retention times (RT) are determined for all single response pesticides, the surrogates, and at least three major peaks of each multi-component analyte.

7.2 For single component pesticides, an RT is measured in each of three calibration standards and the mean RT is calculated as the average of the three values. An RT is measured for the surrogates in each of three analyses of Individual Mixture A during the initial calibration and the mean RT is calculated as the average of the three values.

7.3 A retention time window is calculated for each single component analyte and surrogate by using the following list. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations.

Compound	Retention Time Window in Minutes
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
Aldrin	± 0.05
alpha-Chlordane	± 0.07
gamma-Chlordane	± 0.07
Heptachlor Epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin Ketone	± 0.07
DDD	± 0.07
DDE	± 0.07
DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07
Endosulfan Sulfate	± 0.07
Methoxychlor	± 0.07
Aroclors	± 0.07
Toxaphene	± 0.07
Tetrachloro-m-xylene	± 0.05
Decachlorobiphenyl	± 0.10

7.4 For each multi-component analyte, the RTs for three to five peaks are calculated from the initial calibration standard analysis. An RT window of ± 0.07 minutes is used for all multicomponent analyte peaks.

7.5 Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

8.0 CALIBRATION FACTORS FOR SINGLE COMPONENT PESTICIDES

8.1 The magnitude of the linear ECD response range for each single component pesticide and surrogate on each column and for each GC system is determined by analyzing the Individual Standard Mixtures A and B at three concentrations during the initial calibration sequence.

8.2 The linearity of the instrument is determined by calculating a percent relative standard deviation (% RSD) of the calibration factors from a three-point calibration curve for each single component pesticide and surrogate. Either peak height or peak area may be used to calculate calibration factors used in the % RSD equation, but the method used must be consistent for each analyte.

8.2.1 Calculate the calibration factor (CF) for each single component pesticide and surrogate over the initial calibration range, where

$$CF = \frac{\text{Peak area (or Height) of the Standard}}{\text{mass injected (ng)}}$$

The calibration factors for the surrogates are calculated from the three analyses of Individual Standard Mixture A only.

8.2.2 Calculate the mean (CF) and the % RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range, where

$$\overline{CF} = \sum_{i=1}^{n} \frac{CFi}{n}$$

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{CF} \times 100$$

where,

$$\text{Standard Deviation} = \left| \frac{\sum_{i=1}^{n} (xi - \bar{x})^2}{n-1} \right|^{1/2}$$

where,
xi = each individual value used to calculate the mean
x = the mean of n values
n = the total number of values

8.2.3 The linearity of the calibration is considered acceptable when the % RSD of the three point calibration is less than 20.0% except as noted below.

The % RSD of the two surrogates must be less than or equal to 30.0%. Up to two single component target compounds (but not surrogates) per column may exceed the 20.0% limit for % RSD, but those compounds must have a % RSD of less than or equal to 30.0%.

8.2.4 If the linearity requirements listed above are met, the calibration factor from the mid point concentration standard is used for quantitation of each single component pesticide.

9.0 CALIBRATION FACTORS FOR TOXAPHENE AND AROCLORS

Toxaphene and Aroclors require only a single-point calibration. A set of three to five major peaks is selected for each multicomponent analyte. Retention times and calibration factors are determined from the initial calibration analysis for each peak.

10.0 ACCEPTANCE CRITERIA FOR CHROMATOGRAMS OF CALIBRATION STANDARDS

The following requirements apply to all single component and multicomponent analytes.

10.1 The chromatograms that result from the analyses of the Resolution Check Mixture, the Performance Evaluation Mixture, and Individual Standard Mixtures A and B during the initial calibration sequence must display the single component analytes present in each standard at greater than 10 % of full scale but less than 100 % of full scale.

10.2 The chromatograms of the standards for the multicomponent analytes analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25% and less than 100% of full scale.

10.3 For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

10.4 If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram. Both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

11.0 SAMPLE ANALYSIS

11.1 The gas chromatographic conditions from paragraph 3 must be used.

11.2 The injection must be made on-column by using either automatic or manual injection. If auto-injectors are used, 1.0 ul injection volumes may be used. Manual injections must use at least 2.0 ul injections. The same injection volume must be used for all analyses.

11.3 Analysis of a sample on both GC columns is required for all samples, blanks, matrix spikes, and matrix spike duplicates.

11.4 The requirements for the analysis sequence apply to both GC columns and all instruments used for these analyses.

11.5 The laboratory will identify and quantitate analyte peaks based on RT and calibration factor established during the initial calibration sequence, as long as an acceptable calibration verification is performed every 12 hours.

11.6 The protocol is intended to achieve the quantitation limits shown in table 1, whenever possible. If sample chromatograms have interfering peaks, a high baseline, or off-scale peaks, then those samples must be reanalyzed following dilution, further cleanup or re-extraction. Samples which cannot be made to meet the given specifications after one re-extraction and three-step cleanup (GPC, Florisil, and sulfur removal) are reported in the SDG Narrative and do not need further analysis. No limit is placed on the number of re-extractions of samples that may be required because of contaminated method blanks.

11.7 The sample must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography. If dilution is employed solely to bring a peak within the calibration range or to get a multicomponent pattern on scale, the results for both the more and the less concentrated extract must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

11.8 If there is reason to believe that diluting the final extracts will be necessary, an undiluted run may not be required. If an acceptable chromatogram is achieved with the diluted extract, an additional extract 10 times the concentration of the dilute sample must be injected and reported with the sample data.

11.9 Non-target analyte concentrations may exceed the upper limit of the initial calibration.

11.10 A standard for any identified multicomponent analyte must be analyzed during a valid analytical sequence on the sample instrument, within 72 hours of its detection in a sample.

11.11 The following requirements apply to all data presented for single component and multicomponent analytes.

11.11.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.

11.11.2 Chromatograms must display single component pesticides or multicomponent analyte detected in the sample at less than full scale.

11.11.3 If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100% of full scale and the peaks chosen for quantitation of multicomponent analytes between

25 and 100% of full scale.

11.11.4 For any sample, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution of alpha-BHC and before the elution time of decachlorbiphenyl.

11.11.5 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram. Both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

12.0 QUANTITATION OF ANALYTES

12.1 Quantitation of target analytes and surrogates must be performed and reported on both columns.

12.2 Analytes must be quantitated with an electronic integrator or with a laboratory data system. Peak area is used to quantitate all single component analytes. Peak height is used to quantitate all multi-component analytes.

12.3 The chromatograms of all samples must be reviewed by a qualified pesticide analyst before they are reported.

12.4 In order to be quantitated, the detector response of all of the single component analytes must lie between the response of the low and high concentrations in the initial calibration. The target compound list (TCL) and Contract Required Quantitation Limits (CRQL) are summarized in Table 1. If the analytes are detected below the CRQL, they are reported as present below the CRQL and flagged. If they are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:100,000 or until the response is within the linear range established during calibration. Exceptions to this requirement are as follows:

12.4.1 If the response is still above the high calibration point after the dilution of 1:100,000, Sample Management Office or other designated individuals will be contacted immediately.

12.4.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

12.4.3 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

12.4.4 Data is submitted for only two analyses, i.e., the original sample extract and one dilution, or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

12.4.5 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG narrative.

12.5 The concentrations of the single component pesticides are calculated separately for both GC columns by using the following equations.

12.5.1 - concentration ug/L = $\frac{(Ax)(Vt)(Df)}{(CF)(Vo)(Vi)}$

where,

Ax = Area of the peak for the compound to be measured.
CF = Calibration factor for the midpoint concentration external standard (area per ng).
Vo = Volume of water extracted in milliliters.
Vi = Volume of extract injected in microliters. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

Vt = Volume of the extract in microliters (This volume must be 10,000 ul.)
Df = Dilution factor.

$$Df = \frac{\text{ul most conc. extract used to make dilution + ul clean solvent}}{\text{ul most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

If GPC is performed on a water sample extract, Vt becomes 5000 uL, and a factor of 2 must be added to the numerator, as described below for soil/sediment samples.

12.5.2 Soil/Sediment

Concentration ug/kg (Dry weight basis) = $\frac{(Ax)(Vt)(Df)(2.0)}{(Cf)(Vi)(Ws)(D)}$

where,

Ax, Cf, and Df are given for water, above.

Vt = Volume of the concentrated extract in microliters (this volume must be 5000 uL).

Vi = Volume of extract injected in microliters. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

D = $\frac{100 - \%\ moisture}{100}$

WS = Weight of sample extracted in grams.

The factor of 2.0 in the numerator is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup.

12.5.3 Because of the likelihood that compounds co-eluting with the target compounds will cause positive interferences and increase the concentration determined by the method, the lower of the two concentrations calculated for each single component pesticide is reported on form I. In addition, the concentrations calculated for both the GC columns are reported on form X, along with a percent difference comparing the two concentrations. The percent difference (%D) is calculated as follows,

$$\%\ D = \frac{conc_H - conc_L}{conc_L} \times 100$$

where,

$conc_H$ = The higher of the two concentrations for the target compound in question.

$conc_L$ = The lower of the two concentrations for the target compound in question.

12.6 The concentrations of the surrogates are calculated separately for both GC columns using the midpoint concentration of Individual Standard Mixture A. The recoveries of the surrogate are calculated as follows,

$$\text{surrogate percent recovery} = \frac{Qd}{Qa} \times 100$$

where,

Qd = Quantity determined by analysis

Qa = Quantity added to sample/blank

The limits for the recovery of the surrogates are 60-150% for both surrogate compounds. As these limits are only advisory, no further action is required by the laboratory, but frequent failures to meet the limits for surrogate recovery warrant investigation by the laboratory.

12.7 For Toxaphene or Aroclors, quantitation of peaks with the detector linear range CRQL to > 16 times CRQL is based on a single calibration point assuming linear detector response. A linear calibration range may be established during a run sequence by a three-point calibration curve for any multi-component analyte. If the concentration is calculated to be 10^6 times the CRQL, SMO shall be contacted immediately.

12.8 The quantitation of Toxaphene or Aroclors must be accomplished by comparing the heights or areas of each of the three to five major peaks of the multicomponent analyte in the sample with the calibration factor for the same peaks established during the initial sequence. The concentration of each peak is determined and then a mean concentration for three to five major peaks is determined on both columns. The following table lists the number of potential quantitation peaks for each Aroclor and Toxaphene.

Analyte	No. of Potential Quantitation Peaks
Aroclor 1016/1260	5/5
Aroclor 1221	3
Aroclor 1232	4
Aroclor 1242	5
Aroclor 1248	5
Aroclor 1254	5
Toxaphene	4

12.9 The reporting requirements for Toxaphene and the Aroclors are similar to those for the single component analytes, except that the lower mean concentration is reported on form X, and the two mean concentrations are compared using the percent difference equation.

12.10 If more than one multicomponent analyte is observed in a sample, separate peaks must be chosen to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate either compound.

13.0 SAMPLE DATA ACCEPTANCE CRITERIA

13.1 The requirements below apply to both columns, and quantitation must be performed on both GC columns and reported.

13.2 All samples must be analyzed as part of a valid analysis sequence. They must be bracketed by acceptable instrument blanks, acceptable Performance Evaluation Mixtures, and acceptable Individual Standard Mixtures A and B that were analyzed at the required frequency.

13.3 The retention times for both surrogates must be within the calculated retention time windows for both GC columns.

13.4 Reportable sample data must include chromatograms which meet the criteria in paragraph 11.11.

13.5 If dilution has been applied and if no peaks are detected above 25 percent of full scale, analysis of a more concentrated sample is required.

14.0 BLANKS

There are two types of blanks always required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may be required if all samples associated with a given method blank are not subjected to sulfur cleanup. Both the method and sulfur cleanup blanks must meet the respective acceptance criteria for the sample analysis acceptance criteria to be met.

14.1 Method Blank

14.1.1 - Method blanks are spiked with the surrogate solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A water method blank is one liter of reagent water treated as the water sample aliquot. A soil method blank is 30 g of sodium sulfate treated as the soil sample aliquot.

Method blank analysis must be performed once for the following, whichever is most frequent, and analyzed on each GC/EC system used to analyze samples:

- Each Case, OR
- Each 14 calendar day period (7 calendar day period for 14-day data turnaround contracts) during which samples in a SDG are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- Each 20 samples in a SDG, including matrix spikes and reanalyses, that are of similar matrix (water or soil), OR
- Whenever samples are extracted by the same procedure (separatory funnel, continuous liquid-liquid extraction, or sonication).

14.1.2 In order to be acceptable, a method blank analysis cannot contain any of the analytes listed in Table 1 at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

14.1.3 All samples associated with an unacceptable method blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the Agency.

14.2 Sulfur Cleanup Blank

14.2.1 The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup procedure.

14.2.2 The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and <u>no</u> separate sulfur cleanup blank is required.

14.2.3 In order to be acceptable, a sulfur blank analysis cannot contain any of the analytes listed in Table 1 at greater than the CRQL, assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample. Calculate the concentration of each analyte using the equation in paragraph 12.5.1. Compare the results to the CRQL values for water samples in Table. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

14.2.4 All samples associated with an unacceptable sulfur blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the Agency.

14.3 Instrument Blank

14.3.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

14.3.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable samples analyses are to be bracketed by acceptable instrument blanks, as described in paragraph 4.2.

14.3.3 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Table 1 is

detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of 1 L water sample and calculate the concentration of each analyte using the equation in paragraph 12.5.1. Compare the results to one-half the CRQL values for water samples in Table 1.

14.3.4 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the Agency and must be reported.

14.3.5 Analysts are cautioned that running an instrument blank once ever 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next is highly complex samples are analyzed of if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

15.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

15.1 A matrix spike and matrix spike duplicate must be extracted and analyzed at least once with every 20 samples of each matrix. NOTE: There is no differentiation between "low" and "medium" soil samples in this method. Therefore, only one soil MS/MSD is to be submitted per SDG.

15.2 The surrogate retention times must be within the retention time windows specified.

15.3 The percent recoveries and the relative percent difference between the recoveries of each of the 6 compounds in the matrix spike samples will be calculated and reported by using the following equations:

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{Eq. 12}$$

where, SSR = Spike sample result
SR = Sample result
SA = Spike added

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \times 100 \qquad \text{Eq. 13}$$

where,

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

15.4 Matrix spike and matrix spike duplicate recoveries and percent difference value with the analytical results will be reported. The limits for matrix spike compound recovery and RPD are given below. As these limits are only advisory, no further action by the laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from the Agency.

MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50

16.0 GC/MS CONFIRMATION OF PESTICIDES AND AROCLORS

Any pesticide or Aroclor analyte listed in Table I for which a concentration is reported from a GC/ECD analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. The following paragraph is to be used as guidance in performing GC/MS confirmation.

The GC/MS confirmation may be accomplished by one of three general means.

- Examination of the semivolatile GC/MS library search results (i.e., TIC data).
- A second analysis of the semivolatile extract.
- Analysis of the pesticide/Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

TABLE I

TARGET COMPOUND LIST (TCL) AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)

			Quantitation Limits*		
	Pesticides/Aroclors	CAS Number	Water ug/L	Soil ug/kg	On Column (pg)
98.	alpha-BHC	319-84-6	0.05	1.7	5
99.	beta-BHC	319-85-7	0.05	1.7	5
100.	delta-BHC	319-86-8	0.05	1.7	5
101.	gamma-BHC (Lindane)	58-89-9	0.05	1.7	5
102.	Heptachlor	76-44-8	0.05	1.7	5
103.	Aldrin	309-00-2	0.05	1.7	5
104.	Heptachlor epoxide	1024-57-3	0.05	1.7	5
105.	Endosulfan I	959-98-8	0.05	1.7	5
106.	Dieldrin	60-57-1	0.10	3.3	10
107.	4,4'-DDE	72-55-9	0.10	3.3	10
108.	Endrin	72-20-8	0.10	3.3	10
109.	Endosulfan II	33213-65-9	0.10	3.3	10
110.	4,4'-DDD	72-54-8	0.10	3.3	10
111.	Endosulfan Sulfate	1031-07-8	0.10	3.3	10
112.	4,4'-DDT	50-29-3	0.10	3.3	10
113.	Methoxychlor	72-43-5	0.50	17.0	50
114.	Endrin ketone	53494-70-5	0.10	3.3	10
115.	Endrin aldehyde	7421-36-3	0.10	3.3	10
116.	alpha-Chlordane	5103-71-9	0.05	1.7	5
117.	gamma-Chlordane	5103-74-2	0.05	1.7	5
118.	Toxaphene	8001-35-2	5.0	170.0	500
119.	Aroclor-1016	12674-11-2	1.0	33.0	100
120.	Aroclor-1221	11104-28-2	2.0	67.0	200
121.	Aroclor-1232	11141-16-5	1.0	33.0	100
122.	Aroclor-1242	53469-21-9	1.0	33.0	100
123.	Aroclor-1248	12672-29-6	1.0	33.0	100
124.	Aroclor-1254	11097-69-1	1.0	33.0	100
125.	Aroclor-1260	11096-82-5	1.0	33.0	100

* Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

There is no differentiation between the preparation of low and medium soil samples in this method for the analysis of Pesticides/Aroclors.

REFERENCES: "USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 6/91

ATTACHMENTS: Attachment A - ABB Environmental Instrument Run Log

GLOSSARY: None

ABB ENVIRONMENTAL INSTRUMENT RUN LOG HP5890-02 GC/ECD

METHOD:	
AMT. INJECTED:	

OPERATOR:	REVIEWED:
DATE:	DATE:

	DATE	CLIENT	SITE ID	ABB SAMPLE #	CONC. SURR. INJ. (ug/L)	CHANNEL A: B: TC FILE	QC	DIL. FACTOR	MATRIX H2O OR SOIL	SURR. RECOV.	ANALYSIS ACCEP. (Y OR RE)	COMMENTS
1												
2												
3												
4												
5												
6												
7												
8												
9												
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11												
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ABB ENVIRONMENTAL SERVICES INC. GC PESTICIDE\PCB\HERBICIDE INJECTION LOG INST:H58902 CASE:

FILE:A:\ORG\GC\RUNLOG

PAGE: 1

ATTACHMENT A

STANDARD OPERATING PROCEDURE

Author: Leslie Brewster
Approved by:
Willard C. Warren, III
President, Northeastern Division

Issuing Unit: CCAS - Northeast
SOP No.: CA-087-01
Date: September 1993

TITLE: Analysis of Gasoline in Water by Purge and Trap Gas Chromatography/Flame Ionization Detector

PURPOSE: The method described by this procedure can be used to analyze wastewater, surface water, and groundwater for the presence of gasoline by ME DEP Method 4.2.1 or modified EPA Method 8015.

SCOPE: This method includes the measurement of volatile hydrocarbons with boiling point ranges from -12°C to 210°C . This includes the aliphatic and aromatic hydrocarbons commonly found in gasoline and additives such as methyltertbutyl ether.

RESPONSIBILITIES: Before analyzing any samples, the analyst shall demonstrate competency with this procedure as outlined in the quality control section of this procedure and in the current revision of laboratory training SOP No. AD-002.

The analyst shall use this procedure without any variation unless permission is granted by the section supervisor.

PROCEDURE:

A. APPARATUS

1. 5.0 mL Teflon luer lock syringe - (Hamilton #1005 or equivalent)

2. Gas Chromatograph - Hewlett Packard 5890 equipped with flame ionization detector

3. Gas Chromatograph column: J&W DB-5 30 meter x 0.53 mm ID with 1.0 μm film thickness or equivalent

4. Electronic integrator - Hewlett Packard 3396A series GC terminal or equivalent

5. Tekmar liquid sample concentrator model LCS-2 or equivalent

B. REAGENTS

1. Methanol - Purge and trap grade or equivalent

2. Organic-free water for the blank, Poland Spring or equivalent

C. STANDARDS

1. Gasoline reference materials - gasoline from commercial source

2. Preparation of Standards

a. 1000 mg/L: Syringe 34.0 µl gasoline into a 25.0 mL volumetric flask. Dilute to volume with methanol.

b. 100 mg/L: Syringe 100 µl of the above standard in 900 µl methanol

Standards may be stored for 3 months.

D. ANALYSIS

1. Operating Conditions for the Gas Chromatograph

Initial Temperature:	35°C
Initial Time:	10.0 minutes
Ramp Rate:	8.0°C/minute
Final Temperature:	200°C
Final Time:	5.0 minutes
Injector Temperature:	250°C
Detector Temperature:	300°C

2. Operating Conditions for the Tekmar

Purge Time:	11 minutes
Purge Flow Rate:	30 mL/minute
Purge Ready:	30°C
Desorb Ready:	20°C
Desorb Preheat:	140°C
Desorb Temperature:	200°C
Desorb Time:	1.0 minute
Bake Temperature:	230°C
Bake Time:	15.0 minutes

3. Integrator Operating Conditions

Zero:	5
Attenuation:	1
Chart Speed:	0.5
Area Reject:	500
Threshold:	3
Peak Width:	0.05

Timetable Events

0.000 INTG# = 9
3.500 INTG# = -9
32.500 Stop
Signal 1 = B

4. Loading Samples

a. To load samples, removes plunger from the syringe barrel. Carefully pour the sample into the barrel until it overflows. Allow it to drain out, then refill with the same sample. Insert the plunger and adjust to the desired volume (5.0 mL). Take care to vent any residual air while adjusting the volume.

Transfer to the fritted sparge vessel.

b. Standards are loaded by filling syringe with 5.0 mL of reagent water; then adding 5.0 ul of 100 mg/L gasoline standard.

5. Calculations

Calculate gasoline concentration from the following equation:

$$Csa = \frac{Asa}{Ast} \times \frac{Vst}{Vsa} \times C(st)$$

where,

Csa = concentration of gasoline in sample in µg/L
Asa = total peak area of sample
Ast = total peak area of standard
Vst = mL of standard purged
Vsa = mL of sample purged
Cst = concentration of standard in µg/L

E. QUALITY CONTROL

1. For samples requiring analysis by ME DEP Method 4.2.1, ten replicates of 100 µg/L gasoline standard are run. The average total peak area is used in the calculation.

For samples requiring analysis by modified EPA Method 8015, a five point curve should be analyzed encompassing the range of 20 µg/L to 1000 µg/L.

2. The laboratory established linear range is from 20 ppb total gasoline to 2000 ppb total gasoline. The Practical Quantitation Level (PQL) is 20 µg/L.

a. For samples analyzed by modified EPA Method 8015, sample results should not exceed the highest point analyzed during the initial calibration. Any sample exceeding this level should be reanalyzed at a dilution that corresponds to the mid-point level of the calibration curve.

3. Duplicate samples are run every 20 samples or thirty days, whichever is more frequent.

4. Lab blanks must be analyzed daily and immediately following the initial check standard of the day. The total peak area of the blank chromatogram must be below the practical quantitation level (PQL) for the analysis.

5. A laboratory control sample/laboratory control sample duplicate (LCS/LCSD) must be prepared and analyzed every 20 samples or every 30 days, whichever occurs first. An LCS/LCSD is prepared and analyzed by filling a syringe with 5 ml of reagent water and adding 5 μl of 100mg/L gasoline standard to this syringe and loading it into the appropriate sparger on the purge and trap.

   Nominal acceptance limits for recovery are 75% to 125% and $\leq$25% relative percent difference between recoveries. LCS/LCSD criteria must be met before proceeding with sample analysis. An example LCS/LCSD reporting form is shown as Attachment C.

6. At client request a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed in the same manner as the LCS/LCSD except 5 ml of sample is used instead of 5 ml of reagent water.

   Nominal acceptance limits for recovery are 75% to 125% and $\leq$25% relative percent difference between recoveries. If criteria are not met associated analytical data should be reviewed to determine if unacceptable results are due to laboratory problems. If no laboratory problem is indicated, further action is not needed. Otherwise, re-analyze MS/MSD. An example MS/MSD reporting form is shown as Attachment D.

7. Check instrument logbook for maintenance requirements and enter all maintenance in the instrument logbook.

8. For samples analyzed by ME DEP Method 4.2.1, check standards must be run after the initial calibration, then every 20 samples or twenty-four hours, whichever comes first. Check standards must have a recovery of 80 - 120%.

   All samples analyzed after an unacceptable check standard must be reanalyzed after analysis of an acceptable check standard or recalibration of the instrument.

   a. For samples analyzed by modified EPA Method 8015, check standards at a mid-level concentration should be analyzed after every ten samples, and must be within ± 15% relative percent difference from the initial

calibration curve. If a check standard does not pass this criteria, an additional check standard may be analyzed or the instrument may be recalibrated. All samples analyzed after an unacceptable check standard must be reanalyzed.

F. SAFETY

1. Standards in methanol should be prepared in a hood.

2. Goggles must be worn.

3. Hydrogen is an explosive gas. Make sure that all connections are leak free before using hydrogen.

G. INTERFERENCES

1. Many solvent mixtures and compounds elute in the gasoline range. Therefore, care must be used in identification of gasoline.

2. The water soluble fuel oil components are also present in gasoline and the mixture can be misidentified.

REFERENCES: Maine Department of Environmental Protection SOP No. 4.2.1
EPA Method 8015, SW-846 3rd Edition, Rev. July 1992.

ATTACHMENTS:
Attachment A - Example of Report and Chromatogram
Attachment B - Example of Lotus® Spreadsheet for Initial Calibration
Attachment C - Example of Laboratory Control Sample Form
Attachment D - Example of Matrix Spike/Matrix Spike Duplicate Form

GLOSSARY: Total Hydrocarbons - Total hydrocarbons include all compounds that respond to an FID. This may include compounds that do not fit the classic definition of hydrocarbons.

Weathering - Weathering includes any process that changes the original composition of the petroleum mixture. The main categories that we consider when interpreting the chromatogram are dissolution in water, evaporation, bacterial degradation and oxidation.

Attachment A-1

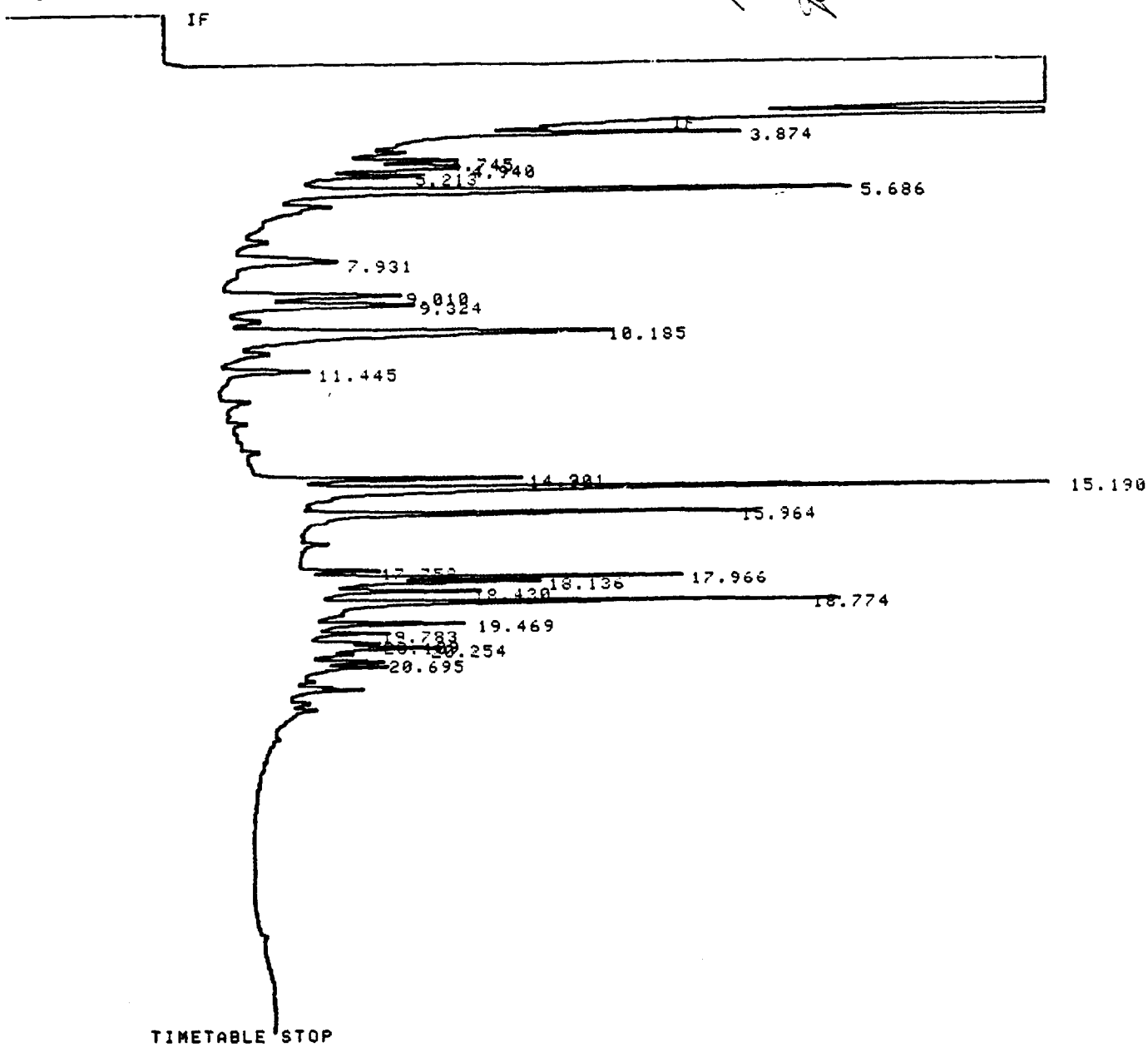
GAS

NO RUN PEAKS STORED

* RUN # 3 FEB 22, 1993 12:45:16

100% gasoline

START-Source

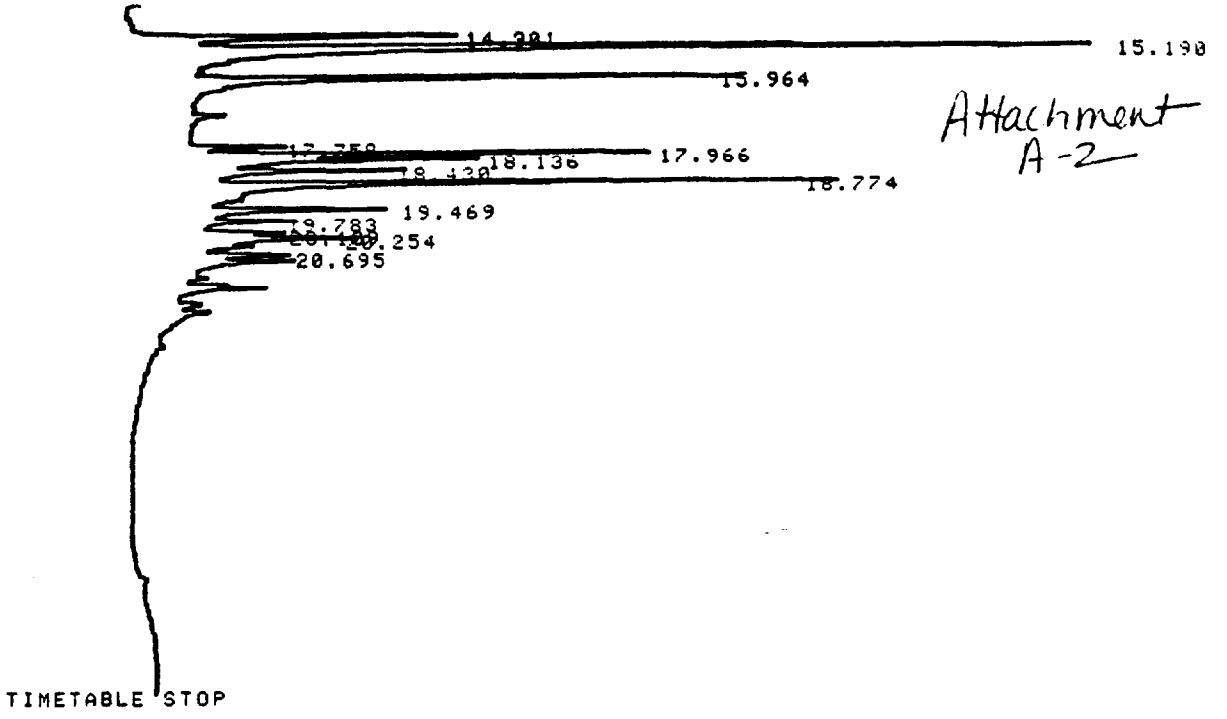


RUN# 3 FEB 22, 1993 12:45:16

GAS

AREA%

RT	AREA	TYPE	WIDTH	AREA%
3.874	20377	BP	.075	2.80650
4.745	11609	PV	.100	1.59889
4.940	24602	VV	.189	3.38840
5.213	11726	VP	.113	1.61501
5.686	83278	PB	.145	11.46977
7.931	26692	BB	.256	3.67625



Attachment A-2

RUN# 3 FEB 22, 1993 12:45:16

GAS

AREA%

RT	AREA	TYPE	WIDTH	AREA%
3.874	20377	BP	.075	2.30650
4.745	11609	PV	.100	1.59889
4.940	24602	VV	.189	3.38840
5.213	11726	VP	.113	1.61501
5.686	83278	PB	.145	11.46977
7.931	26692	BB	.256	3.67625
9.010	32435	BV	.179	4.46723
9.324	39863	VP	.207	5.49028
10.185	97590	BV	.249	13.44095
11.445	15685	PB	.169	2.16028
14.901	26405	PV	.101	3.63673
15.190	105112	VB	.126	14.47694
15.964	41615	BB	.091	5.73158
17.758	6812	PV	.086	.93821
17.966	40194	VV	.104	5.53587
18.136	26325	VV	.111	3.62571
18.430	16137	VP	.095	2.22253
18.774	47311	PB	.089	6.51608
19.469	13875	BV	.092	1.91099
19.783	6756	VP	.090	.93050
20.109	5825	PV	.084	.80227
20.254	16935	VV	.126	2.33244
20.695	8906	VV	.113	1.22661

TOTAL AREA= 726065
MUL FACTOR=1.0000E+00

100% gasoline

* RUN # 4 FEB 22, 1993 14:03:59
START-Source
IF

Attachment B-1

ABB-ENVIRONMENTAL LABORATORY GC CALIBRATION / CCAS

INST: HP5890-04
COLUMN DB-5
< File: A:\FEBB93GAS

METHOD: Me. Dep. GASOLINE in WATER
Cal Date: 02/22/93
Analyte: GASOLINE IN WATER
Calib (AC or HT): AC
Date: 02/23/93

INJECTION/PURGE VOLUME: 5.0 mL

	Std Amt (ng)	Measured Response For Standard 1	2	3	Average Value (Response)	Response Factor (Res/ng)	Calib. Estimate (Response)	Differ. Calib-Aver (%)	Slope	inter
1	100.000	726065			726065	7.26E+03	553123	-24%	ERR	*
2	100.000	805589			805589	8.06E+03	553123	-31%	ERR	*
3	100.000	731061			731061	7.31E+03	553123	-24%	ERR	*
4	100.000	603222			603222	6.03E+03	553123	-8%	ERR	*
5	100.000	636418			636418	6.36E+03	553123	-13%	ERR	*
6	100.000	553123			553123	5.53E+03	553123	0%	ERR	*
7	100.000	674909			674909	6.75E+03	553123	-18%	ERR	*
8	100.000	640940			640940	6.41E+03	553123	-14%	ERR	*
9	100.000	703110			703110	7.03E+03	553123	-21%	ERR	*
10	100.000	617499			617499	6.17E+03	553123	-10%		

Average Response Facto	=	669194	
Standard Deviation	=	73950.51	Res/ng
Relative Standard Dev. (RSD) =		~~1337 %~~	NA

Client: , Work Order: F2-GAS-W 06-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Laboratory Control Sample Results

Gasoline by GC Method: ME DEP 4.2.1

Water Matrix

Date of Analysis: _____

Compound	Units	Spike Conc.	LCS Measured Conc.	LSC Dup. Measured Conc.	LCS % Recovery	LSC Dup. % Recovery	Recovery Acceptance Range (%)*	RPD (%)	RPD Acceptance Range (%)*
Gasoline	ug/L	100					75-125		0-25

* The laboratory has established the following acceptance criteria for the laboratory control sample/laboratory control sample duplicate (LCS/LCSD) sets employed for organic analyses. All spike recoveries must be equal to or greater than ten percent, and a minimum of ninety percent of the total number of calculated recoveries plus relative percent differences (RPDs) must be within the specified acceptance ranges.

See cover letter for additional information.

ATTACHMENT C

Client: , Work Order: F3-GAS-W 19-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Matrix Spike/Matrix Spike Duplicate Results

Gasoline by GC Method: ME DEP 4.2.1

Water Matrix

CCAS Sample No. Spiked: _____

Compound	Units	Spike Conc.	Sample Conc.	MS Measured Conc.	MSD Measured Conc.	Theoretical Spiked Sample Conc.	MS % Recovery	MSD % Recovery	Recovery Acceptance Range (%) *	RPD (%)	RPD Acceptance Range (%) *
Gasoline	ug/L								75-125		0-25

* Acceptance ranges are obtained when available from the applicable US EPA analytical method. These ranges are based upon method performance data generated from the analysis of quality control check samples and not actual environmental samples. The laboratory does not use the MS/MSD acceptance ranges as quality control acceptance criteria; the MS/MSD data are used to evaluate method performance for the environmental sample matrix. Please refer to LCS/LCSD data for assessment of quality control for this method.

NA = Not applicable.

ATTACHMENT D

STANDARD OPERATING PROCEDURE

Author: L. Brewster
Approved by:

Willard C. Warren, III
President, Northeastern Division

Issuing Unit: CCAS Northeast
SOP No.: CA-088-01
Date: September 1993

TITLE: Analysis of Water and Soil Samples for Semivolatile Petroleum Products (Fuel Oil)

PURPOSE: The purpose of this SOP is to described the procedure used by CCAS-NE personnel to analyze samples for fuel oil by ME DEP Methods 4.1.1 and 4.1.2. This procedure can be used to analyze water and soil for the presence of semivolatile petroleum products (fuel oil).

SCOPE: This method is applicable to the measurement of hydrocarbons extractable from water and soils with methylene chloride. Water matrices may include waste water, surface water or groundwater.

Light petroleum hydrocarbons with boiling points below 150°C are completely or partially lost during the concentration step of the extraction procedure.

REQUIREMENTS: Before analyzing any samples, the analyst shall demonstrate competency with this procedure as described in the current version of CCAS-NE SOP No. AD-002, "Personnel Training."

The analyst shall use this procedure for fuel oil analysis without any variation unless permission is granted by the section supervisor. Any deviation shall be noted. Prior to analysis by GC/FID, samples must be extracted and concentrated following the procedures described in the current version of CCAS-NE SOP No. CA-103.

PROCEDURE:

A. APPARATUS

1. Gas Chromatograph - Hewlett Packard 5890 Series II or equivalent equipped with a flame ionization detector

   a. Gas Chromatograph Autosampler with 10 µl syringe, Hewlett Packard or equivalent

2. Data Acquisition System

   a. Integrator - Hewlett Packard 3396 Series II or equivalent

b. Turbochrom Computer Acquisition System - Perkin Elmer Nelson Analytical (optional)

3. Capillary Column - J&W DB-5, 30 meter x 0.53 mm ID with film thickness of 1.5 micron or equivalent

4. 2.0 mℓ autosampler vials with a 200 μl polyspring insert and a teflon lined crimp top or equivalent

B. REAGENTS

1. Methylene Chloride - pesticide grade or better

2. Standards - prepare a standard by weighing 1 g fuel oil in a 25.00 mℓ volumetric flask and dilute to volume with methylene chloride. This standard should be approximately 40,000 mg/L.

   a. Using the above standard, make the following concentrations: 10 mg/L, 50 mg/L, 100 mg/L, 250 mg/L, 500 mg/L and 1000 mg/L. These should be prepared in methylene chloride.

   b. If available, an independent standard should be prepared at a mid-point concentration.

3. Helium carrier gas and auxiliary gas ≥ 99.999%

4. Hydrogen gas ≥ 99.999%

5. Ultra zero air <1 PPM hydrocarbons as methane

C. ANALYSIS

1. Temperature Program: These are set at the GC. They can be saved in the method and stored in the integrator.

Initial Temperature:	50°C
Initial Time:	5.0 minutes
Ramp Rate:	8.0°C/minute
Final Temperature:	280°C
Injector Temperature:	250°C
Detector Temperature:	300°C

2. Injection Parameters: These are set at the integrator in the autosampler.

First Sample:	1 (or desired beginning autosampler tray position)
Last Sample:	100
Injection Volume:	2 μl
Injections per Bottle:	1

Sample Washes:	3
Number of Pumps:	3
Number of Solvent A Washes:	4
Number of Solvent B Washes:	4

3. Integration Parameters: These are set at the integrator and may be saved in the method.

Zero:	5
Attenuation:	0
Chart Speed:	0.5
Area Reject:	25
Threshold:	-3
Peak Width:	0.04

4. Time Table Events:
These are set at the integrator and may be saved in the method.

Time 0.0	Integration #	= 9
Time 10.5	Integration #	= -9
Time 28.0	Integration #	= 9

5. Prepare instrument, autosampler, integrator, and Turbochrom (if used). Consult the instrument manufacturer manuals for further information.

6. Obtain sample extracts and load each into a labeled 2.0 mℓ vial with a 200 µl polyspring insert. Crimp top on tightly. Load these on the autosampler tray.

7. An analytical run sequence consists of the following:

   a. Blank - methylene chloride
   b. 50 mg/L - fuel oil standard
   c. 100 mg/L - fuel oil standard
   d. 250 mg/L - fuel oil standard
   e. 500 mg/L - fuel oil standard
   f. 1000 mg/L - fuel oil standard
   g. Blank - methylene chloride
   h. 500 mg/L - independent standard (if available)
   i. Blank
   j. 500 mg/L - check standard (or mid level on curve)
   k. Blank
   l. 20 samples (or 10 samples if following EPA Method Mod. 8100
   m. Blank
   n. 500 mg/L - check standard (or mid level on curve)

   Repeat sequence "l" through "n" until samples are complete or instrument recalibration is required. See Section E, Quality Control, for calibration curve, method blank, and check standard acceptance criteria.

NOTE: LCS/LCSD samples are run following the check standard and blanks. They are not counted when determining the frequency of check standards.

D. QUANTITATION

Fuel oils are quantitated using a Lotus 1-2-3 spreadsheet which calculates fuel oil concentrations based on a linear fit of the calibration curve. The spreadsheet calculates a linear regression from the calibration curve data. The sample's total area is entered and fuel oil concentration in mg/L is determined. Using results from the spreadsheet (Attachment F-1), reported concentrations are manually calculated using the following equations:

1. Aqueous Matrix

Reported Conc (μg/L) =

$$\frac{Amt_c\ (mg/L) * V_f(L)}{V_i\ (L)} * \frac{1000\ \mu g}{mg}$$

where,

Amt_c = value taken from "Curve Amt (ng)" column in Lotus spreadsheet (this value is equivalent to fuel oil concentration in the extract in mg/L)

V_f = final extract volume in liters

V_i = initial sample volume in liters

2. Soil Matrix

Reported Conc (mg/kg dry wt) =

$$\frac{Amt_c\ (mg/L) * V_f\ (L)}{W_i\ (kg) * \%TS/100}$$

where,

Amt_c = value taken from "Curve Amt (ng)" column on Lotus spreadsheet (this value is equivalent to fuel oil concentration in the extract in mg/L)

V_f = final extract volume in liters

W_i = initial sample weight in kilograms

%TS = percent total solids

A manual check of fuel oil concentrations is done using a point to point comparison of the sample's total area count to a calibration standard's total area count. The result is calculated using the calibration standard whose total area is closest to the sample's total area. Ten percent of the spreadsheet calculations should be confirmed manually using the following equations:

1. Aqueous Matrix Manual Check

$$C(s) = \frac{A(s)}{A(st)} \times \frac{U(st)}{U(s)} \times \frac{V(c)}{V(s)} \times C(st)$$

where,

C(st) = concentration of standard in ug/L
A(s) = total area of sample from 10 minutes to 30 minutes
A(st) = total area of standard from 10 minutes to 30 minutes
U(st) = µl standard injected (2 µl)
U(s) = µl sample extract injected (2 µl)
V(s) = volume sample (mℓ)
V(c) = volume of concentrated sample extract (mℓ)
C(s) = concentration of sample in ug/L

2. Soil Matrix Manual Check

$$C(s) = \frac{A(s)}{A(st)} \times \frac{U(st)}{U(s)} \times \frac{C(st)}{WT(s)} \times V(c) \times \frac{1}{TS}$$

where,

C(st) = concentration of standard in mg/kg, dry weight
A(s) = total area of sample from 10 minutes to 30 minutes
A(st) = total area of standard from 10 minutes to 30 minutes
U(st) = µl standard injected (2 µl)
U(s) = µl sample injected (2 µl)
C(t) = concentration of standard in mg/mℓ
WT(s) = wet weight of sample in kg
V(c) = volume of concentrated sample extract
TS = percent total solids (decimal, e.g., 70% = 0.70)

E. QUALITY CONTROL

1. Neat reference material should be stored in an amber 40 mℓ VOA vial. Neat fuel oil should be changed annually or when

degradation is evident.

2. Lab blanks must be analyzed during and immediately following the highest standard run before samples.

3. The method blank must not contain a hit above the established laboratory practical quantitation level (PQL). The PQL for water samples is 50 μg/L and the PQL for soil samples is 10 mg/kg.

4. Working standard must be made up every six months.

5. Check standard must be within 25% of curve, or 15% of curve if following EPA Method Mod. 8100.

6. Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) must be extracted with each set of twenty samples or once per month, whichever is sooner. Acceptable percent recovery and relative percent difference (RPD) limits are statistically generated on an annual basis. For current limits, see Attachments C-1 and C-2. If LCS/LCSD criteria are not met a Corrective Action Report (CAR) must be completed and associated samples must be re-extracted within hold times or project manager notified for further action.

7. At client request a matrix spike/matrix spike duplicate (MS/MSD) is extracted and analyzed. Nominal acceptance limits for recovery are 50% to 150% and ≤40% relative percent difference between recoveries for both water and soil samples. If criteria are not met associated analytical data should be reviewed to determine if unacceptable results are due to laboratory problems. If no laboratory problem is indicated, further action is not needed. Otherwise, re-extract and re-analyze MS/MSD. Examples of soil and water MS/MSD reporting forms are shown as Attachments D-1 and D-2.

8. Run log and instrument maintenance log must be kept up daily.

REFERENCES: Maine DEP SOP No. 4.1.1 Fuel Oil in Water

Maine DEP SOP No. 4.1.2 Fuel Oil in Soil

ATTACHMENTS:

Attachment A-1 - A-4	-	Sample Report and Chromatogram
Attachment B-1	-	Water Worksheet
Attachment B-2	-	Soil Worksheet
Attachment C-1 - C-2	-	Laboratory Control Sample Form
Attachment D-1 - D-2	-	Matrix Spike/Matrix Spike Duplicate Forms
Attachment E-1	-	Print out of GC Method Parameters

Attachment F-1 - Example of Lotus Calculations Spreadsheet

GLOSSARY:

Flame Ionization Detector (FID) - An FID responds to compounds containing carbon and hydrogen. It also responds to some compounds which contain carbon but no hydrogen.

Total Hydrocarbons - Total hydrocarbons include all compounds that respond to an FID. This may include compounds that do not fit the classic definition of hydrocarbons.

Weathering - Weathering includes any process that changes the original composition of the petroleum mixture. The main categories that we consider when interpreting the chromatogram are dissolution in water, evaporation, bacterial degradation and oxidation.

Software Version: 3.1 <2A23> Attachment A-1

Sample Name : 250MG/L
Sample Number:
Operator :

Time : 3/30/93 9:13
Study :

Instrument : 970 - 0
AutoSampler : NONE
Rack/Vial : 0/0

Channel : A A/D mV Range : 1000

Interface Serial # : 8084920872 Data Acquisition Time: 3/29/93 6:34
Delay Time : 5.00 min.
End Time : 35.00 min.
Sampling Rate : 2.0000 pts/sec

Raw Data File : h:\04\4MAI028.raw
Result File : h:\04\4MAI028.rst
Instrument File: H:\04\04FUEL.ins
Process File : H:\04\04FUEL.prc
Sample File : H:\04\04FUEL.smp
Sequence File : h:\04\04mai.seq

Inj. Volume : 1 ul
Sample Amount : 1.0000

Area Reject : 10.00
Dilution Factor : 1.00

HYDROCARBON SCREEN

COAST TO COAST ANALYTICAL SERVICES

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	10.065	456.00	76.23	0.19	0.19	BB	5.9817
2	10.322	931.50	191.35	0.40	0.40	BB	4.8682
3	10.541	480.50	104.80	0.21	0.21	BB	4.5849
4	10.750	363.25	81.35	0.16	0.16	BB	4.4654
5	10.983	427.50	97.42	0.18	0.18	BB	4.3882
6	11.172	563.75	71.04	0.24	0.24	BB	7.9356
7	11.531	1710.50	383.29	0.73	0.73	BB	4.4627
8	11.717	170.25	47.98	0.07	0.07	BB	3.5482
9	11.893	177.50	48.63	0.08	0.08	BB	3.6504
10	12.044	380.25	82.95	0.16	0.16	BB	4.5843
11	12.229	46.25	12.60	0.02	0.02	BB	3.6700
12	12.335	227.50	69.81	0.10	0.10	BB	3.2589
13	12.476	428.50	113.54	0.18	0.18	BB	3.7741
14	12.677	779.50	172.52	0.33	0.33	BB	4.5183
15	12.863	1029.00	206.16	0.44	0.44	BB	4.9913
16	13.064	416.00	122.55	0.18	0.18	BB	3.3946
17	13.163	115.25	46.74	0.05	0.05	BB	2.4660
18	13.221	80.75	45.48	0.03	0.03	BB	1.7754
19	13.308	222.00	86.55	0.10	0.10	BB	2.5650
20	13.390	255.74	62.86	0.11	0.11	BB	4.0682
21	13.685	3124.01	473.24	1.33	1.33	BB	6.6013
22	14.064	5133.50	1190.26	2.19	2.19	BB	4.3129
23	14.335	919.00	270.15	0.39	0.39	BB	3.4018
24	14.415	92.00	34.90	0.04	0.04	BB	2.6359
25	14.622	1679.50	416.42	0.72	0.72	BB	4.0332
26	14.739	54.00	26.86	0.02	0.02	BB	2.0102
27	14.827	213.50	82.40	0.09	0.09	BB	2.5910

Attachment A-2

28	14.889	[illegible]	[illegible]	[illegible]		
29	15.003	779.00	218.40	0.33	0.33 BB	3.5669
30	15.151	1089.75	183.69	0.46	0.46 BB	5.9325
31	15.368	731.50	246.30	0.31	0.31 BB	2.9700
32	15.510	186.25	83.59	0.08	0.08 BB	2.2282
33	15.639	1307.49	286.39	0.56	0.56 BB	4.5654
34	15.754	850.00	246.52	0.36	0.36 BB	3.4480
35	15.871	138.50	45.79	0.06	0.06 BB	3.0246
36	15.971	192.00	73.58	0.08	0.08 BB	2.6096
37	16.152	195.00	40.87	0.08	0.08 BB	4.7708
38	16.233	7604.51	2105.84	3.24	3.24 BB	3.6112
39	16.423	98.25	39.05	0.04	0.04 BB	2.5163
40	16.484	261.00	115.87	0.11	0.11 BB	2.2526
41	16.607	961.00	230.95	0.41	0.41 BB	4.1611
42	16.719	162.50	63.64	0.07	0.07 BB	2.5533
43	16.827	738.00	188.13	0.31	0.31 BB	3.9229
44	16.963	1038.50	193.47	0.44	0.44 BB	5.3678
45	17.048	288.75	125.85	0.12	0.12 BB	2.2944
46	17.118	329.75	143.17	0.14	0.14 BB	2.3033
47	17.277	1547.00	300.33	0.66	0.66 BB	5.1509
48	17.400	425.24	191.54	0.18	0.18 BB	2.2202
49	17.490	1148.00	322.18	0.49	0.49 BB	3.5632
50	17.625	844.00	264.25	0.36	0.36 BB	3.1939
51	17.791	322.50	87.11	0.14	0.14 BB	3.7023
52	17.968	1885.00	548.91	0.80	0.80 BB	3.4341
53	18.134	9334.00	2749.65	3.98	3.98 BB	3.3946
54	18.311	766.00	222.98	0.33	0.33 BB	3.4353
55	18.427	3243.49	759.63	1.38	1.38 BB	4.2698
56	18.561	98.50	41.79	0.04	0.04 BB	2.3569
57	18.646	254.50	91.40	0.11	0.11 BB	2.7845
58	18.763	812.99	160.06	0.35	0.35 BB	5.0794
59	18.912	2286.75	546.81	0.97	0.97 BB	4.1820
60	19.095	817.51	183.17	0.35	0.35 BB	4.4630
61	19.177	2415.75	817.46	1.03	1.03 BB	2.9552
62	19.261	441.49	206.67	0.19	0.19 BB	2.1363
63	19.448	4405.49	873.05	1.88	1.88 BB	5.0461
64	19.559	115.50	53.92	0.05	0.05 BB	2.1419
65	19.645	6826.50	1400.00	2.91	2.91 BB	4.8761
66	19.851	8780.00	2955.92	3.74	3.74 BB	2.9703
67	20.108	5958.01	920.79	2.54	2.54 BB	6.4706
68	20.427	558.50	145.88	0.24	0.24 BB	3.8286
69	20.517	444.50	185.68	0.19	0.19 BB	2.3940
70	20.640	662.75	203.51	0.28	0.28 BB	3.2565
71	20.804	640.00	257.63	0.27	0.27 BB	2.4842
72	20.884	864.00	362.91	0.37	0.37 BB	2.3808
73	21.000	1672.00	471.92	0.71	0.71 BB	3.5430
74	21.125	2321.75	840.93	0.99	0.99 BB	2.7609
75	21.261	4292.00	904.15	1.83	1.83 BB	4.7470
76	21.433	20205.00	5225.12	8.61	8.61 BB	3.8669
77	21.656	2801.97	994.53	1.19	1.19 BB	2.8174
78	21.707	485.23	289.40	0.21	0.21 BB	1.6767
79	21.885	146.50	42.71	0.06	0.06 BB	3.4301
80	21.980	2254.50	503.22	0.96	0.96 BB	4.4802
81	22.200	4406.49	747.27	1.88	1.88 BB	5.8968
82	22.319	255.75	131.10	0.11	0.11 BB	1.9509
83	22.400	4290.50	1399.00	1.83	1.83 BB	3.0668
84	22.501	1078.00	326.91	0.46	0.46 BB	3.2976
85	22.673	1071.00	351.41	0.46	0.46 BB	3.0477
86	22.904	17962.50	4608.19	7.65	7.65 BB	3.8980
87	23.053	309.50	150.80	0.13	0.13 BB	2.0524
88	23.160	367.00	153.01	0.16	0.16 BB	2.3985
89	23.232	936.00	403.06	0.40	0.40 BB	2.3222
90	23.317	1650.76	591.77	0.70	0.70 BB	2.7896
91	23.535	592.28	200.11	0.25	0.25 BB	2.9598
92	23.595	821.00	348.59	0.35	0.35 BB	2.3552
93	23.721	650.50	237.13	0.28	0.28 BB	2.7433

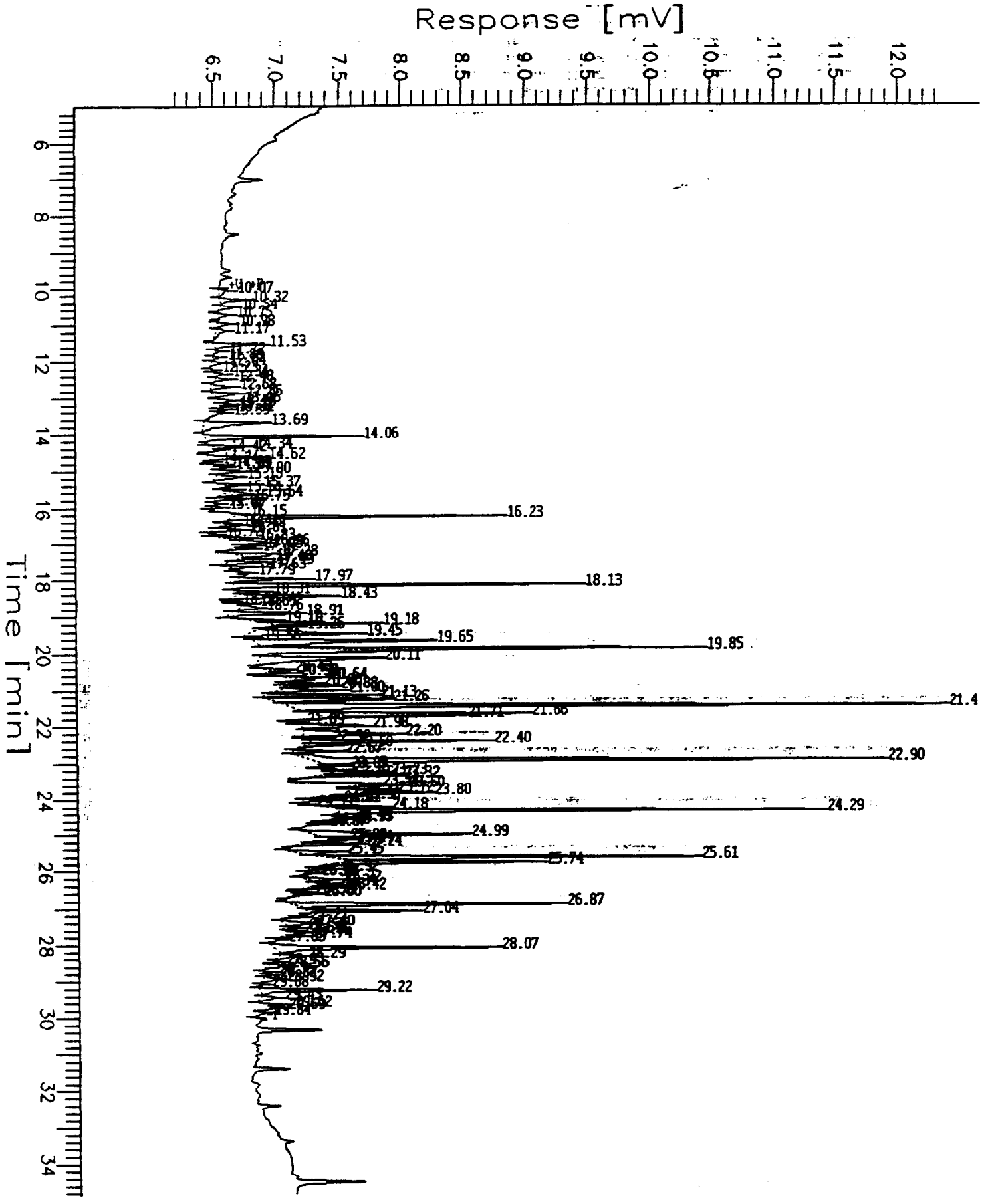
94	23.801	1414.50	[illegible]	[illegible]	[illegible]	[illegible]	
95	23.897	629.75	227.22	0.27	0.27	BB	2.7715
96	24.006	853.75	257.47	0.36	0.36	BB	3.3159
97	24.112	62.50	30.00	0.03	0.03	BB	2.0833
98	24.183	1317.49	434.79	0.56	0.56	BB	3.0302
99	24.292	13162.74	3851.75	5.61	5.61	BB	3.4173
00	24.485	121.00	43.42	0.05	0.05	BB	2.7869
01	24.532	265.50	119.04	0.11	0.11	BB	2.2304
02	24.601	66.25	40.20	0.03	0.03	BB	1.6482
03	24.665	53.25	60.24	0.02	0.02	BB	0.8840
04	24.987	5094.99	1194.50	2.17	2.17	BB	4.2654
05	25.082	148.49	66.14	0.06	0.06	BB	2.2450
06	25.135	398.01	171.36	0.17	0.17	BB	2.3227
07	25.244	1306.99	443.72	0.56	0.56	BB	2.9455
08	25.450	1438.00	347.92	0.61	0.61	BB	4.1331
09	25.607	10105.74	2920.40	4.31	4.31	BB	3.4604
.10	25.743	5543.99	1570.68	2.36	2.36	BB	3.5297
11	25.922	456.25	171.68	0.19	0.19	BB	2.6576
.12	26.027	52.50	16.64	0.02	0.02	BB	3.1552
.13	26.057	68.00	28.59	0.03	0.03	BB	2.3786
.14	26.217	928.75	209.44	0.40	0.40	BB	4.4344
.15	26.340	372.50	99.38	0.16	0.16	BB	3.7484
.16	26.419	657.50	230.00	0.28	0.28	BB	2.8587
.17	26.531	171.00	74.74	0.07	0.07	BB	2.2880
.18	26.595	476.74	142.04	0.20	0.20	BB	3.3564
.19	26.866	7390.25	2123.62	3.15	3.15	BB	3.4800
.20	27.044	2723.50	859.53	1.16	1.16	BB	3.1686
.21	27.213	192.00	79.00	0.08	0.08	BB	2.4304
.22	27.401	1066.25	180.12	0.45	0.45	BB	5.9197
.23	27.514	217.00	88.87	0.09	0.09	BB	2.4418
124	27.590	60.00	27.21	0.03	0.03	BB	2.2052
125	27.657	230.25	86.66	0.10	0.10	BB	2.6569
126	27.743	360.01	144.53	0.15	0.15	BB	2.4910
127	27.835	244.50	55.29	0.10	0.10	BB	4.4224
128	28.068	7727.75	1744.75	3.29	3.29	BB	4.4292
129	28.293	822.00	158.53	0.35	0.35	BB	5.1851
130	28.450	104.00	40.00	0.04	0.04	BB	2.5999
131	28.556	604.50	107.70	0.26	0.26	BB	5.6127
132	28.748	96.50	33.29	0.04	0.04	BB	2.8991
133	28.815	76.50	31.67	0.03	0.03	BB	2.4155
134	28.923	634.50	120.66	0.27	0.27	BB	5.2585
135	29.077	62.50	26.69	0.03	0.03	BB	2.3419
136	29.221	3446.00	861.50	1.47	1.47	BB	4.0000
137	29.426	731.75	122.75	0.31	0.31	BB	5.9614
138	29.623	377.51	133.21	0.16	0.16	BB	2.8339
139	29.693	224.50	49.83	0.10	0.10	BB	4.5051
140	29.843	204.25	41.70	0.09	0.09	BB	4.8982
		234764.50	63482.31	100.00	100.00		

Attachment A-3

Attachment A-4

Sample Name : 250MG/L
FileName : h:\04\4MAI028.raw
Start Time : 5.00 min End Time : 35.00 min
Scale Factor: 1 Plot Offset: 6 mV

Sample #:
Date : 3/30/93 9:13
Low Point : 6.12 mV High Point : 12.32 mV
Plot Scale: 6 mV



Attachment B-1

.oast-To-Coast Analytical Services, Inc.
Iortheast Division

Fuel Oil
GC

:lient:

Vork Order:

Method: GC\FID
Det. Code: FUEL-GA.W
Matrix: Water

Compound	PQL (ug/L)				
		Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: ug/L	Units: ug/L	Units: ug/L	Units: ug/L
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	50				

Compound	PQL (ug/L)				
		Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: ug/L	Units: ug/L	Units: ug/L	Units: ug/L
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	50				

Compound	PQL (ug/L)				
		Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: ug/L	Units: ug/L	Units: ug/L	Units: ug/L
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	50				

Comments:

File: FOILW

Coast-To-Coast Analytical Services, Inc.
Northeast Division

Fuel Oil ATTACHMENT B-2
GC

Client:

Work Order:

Method: GC\FID
Det. Code: FUELS-GA.W
Matrix: Soil

Compound	PQL (mg/Kg) (drywt)	Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: mg/Kg	Units: mg/Kg	Units: mg/Kg	Units: mg/Kg
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	10				

Compound	PQL (mg/Kg) (drywt)	Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: mg/Kg	Units: mg/Kg	Units: mg/Kg	Units: mg/Kg
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	10				

Compound	PQL (mg/Kg) (drywt)				
		Client ID:	Client ID:	Client ID:	Client ID:
		Lab ID:	Lab ID:	Lab ID:	Lab ID:
		File ID:	File ID:	File ID:	File ID:
		Date:	Date:	Date:	Date:
		Units: mg/Kg	Units: mg/Kg	Units: mg/Kg	Units: mg/Kg
		DF:	DF:	DF:	DF:
		Footnote:	Footnote:	Footnote:	Footnote:
Fuel Oil	10				

Comments:

File: FOIL

Client: , Work Order: F2-FUL-S 06-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Laboratory Control Sample Results

Fuel Oil by GC Method: **ME DEP 4.1.2**

Soil Matrix

Date of Extraction: _____
Date of Analysis: _____

Compound	Units	Spike Conc.	LCS Measured Conc.	LCS Dup. Measured Conc.	LCS % Recovery	LCS Dup. % Recovery	Recovery Acceptance Range (%)*	RPD (%)	RPD Acceptance Range (%)*
Fuel Oil	mg/kg	50					50-150		0-40

* The laboratory has established the following acceptance criteria for the laboratory control sample/laboratory control sample duplicate (LCS/LCSD) sets employed for organic analyses. All spike recoveries must be equal to or greater than ten percent, and a minimum of ninety percent of the total number of calculated recoveries plus relative percent differences (RPDs) must be within the specified acceptance ranges.

ATTACHMENT C-1

Client: , Work Order: F2-FUL-W 06-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Laboratory Control Sample Results

Fuel Oil by GC Method: ME DEP 4.1.1

Water Matrix

Date of Extraction: _____
Date of Analysis: _____

Compound	Units	Spike Conc.	LCS Measured Conc.	LSC Dup. Measured Conc.	LCS % Recovery	LSC Dup. % Recovery	Recovery Acceptance Range (%)*	RPD (%)	RPD Acceptance Range (%)*
Fuel Oil	ug/L	500					50-150		0-40

* The laboratory has established the following acceptance criteria for the laboratory control sample/laboratory control sample duplicate (LCS/LCSD) sets employed for organic analyses. All spike recoveries must be equal to or greater than ten percent, and a minimum of ninety percent of the total number of calculated recoveries plus relative percent differences (RPDs) must be within the specified acceptance ranges.

See cover letter for additional information.

ATTACHMENT C-2

Client: , Work Order: F3-FUL-S 19-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Matrix Spike/Matrix Spike Duplicate Results

Fuel Oil by GC Method: ME DEP 4.1.2

Soil Matrix

CCAS Sample No. Spiked: _____

Compound	Units	Spike Conc.	Sample Conc.	MS Measured Conc.	MSD Measured Conc.	Theoretical Spiked Sample Conc.	MS % Recovery	MSD % Recovery	Recovery Acceptance Range (%) *	RPD (%)	RPD Acceptance Range (%) *
Fuel Oil	mg/kg	50							50-150		0-40

* Acceptance ranges are obtained when available from the applicable US EPA analytical method. These ranges are based upon method performance data generated from the analysis of quality control check samples and not actual environmental samples. The laboratory does not use the MS/MSD acceptance ranges as quality control acceptance criteria; the MS/MSD data are used to evaluate method performance for the environmental sample matrix. Please refer to LCS/LCSD data for assessment of quality control for this method.

NA = Not applicable.

ATTACHMENT D-1

Client: , Work Order: F3-FuL-W 19-Jul-93

Coast-To-Coast Analytical Services, Inc.
Northeastern Division
Quality Control Report

Matrix Spike/Matrix Spike Duplicate Results

Fuel Oil by GC Method: ME DEP 4.1.1

Water Matrix

CCAS Sample No. Spiked: _____

Compound	Units	Spike Conc.	Sample Conc.	MS Measured Conc.	MSD Measured Conc.	Theoretical Spiked Sample Conc.	MS % Recovery	MSD % Recovery	Recovery Acceptance Range (%) *	RPD (%)	RPD Acceptance Range (%) *
Fuel Oil	ug/L	500							50-150		0-40

* Acceptance ranges are obtained when available from the applicable US EPA analytical method. These ranges are based upon method performance data generated from the analysis of quality control check samples and not actual environmental samples. The laboratory does not use the MS/MSD acceptance ranges as quality control acceptance criteria; the MS/MSD data are used to evaluate method performance for the environmental sample matrix. Please refer to LCS/LCSD data for assessment of quality control for this method.

NA = Not applicable.

ATTACHMENT D-2

* LIST: METH @
METHOD NAME: M:FUELOIL.MET

Attachment E-1 Page 1 of 2

RUN PARAMETERS
ZERO = 5
ATT 2^ = 0
CHT SP = 0.5
AR REJ = 25
THRSH = -3
PK WD = 0.04

TIMETABLE EVENTS
0.000 INTG # = 9
10.500 INTG # = -9
28.000 INTG # = 9

CALIBRATION
NO CALIB TBL

INTEGRATION PLOT TYPE ..... FILTERED
Presentation plot ..... YES

RUN DATA STORAGE
Store signal data ..... NO
Store processed peaks ..... NO

REPORT OPTIONS
Suppress local report ..... NO
HEIGHT% report ..... NO
Report title:
FUEL OIL
Report uncalibrated peaks ... NO
Extended report ..... NO

PRINT & POST-RUN LIST OPTIONS
Large font ..... NO
Store post-run report ..... NO
External post-run report .... NO
List run parameters ..... NO
List timetable ..... NO
List calibration table ..... NO
List remote method ..... NO
Form-feed before report ..... NO
Form-feed after report ..... NO
Skip perforations in report . NO
Skip perforations in plot ... NO

HP 5890A GAS CHROMATOGRAPH
LOOP ADDRESS: 9

OVEN TEMP = 50 SETPT = 50
EQUIB TIME = 1.00 CRYO OFF
OVEN MAXIMUM = 375 CRYO BLAST OFF
INITIAL TEMP = 50
INITIAL TIME = 5.00

TEMP PRGM:	RATE	FINAL TEMP	FINAL TIME
	8.0	280	5.00
RAMP A	10.0	280	0.00

RUN LENGTH = 38.75 MIN

INJ A TEMP = 250 SETPT = 250
INJ B TEMP = 250 SETPT = 250
DET A TEMP = 300 SETPT = 300
DET B TEMP = 300 SETPT = 300

```
SIGNAL 1 = A
 INET FULL RANGE DATA ON
 RANGE = 0
 ZERO  = 0.0
 ATTN  = 0

SIGNAL 2 = B
 INET FULL RANGE DATA ON
 RANGE = 0
 ZERO  = 0.0
 ATTN  = 0

DETECTOR A = FID  (ON)
DETECTOR B = FID  (ON)

PURGE A  = ON
 ON TIME = 0.75     OFF TIME = 0.00
PURGE B  = ON
 ON TIME = 0.75     OFF TIME = 0.00

VALVE 1  = OFF
VALVE 2  = OFF

- TIME TABLE IS EMPTY -

*
```

Coast to Coast Analytical Services, Inc.

INST: 5890-07 METHOD: DEP
COLUMN DB-5 Cal Date: 03-SEP-93
< File: Analyte: FUEL OIL
DISK: FUEL OIL Calib (AC or HT): TOT AREA
spreadsheet: qa-qc-003:\calib\dmf-01.wk1 (912019) Date: 03-SEP-93
INJECTION VOLUME: (uL) 2.0uL

	Std Amt (ng)	Measured Response For Standard 1	2	3	Average Value (Response)	Response Factor (Res/ng)	Calib. Estimate (Response)	Differ. Calib-Aver (%)	Slope	Y-Inter
	0.000				0.0	0.00E+00	ERR		ERR	ERR
1	50.000				ERR	ERR	ERR	ERR	ERR	ERR
2	100.000				ERR	ERR	ERR	ERR	ERR	ERR
3	250.000				ERR	ERR	ERR	ERR	ERR	ERR
4	500.000				ERR	ERR	ERR	ERR	ERR	ERR
5	1000.000				ERR	ERR	ERR	ERR		
6										
7										
8										

*	Average Response Factor =	ERR	Res/ng
	Standard Deviation =	ERR	Res/ng
	Relative Standard Dev. (RSD) =	ERR	%
	Surrogate Response Factor =		Res/ng

Analyst: Analysis Date: 00-XXX-00 Injection Volume: (uL) 2.0

WATER/SOIL RESULTS POL (mg/L or Kg): QC flags only (1=Y/0=N): 1 RAW RESULTS

RUN #	Sample ID	STD AMT (ng)	RT (min)	RESPONSE (AREA) or (HT)	Date Analyzed	Sample Amount (mL or g)	Extract Volume (mL)	Dilution (# times) and 1/TS	Linear Conc. (mg/L or Kg)		Curve Conc. (mg/L or Kg	QC CODE-% REC	Surr Resp (AREA) or (HT)	Surr % REC	Linear Amt (ng)	Curve Amt (ng)
1					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
2					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
3					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
4					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
5					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
6					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
7					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
8					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
9					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
10					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
11					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
12					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
13					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
14					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
15					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
16					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
17					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR
18					00-XXX-00	1.0	1.0	1.00	ERR	*	ERR	ERR		ERR	ERR	ERR

ATTACHMENT F-1

STANDARD OPERATING PROCEDURE

Author: K. Gross
Approved by:

Willard C. Warren, III
President, Northeastern Division

Issuing Unit: CCAS-Northeast
SOP No.: CA-033-00
Date: February 1993

TITLE: CLP Sample Preparation and Clean-up for Pesticides/PCBs in Water or Soil/Sediment.

PURPOSE: To describe procedures utilized by the Northeastern Division for the preparation of pesticide and PCB samples in accordance with the U.S. Environmental Protection Agency's (EPA) Contract Laboratory Program (CLP) protocol.

SCOPE: The goal of this procedure is to ensure uniformity involving the preparation of samples for subsequent pesticide and PCB analysis utilizing EPA CLP protocols. This SOP is specifically applicable to the EPA CLP Statement of Work (SOW) OLM01.8, dated August, 1991.

REQUIREMENTS: Chemists and technicians must be properly trained in accordance with the current revision of CCAS-NE SOP No. AD-002, "Personnel Training."

PROCEDURE:

1.0 Summary of Sample Preparation Methods

1.1 Water Samples

A 1-L volume of water is spiked with the surrogate solution and is extracted with methylene chloride by using a continuous extractor. The methylene chloride extract is dried and concentrated (5.2). The extract is then cleaned up by gel permeation chromatography (GPC) if the sample appears heavily colored or suspected to contain hydrocarbons, exchanged to hexane, cleaned up by Florisil cartridge, and adjusted to a final volume of 10.0 mL (5.0 mL if GPC cleanup is performed) as described beginning at paragraph 7.3. The holding time for water samples is 5 days from Validated Time of Sample Receipt (VTSR).

1.2 Soil/sediment Samples

A 30 g aliquot of sample is spiked with the surrogate solution and then mixed with sodium sulfate and extracted with a 1:1 acetone/methylene chloride solvent mixture by sonication. The extract is then filtered, dried, concentrated by K-D, and then solvent exchanged into methylene chloride (6.0). The extract is then cleaned up by GPC (mandatory), exchanged to hexane, cleaned up by Florisil cartridge, and adjusted to a final volume of 5.0 mL (7.0).

2.0 Interferences

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves which have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or teflon or other non-phthalate plastic substitute.

2.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits. Matrix interferences are removed by the use of florisil cleanup, GPC and/or sulfur cleanup. Florisil is mandatory for all samples, while GPC is mandatory for soils, and sulfur is optional. All three techniques may be required to remove matrix interference.

3.0 Apparatus and Materials

3.1 Continuous liquid-liquid extractors - with glass connecting lines for use with methylene chloride, (Kontes Glass Company, P/N 5824-00 or equivalent), Corning One-Step Extractor/Concentrator. Both extractors are available but the Corning One-step is the first extractor of choice, after the MDL requirements are met.

3.2 Apparatus for determining percent moisture:

3.3.1 Oven - drying.
3.3.2 Desiccator.
3.3.3 Aluminum drying pans.
3.3.4 Aluminum weighing pans.

3.3 Sonic cell disruptor - Branson Sonifier 450 with 3/4-inch tapped disruptor horn with a 400 Watt output capability.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface. Manufacturer's instructions specify that tuning is not required.

3.4 Sonabox (or equivalent) for use with disruptor to decrease noise level.

3.5 Beakers - 400-mL (KIMAX, 14005 or Pyrex, 1003).

3.6 Kuderna-Danish (K-D) apparatus (Exeter Scientific, Birdsborough, PA):

3.6.1 Concentrator tube - 10-mL, graduated.

3.6.2 Evaporative flask - 500-mL.

3.6.3 Snyder column - three-ball macro and three-ball micro

3.7 Funnels and Filter Paper:

3.7.1 Buchner funnels - 9-cm diameter, for filtration.

3.7.2 Filter paper - No. 41 Whatman, 7.0-cm and 15-cm.

3.8 Boiling chips:

3.8.1 Organic-free boiling chips - approximately 10/40 mesh. Rinse with methylene chloride three times before use (Alltech Associ., Inc., Stk #5785).

3.9 Water bath - heated, with concentric ring cover, capable of temperature control. NOTE: The water bath must be used in a hood (Bockel, Philadelphia, PA).

3.10 Top loading balance - capable of weighing accurately to ± 0.01 g (O'Haus 1500 D).

3.11 Balance - analytical, capable of weighing accurately to ± 0.0001 g. The balance must be calibrated with class S weights once per each 12-hour workshift when in use. The balances must also be checked annually by a certified technician (Sartorius A200S).

3.12 Vials and caps - 2-mL for GC auto sampler.

3.13 Gel permeation chromatography (GPC) cleanup device. NOTE: GPC cleanup is <u>required</u> for all extracts for <u>all</u> soils. GPC is required for all water samples containing high molecular weight contaminants or other contaminants which can be removed by GPC and interfere with the sample analysis.

Gel permeation chromatography system - GPC Waters Model 440.

3.13.1 Chromatographic column - 700 mm x 25 mm i.d. glass column. Flow is upward. Automated switching is accomplished utilizing an ISCO "Foxy" fraction collector.

3.13.2 Guard column - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319).

3.13.3 Bio Beads (S-X3) - 200-400 mesh, 700 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750). An additional 5 gm of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they also can pass through the column screens and damage the valve.

3.13.4 Ultraviolet detector - fixed wavelength (254 nm) with a semi-prep flow-through cell (Waters Co. Model 440).

3.13.5 Strip chart recorder, recording integrator or laboratory data system (ABB Model SE120 Plotter).

3.13.6 Syringe - 10-ml with Luerlok fitting.

3.13.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and .45 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

3.14 Florisil - 500-mg cartridges with Teflon frits, (Burdick & Jackson Division).

3.15 Vacuum system for eluting multiple cleanup cartridges:

3.15.1 Vac Elute Manifold - Burdick & Jackson Division. The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.

3.15.2 Vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing.

3.15.3 Vacuum pressure gauge.

3.15.4 Rack for holding 10-mL concentrator tubes in the manifold.

3.16 Pyrex glass wool - rinsed with methylene chloride and dried before use.

3.17 Bottle - 20-mL for sulfur removal.

3.18 Glass funnel with glass wool plug for drying extracts.

3.19 Glass vials - minimum of 20-mL, with screw cap and Teflon liner.

3.20 Spatula - stainless steel.

3.21 pH Paper - wide range, (color, pHast pH 0-14, EM Science).

3.22 Pipet - Volumetric 1.00-mL or 2.00-mL (Kimble, 72120).

3.23 Vials - 1.0-mL, with screw cap and Teflon liner (National Scientific Co.).

3.24 Tube - centrifuge, 50 mL Pyrex 8422 with Teflon lined cap.

3.25 Centrifuge - table top.

3.26 Vortex mixer - Sybron thermolyne model # M-16715.

3.27 pH Meter with a combination glass electrode (Orion Research, ionanalyzer model 701A, or equivalent).

3.28 Magnetic stirrer motor - Model 120MR, Fisher, Thermix stirrer, or equivalent.

3.29 Magnetic stir bar - Teflon coated, at least 4 cm long.

3.30 Graduated cylinder - minimum 1 L capacity.

3.31 Filter flask - 500 mL

3.32 10 mL syringe with removable needle

3.33 Graduated cylinder - 100 mL

3.34 Disposal Pasteur pipets - 5 3/4 inches

3.35 250 mL amber bottles with Teflon lined caps

3.36 Teflon stoppers and stopcocks

3.37 Iron rings and ring stands

3.38 Chain clamps

3.39 2000 mL separatory funnel

3.40 KD apparatus clips

3.41 1 mL amber vials - crimp top with Teflon/silicone liner

4.0 <u>Reagents</u>

All reagents and solvent lots must be checked for possible contamination. The extraction staff are responsible for submitting samples to the GC or GC/MS sections for appropriate analysis. All information concerning

preparation of the reagent/solvent lot sample will be recorded in the Organic Extraction Log (Attachment B) and acceptance or rejection of these lots must be recorded in the solvent/reagent lot check logbook (Attachment C). All reagents and solvents must be free (<CRQL) of any target compounds.

4.1 Sodium sulfate - granular-anhydrous reagent grade, heated at 400°C for 4 hours, or at 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by GC/ECD to demonstrate that it is free of interference before use. Mallinkrodt ACS anhydrous granular, Catalog No. 8024, or equivalent. CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory. To prepare a lot check sample for analysis, rinse 40 grams of sodium sulfate (contained in a funnel stopped with glass wool) with 100 mL aliquots of hexane; concentrate to 1 ml and analyze by GC/ECD.

4.2 Methylene chloride, hexane, acetone, toluene, iso-octane, and methanol (optional) - pesticide quality or equivalent. It is required that each lot of solvent used be analyzed to demonstrate that it is free of interference before use. One liter of each lot of extraction solvent is concentrated to one ml and analyzed for the appropriate fraction analytes. If no compounds are detected above or equal to the CRQL the lot is acceptable and may be used for sample extraction. Results are filed with the appropriate section supervisor and recorded in the solvent check logbook located in the extraction laboratory. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid. Check each solvent lot for acidic conditions on the bottle. If the solvent is not acid free, notify the extraction lab supervisor.

4.3 Nitric acid (Reagent grade) for removal of oxides from copper.

4.4 Copper-powder (optional) - fine, granular (Mallinkrodt 4649 or equivalent). Copper is used for sulfur cleanup. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

4.5 Sodium hydroxide solution (10 N) - Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

4.6 Concentrated sulfuric acid - 18 N.

4.7 Reagent water - defined as a water in which no interferent is observed at one-half the CRQL of any pesticide/Aroclor when one liter of the reagent water is extracted and prepared by using the same workup procedure as for a water sample. Use deionized water filtered through activated charcoal.

4.8 Ten percent acetone in hexane (v/v) - prepare by adding 10.0 mL of acetone to 90.0 mL of hexane in a graduated cylinder. NOTE: Prepare this mixture

accurately or the results from the Florisil cartridge cleanup will be adversely affected. Water in the acetone also will adversely affect Florisil performance.

4.9 Standards

4.9.1 All standards may be used only after they have been certified according to the procedure in USEPA CLP SOW OLM01.8. The laboratory must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the laboratory. Purchase all standards from Restek or Supelco; all standards must have the manufacturer's certificate filed in either the GC or GC/MS lab as appropriate.

For all standard preparations, see the current revisions of the following CCAS-NE SOPs:

- For standard preparation and labeling, "Analysis of Pesticides/PCBs by USEPA CLP August, 1991, Statement of Work (OLM01.8) Utilizing GC/ECD," (CA-035)

- For standard certification, "Traceability of Standards - Organics," (QA-004)

- For recording information, "Records of Sample Preparation and Analysis for Samples Requiring CLP Protocols," (SD-003)

- For balance information, "Balance Calibration," (CA-003)

4.9.2 Stock standard solutions (1.00 ug/uL) - can be prepared from pure standard materials or purchased as certified solutions.

4.9.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10-mL volumetric flask with toluene or acetone.

4.9.2.2 Transfer the stock standard solutions into a bottle/vial with Teflon-lined cap or septa. Store at 4°C (±2°C) and protect from light. Stock standard solutions must be replaced after <u>six months</u> or sooner, if comparison with check standards indicates a problem.

4.9.3 GPC calibration solution - prepare a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
corn oil	25
bis-2-ethylhexyl phthalate	1.0
methoxychlor	0.2
perylene	0.02
sulfur	0.08

See Attachment A (Standards Prep).

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4°C, and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves). Replace the calibration standard solution every six months, or more frequently if necessary.

4.9.4 Surrogate solution - the surrogates, Tetrachloro-m-xylene and Decachlorobiphenyl, are added to all standards, samples, matrix spikes, and blanks. Prepare a surrogate spiking solution of 0.2 ug/mL of each of the two compounds in acetone. See Attachment A. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner, if comparison with quality control check samples indicates a problem. CAUTION: Analysts must allow all spiking solutions to equilibrate (for one hour) to room temperature before use.

4.9.5 Pesticide matrix spiking solution - prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified:

Pesticide	ug/mL
gamma-BHC (Lindane)	1.0
4,4'-DDT	4.0
Endrin	4.0
Heptachlor	1.0
Aldrin	1.0
Dieldrin	4.0

The solution must be prepared every six months, or sooner if the solution has degraded or concentrated. See Attachment A (Standards Prep).

4.9.6 Florisil cartridge check solution.

Prepare a solution of 2,4,5-trichlorophenol in acetone, at a concentration of 0.1 ug/mL. See Attachment A (Standards Prep).

5.0 Extraction of Water Samples

Water samples must be extracted by the continuous liquid-liquid extraction procedure. Prerinse all glassware three times with methylene chloride.

5.1 Continuous Liquid-Liquid Extraction

5.1.1 Add methylene chloride (100 to 250 mL) to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

5.1.2 Measure out each 1.0 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper by withdrawing a couple drops with a clean, disposable pipet and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the Sample Delivery Group (SDG) Narrative and the Organic Extraction Log (Attachment B). Place the sample into the continuous extractor.

5.1.3 With some samples it may be necessary to place a layer of glass wool between the methylene chloride and the water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction. Addition of glass wool must be noted in the comments section of the Organic Extraction Log.

5.1.4 For each sample selected for matrix spike and matrix spike duplicate analysis, measure out two additional 1-L portions in a clean 1-L graduated cylinder and transfer those portions into separate extractors. Adjust the pH of each, if required, and fortify each with 1.0 mL of matrix spike solution, using a disposable pipet, before continuing the extraction. Spike standard codes and volumes must be recorded in the Organic Extraction Log.

5.1.5 Using a syringe, a volumetric pipet, or a disposable pipet add 1.0 mL of the surrogate solution to all water samples, matrix spikes, and blanks. Record all standard code information and volumes added in the Organic Extraction Log.

5.1.6 Adjust the level of methylene chloride in the extractor so that the bottom sidearm is half filled with solvent.

5.1.7 Add sufficient methylene chloride to the distilling flask to ensure proper solvent cycling during operation and extract the solution for 18 hours.

5.1.8 Prepare a method blank with each group of water samples extracted. For pesticide/Aroclor analyses, a method blank for water samples consists of a 1 L volume of reagent water (see paragraph 4.7), spiked with the surrogate and carried through the entire analytical procedure.

5.2 Extract Drying and Concentration

NOTE: Prerinse all glassware three times with methylene chloride.

5.2.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the pesticide/Aroclor target compounds. The Corning One-step extractor/concentrator is an acceptable substitute and should be used if available and meets MDL requirements.

5.2.2 Prepare a funnel with filter paper or glass wool and about 40 grams of anhydrous granular sodium sulfate. Prerinse the funnel and sodium sulfate with methylene chloride. Pour the extract through the funnel containing the sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the funnel with at least two additional 20 to 30 mL portions of methylene chloride to complete the quantitative transfer, and add the rinsate to the K-D concentrator. As an alternative, the Corning One-step drying tube may be used after rinsing as above.

5.2.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (70° - 85° C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with the condensed solvent. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. <u>DO NOT ALLOW THE EVAPORATOR TO GO DRY</u>. If the sample extract goes dry, re-extraction must occur immediately. If the Corning One-step is used, ensure the water in the jacketed concentrator tube is 80°C, then turn the stopcock turning off the flow of solvent from the extractor. When the extract reaches <1.0 mL, turn off the hot water and remove the concentrator tube.

5.2.4 If no GPC cleanup is required, proceed with the hexane exchange (Section 7.3). If GPC cleanup is to be used, remove the Snyder column, rinse the flask and its lower joint with methylene chloride and collect the rinsate in the concentrator tube, adjust the volume

to 3.0 mL with methylene chloride. Proceed to GPC cleanup (Section 7.0).

6.0 Extraction of Soil/Sediment Samples

NOTE: Prerinse all glassware three times with methylene chloride.

6.1 Sample Preparation

6.1.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks. Also, decant and discard any standing aqueous phase.

6.1.2 pH Determination - transfer 50 g of soil/sediment to a 100-mL beaker. Add 50 mL of water and stir the solution with a magnetic stirrer for 1 hour. Determine the pH of the sample by using a glass electrode and the pH meter while the sample is stirred. Report pH value in the extractions logbook. If the pH of the soil is > 9 or < 5, note the pH in the SDG Narrative, but do not attempt to adjust the pH of the sample. Discard the portion of the sample used for pH determination.

NOTE: If insufficient volume of soil is received, use 5 g of soil and 5 mL of water for the pH determination and note in the SDG Narrative and lab pH logbook.

6.1.3 Percent Moisture - Weigh 5 to 10 g of the sediment to the nearest 0.01 g into a tared aluminum weighing pan. Determine the weight percent volatized by drying overnight at 105°C (hereafter referred to as percent moisture). After the sample is dry, remove the sample and pan and allow them to cool in a desiccator before weighing. Calculate the percent moisture according to Equation 1 below. Concentrations of individual analytes will be reported relative to the dry weight of sediment. CAUTION: Gases volatized from some soil/sediment samples require that this drying procedure be carried out in a hood.

$$\text{Percent Moisture} = \frac{\text{Wt of Sample} - \text{Wt of Dry Sample}}{\text{Wt of sample}} \times 100 \quad \text{EQ. 1}$$

6.2 Extraction with Sonication

6.2.1 Weigh approximately 30 g of sample (to the nearest 0.1 g) into a 250 or 400-mL beaker and add 60 g of anhydrous sodium sulfate (granular).

6.2.2 For a sample to be used for matrix spike and matrix spike duplicate analysis, weigh out two additional 30 g (record weight to nearest 0.1 g) portions of sample and add 1.0 mL of the pesticide matrix

spike solution to each soil aliquot. Record standard code and volumes added in the Organic Extraction Log (Attachment B). An MS/MSD sample set must be prepared for each group of 20 samples for each matrix per sample delivery group (SDG). A minimum of one set per matrix and SDG is required.

6.2.3 Add 2.0 mL of surrogate solution to all soil samples, matrix spikes, and blanks by using a disposable pipet or a syringe. Mix the solution well. The sample and the added sodium sulfate should be a homogeneous, granular mixture at this point. Record standard code and volumes added in the Organic Extraction Log.

6.2.4 Immediately add 80 to 100 mL of 1:1 methylene chloride/acetone to the sample.

6.2.5 Place the bottom surface of the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

6.2.6 Sonicate with the Branson Sonifier 450 for 3 minutes using a 3/4-inch horn at full power (output control knob at 10) with pulse on and percent duty cycle knob set at 50 percent. Do <u>not</u> use a microtip.

6.2.7 The extracted sample can be filtered by using gravity or vacuum filtration.

6.2.7.1 For vacuum filtration, use Whatman No. 41 paper in the Buchner funnel. Pre-wet the paper with methylene chloride/acetone before decanting the solvent.

6.2.8 Repeat the extraction two more times with additional 80 to 100 mL portions of the 1:1 methylene chloride/acetone. Before each extraction, thoroughly mix the solid residue, and make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula. Decant and filter the extraction solvent after each sonication by using the same funnel described in paragraph 6.2.7. After the final sonication, pour the entire sample into the funnel and rinse the beaker and funnel with 60 mL of 1:1 methylene chloride/acetone.

6.2.9 Prepare a method blank with each group of soil/sediment samples extracted. For pesticide/Aroclor analyses, a method blank for soil/sediment samples consists of 30 g of sodium sulfate (see paragraph 4.1), spiked with the surrogates and carried through the entire analytical procedure.

6.3 Soil Extract Concentration

6.3.1 Add one or two clean boiling chips to the evaporative flask and attach a three-ball macro Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-

D apparatus on a hot water bath (60 to 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. Reduce the volume of liquid to less than 10 mL. Remove the K-D apparatus and allow it to drain and cool for at east 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. If the sample extract goes dry, re-extraction must occur immediately.

6.3.2 In order to remove most of the acetone, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1.0 mL. This is best accomplished using the micro snyder technique. (See current revision of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Clean-up for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment.") The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups.

6.3.3 Adjust the extract volume to 3.0 mL with methylene chloride. Proceed to 7.0 below, for mandatory GPC and Florisil cartridge cleanup of soil extracts.

7.0 Extract Cleanup by Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated. A cross-linked divinyl benzenestyrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

GPC is required for all soil/sediment samples, regardless of concentration level, for the elimination of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds from the sample extract. GPC is appropriate for both polar and non-polar analytes, therefore, it can be used effectively to clean up extracts containing a broad range of analytes.

Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or in the front of the GC column. This residue ultimately will reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol especially is susceptible to this problem.

The analyst performing the GPC cleanup will maintain a file containing all recorded information for the present run. All recorder traces, calculations, and notes should be contained in this file.

For a detailed procedure on the operation of the GPC, the current revision of CCAS-NE SOP No. CA-082, "Sample Cleanup by Gel Permeation Chromatography".

Before use of the GPC, calibration must occur according to Section 7.2. All GPC runs will be recorded in the GPC run log. Seven day calibrations are also recorded in the run log. UV printouts and copies (or originals, if available) of run logs and column calibrations are placed in a manila folder (labeled by SDG) stored in the organic extraction laboratory until the samples are ready for analysis, at which time, they are given to the project manager or designee. Any repairs or maintenance to the GPC are recorded in the GPC maintenance and repair logbook. Column calibrations are maintained by the organic prep lab while analytical calibrations (GPC calibration check solutions) are maintained by the appropriate analytical section.

7.1 GPC Column Preparation

7.1.1 Weigh out ≥ 80 gm of Bio Beads (SX-3). Transfer them to a ≥ 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 6 hours. Maintain enough solvent to cover the beads sufficiently at all times. Use the same mix of BioBeads to pack the guard column.

7.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture. Drain the excess methylene chloride from the separatory funnel directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a kimwipe. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make

the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat the step in paragraph 7.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is inserted successfully.

7.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.1.8 Pack the 5 cm column with approximately 5 gm of preswelled beads. Connect the guard column to the inlet of the analytical column.

7.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly outward to reduce pressure.

7.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

7.2 Calibration of the GPC Column

7.2.1 The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column. Care must be taken to account for any difference in volume (elution time) between the GC column and the detector and between the GPC column and the collection vial.

7.2.2 Using an HP 1050 autosampler, load the 1.5 mL loop with 15-100 ul injections.

7.2.3 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace that meets the following requirements. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell and, therefore, the analytical cell is not acceptable for use. The results of this check should be recorded and maintained in the current GPC calibration file.

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.4 Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of methoxychlor and after the elution of the bis(2-ethylhexyl)phthalate. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Collect and dump times must be recorded in the GPC logbook and entered into the Foxy collector.

7.2.5 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in paragraph 7.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.6 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established. The analyst should record and maintain necessary data in the current GPC logbook. If any of the required calibrations fail to meet the given criteria, corrective action must be taken and no samples may be processed until corrective actions have been taken and all required calibrations are met. See the current revision of CCAS-NE SOP No. CA-082, "Sample Clean-up by Gel Permeation Chromatography," for corrective actions.

7.2.6.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.6.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

7.2.6.3 Analyze a GPC blank by loading 1.5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by GC/MS. If the blank exceeds one half the CRQL of any analyte, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

7.2.7 GPC Calibration Check

No Florisil cleanup is used in the GPC calibration check.

7.2.7.1 At least once every 7 days, the calibration of the GPC must be verified with two check mixtures. The first mixture is prepared by concentrating 2.0 mL of the matrix spiking solution (paragraph 4.9.5) to less than

1 mL using the micro technique and adjusting the final volume to 3.0 mL with methylene chloride. The second mixture is prepared with 2 ug of Aroclor 1016 and 2 ug of Aroclor 1260 in a final volume of 3.0 mL methylene chloride. No samples may be analyzed if GC analysis indicates the calibration check is out of criteria.

7.2.7.2 Load the 1.5 mL sample loop with the MS spike solution (paragraph 7.2.7.1) by using the HP 1050 autosampler. The Aroclor mixture is loaded in the same manner. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Section 7.2).

7.2.7.3 The collected GPC calibration fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10-mL portions of methylene chloride to complete the quantitative transfer. The volume of methylene chloride is reduced by concentration. After cooling, the solvent is exchanged to hexane. The final volume is adjusted to 10.0 mL, and the sample is analyzed by GC according to the procedures outlined in the current revision of CCAS-NE SOP No. CA-035, "Analysis of Pesticides/PCBs by USEPA CLP August, 1991, Statement of Work (OLM01.8) Utilizing GC/ECD." The analysis must be performed on at least one of the GC columns used for sample analysis.

7.2.7.4 The pattern of the Aroclor quantitation peaks and the recovery of each single component analyte must be determined for evaluation and reporting purposes. If the recovery of each of the analytes is 80 to 110 percent and if the Aroclor pattern is the same as with previously run standards, then the analyst may continue to use the column. If recoveries are out of the acceptance window or if changes in the relative peak heights of the patterns of the Aroclor are observed, the column must be replaced and recalibrated according to the instructions in 7.1 and 7.2.

7.2.7.5 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every seven days, assuming usage of the GPC is required. In many cases, the SX-3 Bio Beads may be used for several months as long as the column calibration and flow rate remain constant.

7.2.8 Daily UV calibration check

If the column has been heavily colored by a sample and column conditions may be suspect, the calibration of the GPC should be monitored daily by use of the UV-GPC calibration solution (paragraph 4.9.3) and the UV Detector Calibration Procedure (7.2). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" >85 percent of the corn oil and should "COLLECT" >95 percent of the phthalate, methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., > 0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

7.2.9 Sample Extract Cleanup

It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F. The room temperature must be kept between 64°-72°F and must be recorded in the GPC run log at least once per day. No samples may be cleaned up by GPC until the calibration solutions pass GC analysis criteria.

7.2.9.1 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 500 mg of nonvolatile residue per 5 mL of extract must be diluted and loaded into several loops. The nonvolatile residue may be determined by evaporating a 100 uL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container.

7.2.9.2 Particles greater than 5 micron may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract (3.0 mL) through a 0.45 micron (or finer) filter disc by attaching a syringe filter assembly containing the filter disc to a 5 mL syringe. Draw the sample extract through the filter assembly and into the 5 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g., a 3.0 mL sample vial with a Teflon lined crimp top or screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly

and force the extract through the filter and into the glass container. Draw 3.0 mL of extract into a 5 mL syringe. INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

7.2.9.3 Using and HP 1050 autosampler, load 1.5 mL of sample by setting the autosampler for 15-100 uL injections.

7.2.9.4 Load positions one and two on the HP 1050 autosampler with vials of methylene chloride and set #1 for rough rinse and #2 for final rinse.

7.2.9.5 Collect each sample in a 250-mL prerinsed amber sample bottle. Monitor sample volumes collected. Mark one flask at the meniscus for the correct volume to be collected (collect time x flow) and visually compare all collected samples against the correct volume. If the volume appears to be slightly off, measure the volume. If the sample is off by more than 5%, the sample must be re-GPC'd. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the adsorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.
- Leaks in the system or significant variances in room temperature.

7.2.9.6 After the appropriate GPC fraction has been collected for each sample, exchange the sample extract solvent to hexane. <u>DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS</u>. Adjust the final volume of the hexane extract to 5.0 mL.

7.2.9.7 Since a GPC autosampler is used, the samples must first be filtered as in 7.2.9.2. Since the autosampler injects smaller volumes (1.5 ml) the sample extract must be concentrated to twice the injection volume before GPC (3.0 ml).

7.2.9.8 NOTE: A final volume of 5.0 mL is required for extract concentrates after GPC cleanup because only half of the sample is used in the GPC sample loop.

7.3 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil samples. See the current revision of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Clean-up for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment," for the micro-Snyder technique.

7.3.1 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

7.3.2 Remove the Snyder column; using 1 to 2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a vial by using hexane. Adjust the volume of the hexane extract to 10.0 mL or 5.0 ml if GPC cleanup was used.

7.4 Florisil Cartridge Procedure

Florisil cartridge cleanup is required for all extracts. Cleanup significantly reduces matrix interferences caused by polar compounds.

7.4.1 Cartridge Performance Check - Every lot number of florisil cartridges must be tested by the following procedure before they are used for sample cleanup. Add 0.5 mL of 2,4,5-trichlorophenol solution (0.1 mg/mL in acetone) and 0.5 mL of Individual Standard Mixture A, midpoint concentration (see current revision of CCAS-NE SOP No. CA-035, "Analysis of Pesticides/PCBs by USEPA CLP August, 1991, Statement of Work (OLM01.8) Utilizing GC/ECD") to 4 mL of hexane. Reduce the final volume to 0.5 mL using the micro Snyder technique. (See current revision of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Clean-up for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment," for micro-Snyder technique.) Place the mixture onto the top of a washed Florisil cartridge (paragraph 7.4.2.4), and elute it with 9 mL of hexane/acetone [(90:10)(V/V)]. Use two additional 1-mL hexane rinses to ensure quantitative transfer of standard from the cartridge. Reduce the final volume to 1.0 mL using micro Snyder technique and analyze the solution by GC/ECD. The recovery of each analyte must be determined for evaluation and reporting purposes. The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110 percent, if the recovery of trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected. The GC analyst is responsible for documenting and filing the florisil cleanup recovery results. This data is filed in the GC Lab filing system. No samples may be cleaned up by the florisil procedure until the florisil lot check passes GC analysis criteria.

7.4.2 Florisil cartridge cleanup

7.4.2.1 Attach the vacuum manifold to a water aspirator with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 pounds of vacuum.

7.4.2.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.

7.4.2.3 The required Florisil cartridge size and the final volume of the extract after Florisil cleanup are a function of the GC autosampler that a laboratory uses. If the autosampler operates reliably with 1.0 mL of sample extract, then a 500-mg cartridge is used and the required final volume is 1.0 mL. Manual injection requires only a 1.0 mL final extract volume and a 500-mg cartridge.

7.4.2.4 Prior to cleanup of samples, the cartridge must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge in the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

7.4.2.5 After the cartridges in the manifold are washed, the vacuum is released, and a rack containing labelled 10-mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

7.4.2.6 After the volumetric flasks are in place, vacuum to the manifold is restored, and a volume of extract equal to the required final volume (1.0 mL) from each sample, blank or matrix spike extract is transferred to the top frit of the appropriate Florisil cartridge.

7.4.2.7 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1-mL level, the use of a syringe or a volumetric pipet is required to transfer the extract to the cleanup cartridge.

7.4.2.8 The pesticides/Aroclors in the extract concentrates are then eluted through the column with 9 mL of hexane/acetone (90:10 V/V) and are collected into the 10-mL volumetric flasks held in the rack inside the vacuum manifold.

7.4.2.9 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10-mL vial. Use two additional 1-mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

7.4.2.10 Concentrate the extract to 1.0 mL as required in paragraph 7.4.2.3 by using the micro-Snyder column technique. Measure the final volume with a syringe and record the final volume in the extraction logbook.

7.4.2.11 Sulfur contamination will cause a rise in the baseline of the chromatogram that may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, proceed to 7.5. Sample analyses showing the presence of sulfur are not acceptable and must be cleaned up and reanalyzed.

7.4.2.12 If sulfur is not present, transfer the sample to a GC vial and label the vial. The vial should be labelled with sample ID, date of extraction, fraction, initial volume, and final volume. The extract is ready for GC/ECD analysis. Store the extracts at 4°C in the dark.

7.5 Sulfur Removal

Sulfur can be removed by one of two methods, according to laboratory preference. CCAS-NE utilizes the copper technique, which is described in paragraph 7.5.2. Interference which is due to sulfur is not acceptable. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the samples, extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

7.5.1 If only part of a set of samples requires sulfur cleanup, then two method blanks are required for that set; one that is shaken with mercury or copper, and one that is not.

Sulfur cleanup blank - add 1.0 mL of surrogate to 10 mL of hexane in a clean centrifuge tube or 10-mL vial. Concentrate the solution to 2.0 mL by using the micro Snyder column technique. (See current revision of CCAS-NE SOP No. CA-034, "CLP Sample Preparation and Clean-up for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment.") The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. Measure the volume with a syringe or by transferring the solution to a volumetric flask. Proceed with the sulfur removal using the same technique as the samples associated with the blank.

7.5.2 Copper Technique

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 2.0 mL final volume. The separation of the extract from the copper powder is necessary to prevent degradation of the pesticides. If the copper appears bright, see current revision of CCAS-NE SOP No. CA-035, "Analysis of Pesticides/PCBs by USEPA CLP August, 1991, Statement of Work (OLM01.8) Utilizing GC/ECD," and analyze the extract. If the copper changes color, repeat the sulfur removal procedure as necessary.

REFERENCES:

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 02/88.

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 03/90, Document No. 01M01.0.

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 12/90, Rev. 1/91, Document No. OLM01.0.

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. August, 1991, Document No. OLM01.8.

ATTACHMENTS:
Attachment A - Standard Preparation Summary
Attachment B - Example of Extractions Logbook
Attachment C - Example of Solvent/Reagent Lot Check Logbook

ATTACHMENT A

Page 1

STANDARDS PREP

USEPA CLP 6/91 SOW

Pest Surrogate Mix - Stock

Restek Surrogate Pesticide Mix contents:

Tetrachloro-m-xylene	200 ug/ml
Decachlorobiphenyl	200 ug/ml

Pest Surrogate Mix - Spiking Mix

Stock	Initial Concentration (ug/mL)	Amount Added (uL)	Final Volume (uL)	Final Concentration (ng/uL)
Pest Surrogate Mix	200	25	25000	0.2

* All standards are diluted to final volume with pesticide grade methanol.

Florisil Cartridge Check - Stock

Restek Florisil Cartridge Check contents:

2,4,5-Trichlorophenol	100 ug/ml

Florisil Cartridge Check - Working Standard

Stock	Initial Concentration (ug/mL)	Amount Added (uL)	Final Volume (uL)	Final Concentration (ng/uL)
Florisil Cartridge Check	1000	10	1000	10
Florisil Cartridge Check	10	10	1000	0.1

*All standards are diluted to final volume with pesticide grade hexane.

ATTACHMENT A
Page 2

STANDARDS PREP

USEPA CLP 6/91 SOW

Pesticide Matrix Spike – Stock

Restek Pesticide Matrix Spike Mix contents:

gamma-BHC	0.5 ug/ml	Dieldrin	1.0 ug/ml
Heptachlor	0.5 ug/ml	Endrin	1.0 ug/ml
Aldrin	0.5 ug/ml	4,4'-DDT	1.0 ug/ml

Pesticide Matrix Spiking Mix

Stock	Initial Concentration (ug/mL)	Amount Added (uL)	Final Volume (uL)	Final Concentration (ng/uL)
Pest Surrogate Mix	10,40 ug/ml	500	5000	0.5,1.0 ug/ml

* All standards are diluted to final volume with pesticide grade methanol.

STANDARDS PREP

USEPA CLP 6/91 SOW

GPC Calibration Solution

Stocks	Concentration
Sulfur	neat
Methoxychlor	neat
Perylene	neat
Bis(2-ethylhexyl)phthalate	neat
Corn Oil	neat

GPC Calibration Solution Mix

Stock	Initial Concentration (ug/mL)	Amount Added (g)	Final Volume (mL)	Final Concentration (mg/mL)
Corn Oil	neat	25	1000	25
Sulfur#	neat	0.08	1000	0.08
Methoxychlor	neat	0.2	1000	0.2
Perylene	neat	0.02	1000	0.02
Bis(2-ethylhexyl)phthalate	neat	1.0	1000	1.0

* All standards are diluted to final volume with methylene chloride.

Sulfur should be dissolved in heated Corn Oil before adding Methylene Chloride.

GPC Check Mixtures

Stock	Initial Concentration (ug/mL)	Amount Added	Final Volume (mL)	Final Concentration (ug/mL)
Pest Matrix Spiking Mix	1.0, 4.0	2.0 ml	10.0^	0.1, 0.4
AROCLOR 1016	neat	2.O ug	10.0	0.2
AROCLOR 1260	neat	2.O ug	10.0	0.2

^ Concentrate 2.0ml's to 1.0ml then dilute to 10ml in Methylene Chloride.

Coast-To-Coast Analytical, Inc.
NON-CLP Organic Extraction Log

Date of Extraction	Ext. Analyst	Client	Sample #	Fraction	Matrix / Ext. Method	Initial Volume	Surrogate (Name, Code, & Conc.)	Spike (Name, Code, & Conc.)	OBS	pH	Clean Up*	Final Vol	Date of Conc.	Tray Location	Conc. Analyst	Comments
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				
												BNA:				
												P/P:				

*Clean Up: G=GPC; F=Florisil; AW=Acid Wash

Reviewed by: Date:

File: A:\ORG\EXTNONCLP\EXTLOG3.wk1

ATTACHMENT B

SOLVENT / REAGENT LOT NUMBER CHECK

Solvent or Reagent	Manufacturer	Catalogue Number	Lot Number	Date of Receipt	Expiration Date	Date Conc. (1L to 1ml)	Date Analyzed	Approval or Rejection	Approved by or Rejected by

ATTACHMENT C

Reviewed by:_____ Date:_____

STANDARD OPERATING PROCEDURE

Author: K. Gross
Approved by:

Issuing Unit: ABB-ES Portland
SOP No.: ALSCA-034-00
Date: July 1991

Willard C. Warren, III.
Director, Analytical Laboratory Services

TITLE: CLP Sample Preparation and Clean-up for Extractable Semivolatiles (SVOA) in Water or Soil/Sediment.

PURPOSE: To describe procedures utilized by the Analytical Laboratory Services Division (ALSD) in the preparation of all semivolatile (SVOA) samples associated with the U.S. Environmental Protection Agency's (EPA) Contract Laboratory Program (CLP).

SCOPE: The goal of this procedure is to ensure uniformity involving the preparation of all USEPA CLP samples for subsequent SVOA analysis. This SOP is specifically applicable to the EPA CLP statement of Work (SOW) OLM01.0, OLM01.1, and OLM01.2.

REQUIREMENTS: Only properly trained and approved sample preparation chemists/technicians may perform this procedure on samples for CLP.

Sonication extractions for semivolatiles in soil samples must be completed within ten days of Verified Time of Sample Receipt (VTSR). Continuous liquid-liquid extractions for semivolatiles must be started within five days of VTSR.

PROCEDURE:

1.0 SUMMARY OF SAMPLE PREPARATION METHOD FOR EXTRACTABLE SEMIVOLATILES (SVOA) IN WATER

1.1 A one liter aliquot of sample is acidified to pH 2 and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. The methylene chloride extract is dried and concentrated to a volume of 1.0 mL.

2.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by

contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.0 APPARATUS AND MATERIALS

3.1 Glassware (brand names and catalog numbers are included for illustration purposes only)

3.1.1 Continuous liquid-liquid extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent), Corning One-Step Extractor/Concentrator.

3.1.2 Glass funnels with glass wool plug for drying of extracts.

3.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

3.1.4 Evaporate flask - Kuderna-Danish, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

3.1.5 Snyder column - Kuderna-Danish, three-ball macro (Kontes K-503000-0121 or equivalent).

3.1.6 Snyder column - Kuderna-Danish, two-ball micro or preferably three-ball micro.

3.1.7 Vials - amber glass, 2 mL capacity with Teflon-lined screw cap.

3.2 Organic Free Boiling Chips - approximately 10/40 mesh. Rinsed with methylene chloride, dried, and baked at 400°C for 30 minutes.

3.3 Water bath - heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

3.4 Balance - analytical, capable of accurately weighing ± 0.0002 g.

4.0 REAGENTS

4.1 Reagent water - defined as water in which an interferent is not observed at or above the CRQL of each parameter of interest. Deionized water filtered through activated charcoal.

4.2 Sodium thiosulfate - (ACS) granular.

4.3 Sulfuric acid solution (1+1) - slowly add 50 mL of H_2SO_4 (sp gr 1.84) to 50 mL of reagent water.

4.4 Acetone, methanol, methylene chloride - pesticide residue analysis grade or equivalent.

4.5 Sodium sulfate - (ACS) powdered, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a glass bottle (Baker anhydrous powder, catalog #73898, or equivalent).

4.6 Surrogate standard spiking solution.

4.6.1 Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are Phenol-d_5, 2,4,6-Tribromophenol, 2-Fluorophenol, Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Fluorobiphenyl, 2-Chlorophenyl-d_4, and 1,2-Dichlorobenzene-d_4.

4.6.2 Prepare a surrogate standard spiking solution that contains Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Fluorobiphenyl, and 1,2-Dichlorobenzene-d_4 at a concentration of 100 µg/mL; Phenol-d_5, 2,4,6-Tribromophenol, 2-Fluorophenol, and 2-Chlorophenol-d_4 at a concentration of 150 µg/mL. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

4.7 SVOA Matrix standard spiking solution - the matrix spike solution consists of the following:

Bases/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

Prepare a spiking solution that contains each of the base/neutral compounds above at 100 µg/mL in methanol and the acid compounds at 150 µg/ml in methanol. Analyze duplicate aliquots of a sample spiked with SVOA matrix spiking solution.

5.0 WATER SAMPLE EXTRACTION

5.1 Continuous liquid-liquid extraction is used to extract the samples.

NOTE: Prerinse all glassware three times with methylene chloride.

5.1.1 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom side arm.

5.1.2 Using a liter graduated cylinder, measure out a 1.0 liter sample aliquot. Transfer the 1 liter sample aliquot to the continuous extractor. Pipet 0.5 mL of surrogate standard spiking solution into the sample and mix well. Check the pH of the sample with wide range pH paper and adjust the pH to 2.0 with 1:1 H_2SO_4.

5.1.3 Following the procedures in 5.1.1 and 5.1.2 above, prepare two additional 1.0 liter aliquots of the sample chosen for spiking. Add 0.5 mL of the SVOA Matrix Spiking Solution to each of the additional aliquots.

5.1.4 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation. Extract for 18 hours. Allow to cool, then detach the distilling flask, and label the flask.

5.1.5 Prepare a method blank with each group of water samples extracted. For semivolatile analyses, a method blank for water samples consists of a 1 L volume of reagent water (see Paragraph 4.1), spiked with the surrogates and carried through the entire analytical procedure.

5.2 Concentrating the Extracts

NOTE: Prerinse all glassware three times with methylene chloride.

5.2.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. The Corning One-Step Extractor/Concentrator is an acceptable substitute.

5.2.2 Prepare a glass funnel containing a glass wool plug and about 40 grams of anhydrous granular sodium sulfate; prerinse the funnel and sodium sulfate with methylene chloride. Transfer the sample extract by pouring the extract through the glass funnel containing anhydrous granular sodium sulfate, and collect the extract in a K-D concentrator. Rinse the Erlenmeyer flask and funnel with 20 to 30 mL of methylene chloride to complete the quantitative transfer, collecting the rinsate in the K-D. As an alternative, the Corning One-Step drying tube may be used after rinsing as above.

5.2.3 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60°C to 80°C) so that

the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. If the Corning One-Step is used, ensure the water in the jacketed concentrator tube is 80°C then turn the stopcock turning off the flow of solvent from the extractor. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride.

5.2.4 Final Concentration

NOTE: Prerinse the micro Snyder column three times with methylene chloride.

5.2.4.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball or three-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60°C to 80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. Transfer the extract to a Teflon-sealed screw-cap bottle, label the bottle, and store at 4°C (±2°C).

6.0 THE SAMPLE EXTRACTS ARE READY FOR GC/MS ANALYSIS

If the sample is suspected of having high concentrations of organic contamination proceed (e.g., highly colored extract) to the GPC clean-up Section (10.0); or proceed to the optional GC/FID screen (Section 7.0) before performing GPC clean-up or sample dilution if high concentrations of target compounds are present.

7.0 SAMPLE PREPARATION FOR EXTRACTABLE SEMIVOLATILES (SVOA) IN SOIL/SEDIMENT

It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol is chosen to ensure proper quantitation limits for the sample. Note that the terms "low level" and "medium level" are not used here as a judgement of degree of contamination but rather as a description of the concentration ranges that are encompassed by the "low" and "medium" level procedures.

The laboratory is at liberty to determine the method of characterization. The following two screening methods may be used for soil/sediment sample characterization:

- Screen an aliquot from the "low level" 30 g extract or an aliquot from the "medium level" 1 g extract.
- Screen using either GC/FID or GC/MS as the screening instrument.

The concentration ranges covered by these two procedures may be considered to be approximately 330 µg/kg for the low level analysis and >10,000 µg/kg for medium level analysis for semivolatile extractables.

7.1 Screen from the Medium Level Method

Take 5.0 mL from the 10.0 mL total extract and concentrate to 1.0 mL and screen. If the sample concentration is <10,000 µg/kg, discard the medium level extract and follow the low level method.

7.2 Screen from the Low Level Method

Take 5.0 mL from the 300 mL (approximate) total extract from the 30 g sample and concentrate to 1.0 mL and screen. If the original sample concentration is >10,000 µg/kg, discard the 30 g extract and follow the medium level methods for organics, using medium level surrogates. If the sample concentration is method.

7.3 Mandatory GPC Clean Up

Regardless of the concentration level, all soil/sediment sample extracts must be subjected to clean up by Gel Permeation Chromatography (GPC). Because the effectiveness of GPC can be adversely affected by the amount of material loaded onto the GPC column, it may be advisable to screen the sample extracts described here prior to employing GPC.

8.0 MEDIUM LEVEL PREPARATION FOR SCREENING AND ANALYSIS OF SEMIVOLATILES

8.1 Scope and Application

This procedure is designed for the preparation of sediment/soil samples which may contain organic chemicals at a level greater than 20,000 µg/kg. (NOTE: The 20,000 µg/kg quantitation limit assumes the extract will be screened prior to GPC clean up; if the extract is to be cleaned up using GPC without screening then the quantitation limits for the screening procedure outlined in paragraph 7.1 are approximately 10,000 µg/kg.)

8.1.1 The extracts and sample aliquots prepared using this method are screened by GC/MS or FID, using capillary columns for semivolatile priority pollutants, and related organic chemicals. The results of these screens will determine whether sufficient quantities of pollutants are present to warrant analysis by low or medium level protocol.

8.1.2 If the screenings indicate no detectable pollutants at the lower limits of quantitation, the sample should be prepared by the low level protocol in Section 9.0.

8.2 Summary of Method

8.2.1 1 g portions of sediment/soil are transferred to vials and extracted with methylene chloride. The methylene chloride extract is screened for extractable organics by GC/FID or GC/MS.

8.2.2 If organic compounds are detected by the screen, the methylene chloride extract is subjected to GPC clean up and analyzed by GC/MS for extractable organics.

8.2.3 If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

8.3 Interferences

8.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

8.4 Limitations

8.4.1 The procedure is designed to allow quantitation limits for screening purposes as low as 20,000 µg/kg for extractable organics. For analysis purposes, the quantitation limits are 20,000 µg/kg for extractable organics. If peaks are present based on the GC/FID

screen, the sample is determined to require a medium level analysis by GC/MS. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.

8.4.2 These extraction and preparation procedures were developed for rapid and safe handling of high concentration hazardous waste samples. The design of the methods thus does not stress efficient recoveries or low limits of quantitation of all components. Rather, the procedures were designed to screen, at moderate recovery and sufficient sensitivity, a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples.

8.5 Reagents

8.5.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, catalog # 73898 or equivalent).

8.5.2 Acetone, Methanol, Methylene chloride - pesticide residue analysis grade or equivalent.

8.5.3 Base/Neutral and Acid (SVOA) Surrogate Spiking Solution

Surrogate standards are added to all samples and calibration solutions. The compounds specified are Phenol-d_5, 2,4,6-Tribromophenol, 2-Fluorophenol, Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Fluorobiphenyl, 2-Chlorophenol-d_4, and 1,2-Dichlorobenzene-d_4. Prepare a surrogate standard spiking solution that contains Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Fluorobiphenyl, and 1,2-Dichlorobenzene-d_4 at a concentration of 100 µg/mL; Phenol-d_5, 2,4,6-Tribronophenol, 2-Fluorophenol, and 2-Chlorophenol-d_4 at a concentration of 150 µg/mL. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

8.5.4 Base/Neutral and Acid (SVOA) Matrix Spiking Solution

Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 µg/mL for base/neutrals and 150 µg/mL for acids. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

Bases/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

8.6 Equipment

8.6.1 Glass scintillation vials - at least 20 mL, with screw cap and teflon or aluminum foil liner.

8.6.2 Spatula - stainless steel or Teflon.

8.6.3 Balance - capable of weighing 100 g to ± 0.01 g.

8.6.4 Vials and caps - 2 mL for GC auto sampler.

8.6.5 Disposable pipets - Pasteur; glass wool rinsed with methylene chloride.

8.6.6 Concentrator tubes - 15 mL.

8.6.7 Ultrasonic cell disruptor - Heat Systems, Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200, 1/2 inch tapped MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe <u>must</u> be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

8.6.8 Sonabox acoustic enclosure or equivalent - recommended with above disruptors for decreasing cavitation sound.

8.6.9 Test tube rack.

8.6.10 Oven - drying.

8.6.11 Desiccator

8.6.12 Aluminum drying pans

8.7 Medium Level Sample Preparation

NOTE: Prerinse all glassware three times with methylene chloride.

8.7.1 Transfer the sample container into a fume hood. Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a kimwipe to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

8.7.1.1 Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Technical Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the SDG Narrative. Discard this portion of sample. NOTE: If limited sample volume is received, use 5 g of soil and 5 mL of water for the pH determination. Note this on the SDG Narrative.

8.7.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared aluminum pan. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

8.7.3 Add 2.0 g of anhydrous <u>powdered</u> sodium sulfate to the sample in the 20 mL vial from paragraph 8.7.1 and mix well.

8.7.4 Surrogates are added to all samples, spikes, and blanks. Add 0.5 mL of surrogate spiking solution to sample mixture.

8.7.5 Add 0.5 mL of matrix standard spiking solution to each of two 1 g portions from the sample chosen for spiking.

8.7.6 Immediately add 9.5 mL (9.0 mL for matrix spikes) of methylene chloride to the sample and disrupt the sample with the 1/8 inch tapered MICROTIP ultrasonic probe for 2 minutes at output control setting 5, in continuous mode (if using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings). Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula or, <u>very carefully</u>, with the tip of the unenergized probe.

Only 9.0 mL of methylene chloride is added to the matrix spike samples to achieve a final volume of 10 mL.

8.7.7 Prepare a method blank with each group of medium soil/sediment samples extracted. For semivolatile analyses, a method blank for medium soil/sediment samples consists of 1 g of sodium sulfate (see Paragraph 8.5.1), spiked with the surrogates and carried through the entire analytical procedure.

8.7.8 Loosely pack disposable Pasteur pipets with 2-3 cm prerinsed glass wool plugs. Filter extract through the glass wool and collect at least 8.0 mL in a concentrator tube.

8.7.9 If the extract is to be screened prior to GPC, concentrate 5.0 mL of the extract collected in paragraph 8.7.8 to 1.0 mL using the technique described in Section 5.2. Transfer the concentrate to an autosampler vial for GC/FID or GC/MS for screening. The quantitation limits for the screening procedure are approximately 20,000 µg/kg.

8.7.10 If the extract is to be cleaned up using GPC without screening, take at least 8.0 mL of the extract in paragraph 8.7.8 and proceed to Section 10.0. Following GPC, the 5.0 mL of extract collected must be concentrated to 0.5 mL by the micro snyder technique described in paragraph 5.2.4, and screened. In this case, the quantitation limits for the screening procedure are approximately 10,000 µg/kg.

9.0 LOW LEVEL PREPARATION FOR SCREENING AND ANALYSIS OF SEMIVOLATILES

9.1 Summary of Method

A 30 gram portion of sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. If the optional low level screen is used, a portion of this dilute extract is concentrated fivefold and is screened by GC/FID or GC/MS. If peaks are present at greater than 20,000 µg/kg, discard the extract and prepare the sample by the medium level method. If no peaks are present at greater than 20,000 µg/kg, the entire extract is concentrated, subject to GPC clean up, and analyzed by GC/MS for extractable organics.

9.2 Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are

coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

9.3 Apparatus and Materials

9.3.1 Apparatus for determining percent moisture

9.3.1.1 Oven - drying.

9.3.1.2 Desiccator.

9.3.1.3 Aluminum pan.

9.3.2 Disposable Pasteur glass pipets - 1 L.

9.3.3 Ultrasonic cell disruptor, Heat Systems, Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 305, 3/4 inch tapped high gain "Q" disruptor horn), or equivalent device with a minimum of 375 Watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

Sonabox or equivalent acoustic enclosure - recommended with above disruptors for decreasing cavitation sound.

9.3.4 Beakers - 400 mL.

9.3.5 Vacuum filtration apparatus.

9.3.5.1 Buchner funnel.

9.3.5.2 Filter paper - Whatman No. 41 or equivalent.

9.3.6 Kuderna-Danish (K-D) apparatus.

9.3.6.1 Concentrator tube - 10 mL, graduated (Kontes K-570040-1025 or equivalent).

9.3.6.2 Evaporative flask - 500 mL (Kontes K-570001-0500 or equivalent).

9.3.6.3 Snyder column - three-ball macro (Kontes K-50300-0121 or equivalent).

9.3.6.4 Snyder column - two-ball micro or three ball micro.

9.3.7 Organic free boiling chips - approximately 10/40 mesh. Rinse in methylene chloride, dry, and bake at 400°C for 30 minutes.

9.3.8 Water bath - heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

9.3.9 Balance - capable of accurately weighing ± 0.01 g.

9.3.10 Vials and caps - 2 mL for GC auto sampler.

9.3.11 Balance - analytical, capable of accurately weighing ± 0.0001g.

9.3.12 Pyrex glass wool.

9.3.13 Pasteur pipets - disposable.

9.4 Reagents

9.4.1 Sodium Sulfate - anhydrous powdered reagent grade, heated at 400°C for four hours, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, catalog #73898 or equivalent).

9.4.2 Methylene chloride, methanol, acetone, isooctane, 2-propanol, and benzene - pesticide residue analysis grade or equivalent.

9.4.3 Reagent water - defined as water in which an interferent is not observed at or above the CRQL of each parameter of interest. Deionized water filtered through activated charcoal.

9.4.4 Sodium Sulfite - reagent grade.

9.4.5 Base/Neutral and Acid (SVOA) Surrogate Spiking Solution

Surrogate standards are added to all samples and calibration solutions. The compounds specified are Phenol-d_5, 2,4,6-Tribromophenol, 2-Fluorophenol, Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Flurobiphenyl, 2-Chlorophenol-d_4, and 1,2-Dichlorobenzene-d_4. Prepare a surrogate standard spiking solution that contains Nitrobenzene-d_5, Terphenyl-d_{14}, 2-Fluorobiphenyl, and 1,2-Dichlorobenzene-d_4 at a concentration of 100 µg/mL; Phenol-d_5, 2,4,6-Tribromophenol, 2-Fluorophenol, and 2-Chlorophenol-d_4 at a concentration of 150 µg/mL. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

9.4.6 Base/Neutral and Acid (SVOA) Matrix Spiking Solution

Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 µg/mL for base/neutrals and 150 µg/mL for acids. Store the spiking solution at 4°C (±2°C) in Teflon-sealed containers. These solutions must be replaced after

six months, or sooner if comparison with quality control check samples indicates a problem.

Bases/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

9.5 Low Level Sample Preparation

9.5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

Transfer 50 g of soil/sediment to 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Technical Project Officer cited in the contract for instructions on how to handle the sample. Document the instructions in the SDG Narrative. Discard this portion of sample. NOTE: If limited sample volume is received, use 5 g of soil and 5 mL of water for the pH determination. Note this in the SDG Narrative.

9.5.2 The following steps should be performed <u>rapidly to avoid loss of the more volatile extractables</u>. Weigh approximately 30 g of sample to the nearest 0.1 g into a 400-mL beaker and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride-acetone to the sample, then add the surrogates according to paragraph 9.5.2.3.

9.5.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared aluminum pan. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

9.5.2.2 Weigh out two 30 g (record weight to nearest 0.1 g) portions for use as matrix spike and matrix spike duplicate according to paragraph 9.5.2. Add 0.5 mL of the SVOA matrix spike solution to each of two portions.

9.5.2.3 Add 0.5 mL of base/neutral and acid (SVOA) surrogate standard to the sample and each of the aliquots in 9.5.2.2.

9.5.2.4 Prepare a method blank with each group of low soil/sediment samples extracted. For semivolatile analyses, a method blank for low soil/sediment samples consists of 30 g of sodium sulfate (see paragraph 9.4.1), spiked with the surrogates and carried through the entire analytical procedure.

9.5.3 Place the bottom surface of the tip of the 3/4 inch disruptor horn about 1/2 inch below the surface of the solvent but above the sediment layer.

9.5.4 Sonicate for 1½ minutes with the W-385 (or 3 minutes with the W-375), using No. 208, 3/4 inch standard disruptor horn with output control knob set at 10 (or No. 305, 3/4 inch tapped high gain "Q" disruptor horn at 5) and mode switch on "1 sec. pulse" and % duty cycle knob set a 50% (if using a sonicator other than Models W-375 or W-385, contact the Project Officer for appropriate output settings). Do NOT use MICROTIP probe.

9.5.5 Decant and filter extracts through Whatman #41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

9.5.6 Repeat the extraction two more times with 2 additional 100 mL portions of 1:1 methylene chloride-acetone. Before each extraction make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula or, <u>very carefully</u>, with the tip of the probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride-acetone.

9.5.6.1 If the sample is to be screened from the low level method <u>prior to</u> GPC, take 5.0 mL and concentrate to 1.0 mL following paragraph 5.2.4, but note that the final volume for screening is 1.0 mL, not 0.5 mL.

9.5.6.2 After GC/FID or GC/MS screening, transfer the remainder of the 1 mL back to the total extract from paragraph 9.5.6.1. CAUTION: To minimize sample loss, autosamplers which pre-flush samples through the syringe should not be used.

9.6 Concentration and Solvent Exchange

NOTE: Prerinse all glassware three times with methylene chloride.

9.6.1 Low level soil/sediment samples will result in extracts containing a mixture of acetone and methylene chloride. Because all soil/sediment sample extracts must be subjected to GPC clean up prior to analysis, the majority of the acetone must be removed from the extract, otherwise it will have adverse effects on the GPC column. To remove the acetone from the sample extract, employ the following three steps.

9.6.2 Transfer the extract to a Kuderna-Danish (K-D) concentrator consisting of a 10 mL concentrator tube and a 500 mL evaporative flask.

9.6.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reached 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

9.6.4 Dilute the extract to 10.0 mL with methylene chloride, and proceed with GPC clean up. If the GPC has 1.5mL injected volume, dilute the extract to 3.0 mL.

10.0 EXTRACT CLEANUP BY GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated. A cross-linked divinyl benzenestyrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

GPC is required for all soil/sediment samples, regardless of concentration level, for the elimination of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds from the sample extract. GPC is appropriate for both polar and

non-polar analytes, therefore, it can be used effectively to clean up extracts containing a broad range of analytes.

Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or in the front of the GC column. This residue ultimately will reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol especially is susceptible to this problem.

In the event that the laboratory fails to appropriately employ GPC clean-up procedures, the Agency will require the clean up and reanalysis of all affected samples or sample extracts at no additional cost to the Agency.

10.1 Apparatus and Materials

10.1.1 Gel permeation chromatography (GPC) cleanup device. NOTE: GPC cleanup is required for all soil/sediment extracts.

Gel permeation chromatography system - GPC Autoprep Model 1002 A or B (Analytical Biochemical Laboratories, Inc., or equivalent) Systems that perform very satisfactorily also have been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of paragraph 3.4.

10.1.1.1 Chromatographic column - 700 mm x 25 mm i.d. glass column. Flow is upward. To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

10.1.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

10.1.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 gm of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they also can pass through the column screens and damage the valve.

10.1.1.4 Ultraviolet detector - fixed wavelength (254 nm) with a semi-prep flow-through cell.

10.1.1.5 Strip chart recorder, recording integrator or laboratory data system.

10.1.1.6 Syringe - 10 mL with Luerlok fitting.

10.1.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-000, 25 mm, and 0.45 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

10.2 Reagents

10.2.1 GPC Calibration Solution - prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

Compound	mg/mL
corn oil	25.0
bis(2-ethylhexyl)phthalate	1.0
methoxychlor	0.2
perylene	0.02
sulfur (optional)	0.08

NOTE: If used, sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon-lined screw-cap at 4°C, and protect from light (NOTE: refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves). Replace the calibration standard solution every 6 months, or more frequently if necessary.

10.3 Column Preparation

10.3.1 Weight out 70 gm Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon-lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to

cover the beads sufficiently at all times. If a guard column is to be used, repeat the above with 5 gm of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

10.3.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

10.3.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

10.3.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

10.3.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a Kimwipe. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.3.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat the step in paragraph 10.3.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is inserted successfully.

10.3.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

10.3.8 Pack the optional 5 cm column with approximately 5 gm of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

10.3.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

10.3.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as the one in paragraph 10.3.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not affect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.3.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

10.4 Calibration of the GPC Column

10.4.1 The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column. Care must be taken to account for any difference in volume (elution time) between the GC column and the detector and between the GPC column and the collection vial.

10.4.2 Using a 5 mL or 10 mL syringe load sample loop #1 with calibration solution (paragraph 10.2). With the ABC automated system the 5 mL or 10 mL sample loop requires a minimum of 5 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-

through cell. The HP autosampler system requires a minimum 1.5 mL sample size.

10.4.3 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace that meets the following requirements. Differences between manufacturer's cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell and, therefore, the analytical cell is <u>not</u> acceptable for use.

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

10.4.4 Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis(2-ethylhexyl)phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences.

10.4.5 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in paragraph 10.4.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.4.6 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.4.6.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.4.6.2 The retention times for bis(2-ethylhexyl)phthalate and perylene must not vary more than ±5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.4.7 Analyze a GPC blank by loading 5 mL (or 1.5 mL into the HP system) of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a prerinsed Kuderna-Danish (KD) evaporator. Analyze the concentrate by GC/MS. If the blank exceeds one half the CRQL of any analyte, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.5 Sample Extract Cleanup

It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

10.5.1 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 500 mg of nonvolatile residue per 5 mL of extract must be diluted and loaded into several loops. The nonvolatile reside may be determined by evaporating a 100 μL aliquot

of the extract to dryness in a tared aluminum weighting pan, or other suitable container.

10.5.2 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 0.45 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 5 mL syringe. Draw the sample extract into a small glass container, e.g., a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container.

10.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi) the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes (this should be done before sample loading). If the HP system is used, manual injection is not necessary.

10.5.4 Collect each sample in 250-mL prerinsed Erlenmeyer flask or similar container, covered with aluminum foil to reduce solvent evaporation, or directly into a prerinsed Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.
- Leaks in the system or significant variances in room temperature.

10.5.5 Concentrate the extract as per paragraphs 10.6.1 or 10.6.2.

10.5.6 Calibrate the GPC at least once per week, following the procedure outlined in 10.4. The UV trace must meet the requirements in paragraph 10.4.3. In addition, the retention times of the calibration compounds must be within ±5% of their retention times in the previous calibration. A copy of the UV trace of the calibration solution must be submitted with the data for the associated samples.

10.5.7 If the requirements in paragraphs 10.4.3 and 10.5.6 cannot be met, the column may be cleaned by processing several injections of butyl chloride throughout the system. Butyl chloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated.

10.6 Final Concentration of Extract

NOTE: Prerinse all glassware three times with methylene chloride.

10.6.1 Transfer the sample extract to K-D evaporator, attach the micro-Snyder column to the concentrator tube and add a silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with 0.5 mL methylene chloride. Place the K-D apparatus on the hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. When the apparent volume of the liquid reaches 0.4 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with 0.1 mL of methylene chloride. Adjust the final volume to 0.5 mL with methylene chloride. Concentrating the extract to 0.5 mL will account for the volume of extract (5 mL) <u>not</u> recovered after GPC.

10.7 Store all extracts at 4°C (±2°C) in the dark in labeled Teflon-sealed containers.

10.8 If the extract was <u>not</u> screened prior to GPC, proceed to the screening procedures. If the extract <u>was</u> screened prior to GPC, proceed with the GC/MS analysis.

REFERENCES:

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 02/88.

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 05/90, Rev. 12/90, and Rev. 1/91 Document No. 01M01.0.

ATTACHMENTS:

Attachment A - Example of Organic Prep Log Book for CLP Samples
Attachment B - Example of GPC Log Book

ABB Environmental
CLP Organic Extraction Log

CASE#

Date of Extraction	Ext. Analyst	Sample #	Fraction	Matrix	Initial Volume	Surrogate (Name, Code, Conc., & vol.)	Spike (Name, Code, Conc., & vol.)	OBS	pH	Clean Up*	Final Vol	Date of Conc.	Tray Location	Conc. Analyst	Comments
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				
											BNA:				
											P/P:				

*Clean Up: G=GPC; A=Alumina; F=Florisil

Reviewed by: _____ Date: _____

File: a:\ORG\EXT\CLP\EXTLOG2.wk1

ABB Environmental
GPC Logbook

Sample Identification	Extraction Fraction(s)	Date Extracted	Pre-extraction Sample Volume/wt.	Extract Volume	GPC Injection Volume	GPC Fraction Desired Final Volume	GPC Fraction Actual Final Volume	GPC Analyst	Chromatogram ID	Date & Time GPC Performed	GPC Method	GPC Initial Dump Time/ GPC Collect Time	Comments

STANDARD OPERATING PROCEDURE

Author: Timothy Lewis, George Brewer
Approved by:

Issuing Unit: CCAS-Northeast
SOP No.: CA-013-01
Date: November 1993

Willard C. Warren, III
President, Northeastern Division

TITLE: Hot Plate Acid Digestion Procedures for Water Sample Preparation Prior to Determination of Total or Dissolved Metals by Inductively Coupled Plasma (ICP), Flame Atomic Absorption (FAA), or Flame Atomic Emission (FAE) Analysis

PURPOSE: To describe the CCAS-NE procedures utilized to solubilize metals in water samples prior to ICP, FAA, or FAE analyses.

SCOPE: These procedures apply to all water sample preparations for ICP, FAA, and FAE analyses and analysis of antimony and tin by GFAA, unless the client has requested an alternate procedure. They are appropriate for all metals that are to be analyzed by ICP, FAA, or FAE and for samples to be analyzed for antimony and tin by graphite furnace atomic absorption (GFAA). Samples to be analyzed for dissolved metals should be filtered through a 0.45 um membrane filter and preserved as soon as possible after collection. Samples to be analyzed for total metals should be preserved, unfiltered, as soon as possible after collection.

REQUIREMENTS:

A. EQUIPMENT

1. 150 mL pre-cleaned Pyrex Griffin beakers (cleaned according to the current revisions of SOP Nos. CA-001, "Labware Cleaning" and CA-012, "Glassware Preparation and Sample Preservation for Trace Element Analyses")

2. Watch glasses, ribbed and non-ribbed, pre-cleaned as above

3. Adjustable volume pipets - 50 μL to 200 μL, 200 μL to 1000 μL, 1.00 mL to 5.00 mL; Finn pipets or Eppendorf pipets are acceptable

4. Graduated cylinders - HNO_3 acid-rinsed

5. Hot plates

6. Assorted sizes of acid-cleaned volumetric flasks

7. Polyethylene sample containers

B. REAGENTS

1. 16 M nitric acid (HNO_3), 12 M hydrochloric acid (HCl) - spectrometric grade

2. ASTM Type II water (ASTM D1193)

PROCEDURE:

A. PROCEDURE FOR WATER SAMPLES

Sample matrices include groundwater, surface water, domestic wastewater and some industrial wastewater. This procedure must be followed for samples being analyzed according to EPA Contract Laboratory Program (or equivalent) protocols.

1. Mix the sample well and transfer 100 mL of sample to a 150 mL beaker using an acid-rinsed graduated cylinder. A smaller sample aliquot may be used if less than 100 mL of sample is available; however, Client Services must obtain the consent of the client if a non-standard volume is to be used. If less than 100 mL of sample is digested, the volumes of reagents used must be decreased proportionately. Record initial sample volume in the digestion log book. For each 100 mL of sample, add 1 mL of 16 M HNO_3 and 5 mL of 12 M HCl. Cover with a ribbed watch glass and heat for 2 hours at 95° C or until the sample volume is decreased by 50 to 75 percent. Do not boil the sample or take to dryness, as low recoveries may result.

2. Allow the beaker to cool and quantitatively transfer the sample to an appropriately sized acid-cleaned volumetric flask (the final sample volume should equal the initial sample volume, so select the volumetric flask accordingly). Adjust the volume in the flask to the meniscus with Type II water and transfer to an appropriately labeled polyethylene bottle. Bottles are labeled with the sample number, type of digestion, and a letter code denoting the date of digestion as traceable to the digestion logbook.

B. PROCEDURE FOR LEACHATES, TCLP EXTRACTS, AND SAMPLES CONTAINING SUSPENDED SOLIDS

1. A more rigorous digestion may be required for leachates and similar samples. Transfer 100 mL of well-mixed sample to a properly cleaned 150 mL beaker. A smaller sample aliquot may be used if less than 100 mL of sample is available; however, Client Services must obtain the consent of the client if a non-standard volume is to be used. If less than 100 mL of sample is digested, the volumes of reagents used must be decreased proportionately. For each 100 mL of sample, add 3 mL of 16 M HNO_3 and cover with a ribbed watch glass. Evaporate to near dryness. Note: Do <u>not</u> boil the sample and do <u>not</u> let the sample go to dryness. If a sample is allowed to go to dryness, low recoveries may result. Should this occur, discard the sample and reprepare.

2. Cool the sample and add another 3 mL aliquot of 16 M HNO_3. Cover the beaker with a non-ribbed watch glass, return to the hot plate, and reflux gently. Continue heating, adding more acid as necessary until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with repeated refluxing). Replace the non-ribbed watch glass with a ribbed watch glass and evaporate to a volume of approximately 3 mL. Cool and add 5 mL of 12 M HC1 and approximately 5 mL of Type II water. Return to the hot plate and reflux for 15 minutes to dissolve any residue resulting from the evaporation.

3. Allow the beaker to cool and quantitatively transfer the solution to an appropriately sized acid-cleaned volumetric flask. Follow the procedure for water samples above starting with adjusting the sample volume in the volumetric flask (Step A2).

C. QUALITY CONTROL

1. A preparation blank for waters (PBW) is processed with each digestion batch, and is used to assess contamination resulting from the digestion procedure. The PBW consists of a 100 mL aliquot of Type II water, and is processed through the digestion procedure using the same reagents as those used for associated samples. Acceptance criteria for the preparation blank are tabulated in Attachment C.

2. A Laboratory Control Sample for waters (LCSW) is processed with each digestion batch, and is used to assess method recovery. The LCSW consists of a 100 mL aliquot of Type II water that is spiked to contain all analytes of interest at known concentrations, and is processed through the digestion procedure using the same reagents as have been used for associated samples. Analytes should be present in the LCSW at concentrations that are approximately midrange on the

calibration curve. Directions for spiking the LCSW are contained in Attachment A. Acceptance criteria for the LCSW are tabulated in Attachment C.

3. Matrix spike samples are processed along with each digestion batch at a frequency of 5 percent (or at least one per digestion batch, whichever is greater), unless special QC is requested. Matrix spike recoveries are used to assess the effects of sample matrix on digestion and analysis efficiency. The spiking solution should contain all the analytes of interest at levels that are approximately midrange on the instrument calibration curve. The spiking scheme used for EPA CLP protocol samples may differ from that used for non-CLP samples. Directions for spiking matrix spike samples are contained in Attachment A.

4. Duplicate samples are processed in each digestion batch at a frequency of 5 percent (or at least one per digestion batch, whichever is greater). Duplicate samples are used to assess the precision of the digestion and analysis. Sample volumes available may dictate the choice of samples for duplicate digestion. Ideally, the duplicate and spike will be performed on the same sample if sufficient volume is available. For work orders requiring CCAS-NE Level III QC, matrix spike duplicates are prepared instead of duplicate samples.

D. DOCUMENTATION

1. Record all pertinent digestion information in the digestion logbook. At a minimum the information included in the logbook should include: the digestion date, analyst signature, laboratory sample numbers, initial and final volumes, digestion type, QC sample identification, and identification of lot numbers of reagents and spiking solutions used. Example logbook pages are included as Attachment B.

2. Digestion information for each sample is entered into the Laboratory Information Management System (LIMS) by the digestion analyst. This information includes the digestion date, analyst initials, initial and final volumes, and preparation method.

3. Currently, results for QC samples (PBW, LCSW, duplicate samples, and matrix spike and matrix spike duplicate samples) are not reported through the LIMS. Therefore, the digestion analyst who generates these QC samples must prepare worksheets on which to record their analytical results. Examples of these worksheets are included as Attachment C. Blank worksheets are available in the Elements instrument lab. Once the appropriate information has been entered by the digestion analyst, QC sample worksheets are filed in a looseleaf notebook in the Elements instrument lab for use during instrumental analysis.

E. WASTE DISPOSAL

1. Excess spiking solutions must be emptied into the corrosive waste carboy located in the Elements prep lab (or the corrosive waste drum in the waste shed) for subsequent appropriate disposal.

2. Sample digestates should be stored for a minimum of 60 days after digestion to allow for analysis, and reanalysis if necessary. Digestates older than 60 days may be emptied into the corrosive waste carboy in the Elements prep lab (or the corrosive waste drum in the waste shed) for subsequent appropriate disposal.

F. SAFETY

1. The acids used in this procedure are highly corrosive and reactive, and spiking standards contain toxic metals. The toxicity and reactivity of client samples are usually unknown, so samples should always be assumed to present a contact hazard. To reduce or eliminate exposure to potentially harmful chemicals, lab coats, gloves, and safety glasses or goggles must be worn whenever handling samples or reagents. Additional safety apparel, including face shields, rubber aprons, dust masks, and rubber shoe protectors, are available in the Elements prep lab and should be worn whenever circumstances warrant.

2. Acids should be added to samples slowly and carefully, while watching for reactions. This should be done under a hood, in case harmful fumes are evolved.

3. Hood sashes should be lowered as far as possible whenever beakers are being heated on a hot plate. Hot pads or asbestos gloves should be used when handling hot beakers.

4. Read the laboratory's chemical hygiene plan before performing this procedure, and familiarize yourself with the general rules for laboratory safety, personal hygiene, housekeeping, and use of protective clothing and equipment.

REFERENCES:

1. United States Environmental Protection Agency Contract Laboratory Program, Statement of Work for Inorganics Analysis - Multi-Media Multi-Concentration, Document Number ILMO3.0.

2. "Test Methods for the Evaluation of Solid Waste," United States Environmental Protection Agency, SW-846, Third Edition, Final Update I, Revised July, 1992.

3. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Revised March, 1983.

ATTACHMENTS:

Attachment A - Sample matrix spike and LCS spiking instructions

Attachment B - Example page from digestion logbook

Attachment C - Example analytical worksheets for QC samples

ATTACHMENT A

INSTRUCTIONS FOR PREPARING WATER MATRIX SPIKES AND LCSWs FOR ANALYSIS BY ICP, FAA, AND FAE

SAMPLE TYPE	ANALYSIS PROTOCOL	SOLUTION NAME	SOLUTION VENDOR	AMT. ADDED (PER 100 mL)	FINAL METAL CONC. IN DIGESTATE (ug/L)
Water Matrix Spike	Non-CLP	CLPP-SPK-1	Inorganic Ventures	0.100 mL	Al=2000, Ba=2000, Be=50, Co=500, Cu=250, Cr=200, Ag=50, V=500, Zn=500
		CLPP-SPK-2	Inorganic Ventures	0.020 mL	Sb=100 (For GFAA Analysis)
				0.100 mL	Sb=500 (For ICP Analysis)
		CLPP-SPK-3	Inorganic Ventures	0.100 mL	As=2000, Cd=50, Pb=500, Se=2000, Tl=2000
		2007ICS-1	Inorganic Ventures	0.200 mL	B=1000, Mo=600, Si=460, Ti=2000
		2007SPK-B	Inorganic Ventures	0.200 mL	Ca=2000, Mg=4000, K=20000, Na=6000
Water Matrix Spike	CLP	CLPP-SPK-1	Inorganic Ventures	0.100 mL	Al=2000, Ba=2000, Be=50, Co=500, Cu=250, Cr=200, Ag=50, V=500, Zn=500
		CLPP-SPK-2	Inorganic Ventures	0.020 mL	Sb=100 (For GFAA Analysis)
		CLPP-SPK-3	Inorganic Ventures	0.100 mL	As=2000, Cd=50, Pb=500, Se=2000, Tl=2000
LCSW	Non-CLP	CLPP-CICV-1	Inorganic Ventures	1.00 mL	Al=10000, Ba=10000, Be=250, Ca=25000, Cr=1000, Co=2500, Cu=1250, Fe=5000, Mg=25000, Mn=2500, Ni=2500, K=25000, Ag=2500, Na=25000, V=2500, Zn=2500
		CLPP-CICV-2	Inorganic Ventures	0.010 mL	Sb=50 (For GFAA Analysis)
				1.00 mL	Sb=5000 (For ICP Analysis)
		CLPP-CICV-3	Inorganic Ventures	1.00 mL	As=5000, Cd=2500, Pb=5000, Se=5000, Tl=5000
		2007ICS-1	Inorganic Ventures	0.200 mL	B=1000, Mo=600, Si=460, Ti=2000
LCSW	CLP	CLPP-CICV-1	Inorganic Ventures	1.00 mL	Al=10000, Ba=10000, Be=250, Ca=25000, Cr=1000, Co=2500, Cu=1250, Fe=5000, Mg=25000, Mn=2500, Ni=2500, K=25000, Ag=2500, Na=25000, V=2500, Zn=2500
		CLPP-CICV-2	Inorganic Ventures	0.010 mL	Sb=50 (For GFAA Analysis)
		CLPP-CICV-3	Inorganic Ventures	1.00 mL	As=5000, Cd=2500, Pb=5000, Se=5000, Tl=5000

Notes:

1) Instructions assume initial volume = final volume = 100mL. If final volume varies from 100 mL, the amount of solution added must be adjusted proportionally.

2) Matrix spikes and LCSWs must contain all metals to be analyzed in associated samples. If any required metals are not contained in the listed spiking solutions, additional spiking using single element standards is necessary. Consult Section Supervisor for further instructions.

3) Note that two spiking levels are listed for antimony. Spike antimony according to to the analytical method required for associated samples.

ATTACHMENT B
EXAMPLE PAGE FROM DIGESTION LOGBOOK

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PROJECT Hot Plate Digestion- Waters Digestion Code JA01-L (01/01/93)

Notebook No. 100

Continued From Page —

CCAS Sample Number	Digestion Type	Initial Volume	Final Volume	Client
PBW	3010 (ICP)	100 mL	100 mL	
LCSW				
WJ8765-1				ABC Corp. (Rush)
-1 Dup				
-1 Spk				
-2				
-3				
-4				
WJ8321-1				XYZ, Inc.
-2				
-3				
-4				
-5				
-6				
-7				
-7 MS				
-7 MSD				

Reagent/Standard	Lot #	
HNO3	G300417	Note:
HCl	G200557	Antimony
CLPP-SPK-1	112-S	spiking
CLPP-SPK-2	312-S	for analysis
CLPP-SPK-3	113-S	by GFAA.
2007 ICS-1	214-S	
2007 SPK-B	216-S	
CLPPL SPK-1	115-S	
CLPPL SPK-2	312-S	
CLPPL-SPK-3	313-S	

Spiking initiated by: [illegible]

Continued on Page —

Read and Understood By

[illegible]	01/01/93	[illegible]	01/01/93

QC SAMPLE WORKSHEETS FOR WATER DIGESTIONS

COAST-TO-COAST ANALYTICAL SERVICES - ELEMENTS SECTION

AQUEOUS PREPARATION BLANK (PBW)

DIGESTION I.D. / DATE: _____

Method 3010 (HCl)	Initial Volume (mL) =	Final Volume (mL) =	
ELEMENT	MEASURED CONC. (mg/L)	ANALYSIS DATE	ACCEPTANCE LIMIT (mg/L)
Aluminum			0.10
Antimony (GFAA)			0.005
Antimony (ICP)			0.50
Arsenic (ICP)			0.50
Barium			0.005
Beryllium			0.005
Boron			0.10
Cadmium			0.010
Calcium			0.10 (PQL = 0.050)
Chromium			0.015
Cobalt			0.030
Copper			0.025
Iron			0.050 (PQL = 0.025)
Lead (ICP)			0.20
Magnesium			0.050
Manganese			0.005
Molybdenum			0.10
Nickel			0.040
Potassium (FAA)			0.10
Potassium (ICP)			0.50
Silver (ICP)			0.015
Sodium			0.20 (PQL = 0.10)
Tin			0.50
Titanium			0.015
Vanadium			0.025
Zinc			0.025

Method 3020 (HNO3)	Initial Volume (mL) =	Final Volume (mL) =	
ELEMENT	MEASURED CONC. (mg/L)	ANALYSIS DATE	ACCEPTANCE LIMIT (mg/L)
Arsenic (GFAA)			0.005
Lead (GFAA)			0.005
Selenium			0.005
Silver (GFAA)			0.002
Thallium			0.005

Notes: 1) Blank acceptance limits are equivalent to PQLs unless otherwise indicated.

2) A Corrective Action Report (CAR) must be filed for each PBW value outside acceptance limits.

All samples associated with contaminated blanks must be flagged with the appropriate notation.

QC SAMPLE WORKSHEETS FOR WATER DIGESTIONS

COAST-TO-COAST ANALYTICAL SERVICES - ELEMENTS SECTION

AQUEOUS LABORATORY CONTROL SAMPLE (LCSW)

DIGESTION I.D. / DATE: _____

If digestion contains HAZWRAP samples, check here: [ ]

Method 3010 (HCl) — Initial Volume (mL) = — Final Volume (mL) =

ELEMENT	MEASURED CONC. (mg/L) 1	MEASURED CONC. (mg/L) 2	ANALYSIS DATE 1	ANALYSIS DATE 2	INSTR. DILUTION FACTOR 1	INSTR. DILUTION FACTOR 2	TRUE VALUE (mg/L)	CALCULATED RECOVERY (%) 1	CALCULATED RECOVERY (%) 2	CONTROL LIMITS (%)
Aluminum							10.0			80.0-120
Antimony (GFAA)							0.050			80.0-120
Antimony (ICP)							5.00			80.0-120
Arsenic (ICP)							5.00			80.0-120
Barium							10.0			80.0-120
Beryllium							0.250			80.0-120
Boron							1.00			80.0-120
Cadmium							2.50			80.0-120
Calcium							25.0			80.0-120
Chromium							1.00			80.0-120
Cobalt							2.50			80.0-120
Copper							1.25			80.0-120
Iron							5.00			80.0-120
Lead (ICP)							5.00			80.0-120
Magnesium							25.0			80.0-120
Manganese							2.50			80.0-120
Molybdenum							0.600			80.0-120
Nickel							2.50			80.0-120
Potassium (FAA)							25.0			80.0-120
Potassium (ICP)							25.0			80.0-120
Silver (ICP)							1.25			80.0-120
Sodium							25.0			80.0-120
Tin							1.00			80.0-120
Titanium							2.00			80.0-120
Vanadium							2.50			80.0-120
Zinc							2.50			80.0-120

Method 3020 (HNO3) — Initial Volume (mL) = — Final Volume (mL) =

ELEMENT	MEASURED CONC. (mg/L) 1	MEASURED CONC. (mg/L) 2	ANALYSIS DATE 1	ANALYSIS DATE 2	INSTR. DILUTION FACTOR 1	INSTR. DILUTION FACTOR 2	TRUE VALUE (mg/L)	CALCULATED RECOVERY (%) 1	CALCULATED RECOVERY (%) 2	CONTROL LIMITS (%)
Arsenic (GFAA)							0.025			80.0-120
Lead (GFAA)							0.025			80.0-120
Selenium							0.0125			80.0-120
Silver (GFAA)							0.025			80.0-120
Thallium							0.020			80.0-120
										80.0-120

Notes: 1) LCS control limits are nominal values, effective 09/15/93.

2) Enter ALL measurements for each LCS, even those outside of the control limits. Future statistical control limits will be calculated from this database. Space is provided to record up to two measurements for each metal.

3) Enter all results and calculations to three significant figures.

4) A Corrective Action Report (CAR) must be filed for each LCS value outside acceptance limits.

5) For digestions containing HAZWRAP samples, recoveries for highlighted metals must be plotted on control charts.

QC SAMPLE WORKSHEETS FOR WATER DIGESTIONS

COAST-TO-COAST ANALYTICAL SERVICES — ELEMENTS SECTION

FINAL ELEMENT CONCENTRATIONS IN LIQUIDS (DUPLICATE & SPIKE)

Client Name: _____ Dig. ID / Date: _____

CCAS Sample Number: Sample Type (circle one): Dissolved Total

	REPLICATE #1		REPLICATE #2			SPIKE		
SW846 Method 3010 (HCl)	I.V. (mL):		I.V. (mL):			I.V. (mL):		
	F.V. (mL):		F.V. (mL):			F.V. (mL):		
ELEMENT	Conc. (mg/L)	Nota-tions	Conc. (mg/L)	Nota-tions	RPD (%)	Conc. (mg/L)	Added (mg/L)	% Rec.
Aluminum							2.000	
Antimony(GFAA)							0.100	
Antimony(ICP)							0.500	
Arsenic							2.000	
Barium							2.000	
Beryllium							0.050	
Boron							1.000	
Cadmium							0.050	
Calcium							2.000	
Chromium							0.200	
Cobalt							0.500	
Copper							0.250	
Iron							1.000	
Lead							0.500	
Magnesium							4.000	
Manganese							0.500	
Molybdenum							0.600	
Nickel							0.500	
Potassium							20.000	
Silver							0.050	
Sodium							6.000	
Tin							1.000	
Titanium							2.000	
Vanadium							0.500	
Zinc							0.500	
SW846 Method 3020 (HNO3)	I.V. (mL):		I.V. (mL):			I.V. (mL):		
	F.V. (mL):		F.V. (mL):			F.V. (mL):		
ELEMENT	Conc. (mg/L)	Nota-tions	Conc. (mg/L)	Nota-tions	RPD (%)	Conc. (mg/L)	Added (mg/L)	% Rec.
Arsenic							0.040	
Lead							0.020	
Selenium							0.010	
Silver							0.005	
Thallium							0.050	
SW846 Method 7470 (H2SO4)								
ELEMENT	Conc. (ug/L)	Nota-tions	Conc. (ug/L)	Nota-tions	RPD (%)	Conc. (ug/L)	Added (ug/L)	% Rec.
Mercury							1.000	

NOTES:

TEMPLATE: AMFORMROATALIQDAS.WK1

QC SAMPLE WORKSHEETS FOR WATER DIGESTIONS

COAST-TO-COAST ANALYTICAL SERVICES – ELEMENTS SECTION

FINAL ELEMENT CONCENTRATIONS IN LIQUIDS (SPIKE AND SPIKE DUP.)

Client Name: _____ Dig. ID / Date: _____

CCAS Sample Number: | Sample Type (Circle One): Dslvd. Total

	SAMPLE		SPIKE #1				SPIKE #2				
SW846 Method 3010 (HCl)	I.V. (mL): F.V. (mL):		I.V. (mL): F.V. (mL):				I.V. (mL): F.V. (mL):				Spk. Rec. Relative Percent Difference
ELEMENT	Conc. (mg/L)	Nota-tions	Conc. (mg/L)	Added (mg/L)	% Rec.	Nota-tions	Conc. (mg/L)	Added (mg/L)	% Rec.	Nota-tions	
Aluminum				2.000				2.000			
Antimony(GFAA)				0.100				0.100			
Antimony(ICP)				0.500				0.500			
Arsenic				2.000				2.000			
Barium				2.000				2.000			
Beryllium				0.050				0.050			
Boron				1.000				1.000			
Cadmium				0.050				0.050			
Calcium				2.000				2.000			
Chromium				0.200				0.200			
Cobalt				0.500				0.500			
Copper				0.250				0.250			
Iron				1.000				1.000			
Lead				0.500				0.500			
Magnesium				4.000				4.000			
Manganese				0.500				0.500			
Molybdenum				0.600				0.600			
Nickel				0.500				0.500			
Potassium				20.000				20.000			
Silver				0.050				0.050			
Sodium				6.000				6.000			
Tin				1.000				1.000			
Titanium				2.000				2.000			
Vanadium				0.500				0.500			
Zinc				0.500				0.500			
SW846 Method 3020 (HNO3)	I.V. (mL): F.V. (mL):		I.V. (mL): F.V. (mL):				I.V. (mL): F.V. (mL):				SpK. Rec. Relative Percent Difference
ELEMENT	Conc. (mg/L)	Nota-tions	Conc. (mg/L)	Added (mg/L)	% Rec.	Nota-tions	Conc. (mg/L)	Added (mg/L)	% Rec.	Nota-tions	
Arsenic				0.040				0.040			
Lead				0.020				0.020			
Selenium				0.010				0.010			
Silver				0.005				0.005			
Thallium				0.050				0.050			
SW846 Method 7470 (H2SO4)											SpK. Rec. Rel. Pct. Difference
ELEMENT	Conc. (ug/L)	Nota-tions	Conc. (ug/L)	Added (ug/L)	% Rec.	Nota-tions	Conc. (ug/L)	Added (ug/L)	% Rec.	Nota-tions	
Mercury				1.000				1.000			

NOTES:

TEMPLATE: AAFORMS\DATA\LIQSLSD.WK1

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-609
Revision History
Cover Page
Page 1

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

Prepared By: Edward A. Morgan Date: 7-24-96

Approved By:

Group Supervisor: Christopher J. Dodd Date: 7/24/96

Operations Manager: John C. Burton Date: 7/24/96

QA Officer: Julie Riordi Date: 072496

General Manager: Dennis P. Hughes Date: 07/24/96

Revision History:

Revision	Changes	Authorization	Date

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-609-00**, titled **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-609-00**, titled **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

Recipient: _____ Date: _____

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

1.0 SCOPE AND APPLICATION

Inductively coupled plasma atomic-emission spectroscopy (ICP) determines trace elements, including metals, in solution. The purpose of this SOP is to describe the procedures used by Katahdin Analytical Services, Inc. personnel to analyze aqueous and solid samples for trace metals by EPA Methods 200.7 (Methods for Chemical Analysis of Water and Wastes, US EPA 600), 6010A (Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, US EPA SW 846), and 200.7 CLP-M (USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis) using the Thermo Jarrell Ash 61 ICAP spectrometer.

Sample types that may be analyzed using these methods include drinking waters, ground waters, aqueous samples, mobility-procedure extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes. The following elements may be analyzed under this SOP: Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Ni, K, Se, Si, Ag, Na, Sn, V, Y, and Zn.

Aqueous samples analyzed under EPA Method 200.7 may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has a turbidity of <1 NTU at the time of analysis. All other samples require digestion prior to analysis. ICP analysis under EPA Methods 200.7 and 200.7 CLP-M may be performed after sample digestion as described in those methods. EPA Methods 3005, 3010, and 3050 describe appropriate digestion procedures for samples to be analyzed by ICP under EPA Method 6010. Refer to current revisions of Katahdin SOPs CA-604 and CA-605 for sample digestion procedures.

1.1 Definitions

Analytical Spike - An aliquot of a sample to which a known amount of analyte has been added before analysis and after digestion, if digestion is required.

CCB - Continuing Calibration Blank - An analyte-free solution consisting of acidified deionized water used to verify calibration accuracy periodically during analysis.

CCV - Continuing Calibration Verification - A midrange standard used to verify calibration accuracy periodically during analysis.

CRI - Contract Required detection limit sample for ICP - A low concentration standard used to verify calibration accuracy near the low end of the calibration range.

Duplicate - A second aliquot of a sample that is prepared and analyzed in the same way as the original sample in order to determine the precision of the method.

ICB - Initial Calibration Blank - An analyte-free solution consisting of acidified deionized water used to verify calibration accuracy.

ICS - Interference Check Sample - Two standards (ICSA and ICSAB) used to verify the effectiveness of interelement correction and background correction. Solution ICSA contains only interferents (Al, Ca, Fe, and Mg) at high concentrations (hundreds of mg/L);

solution ICSAB contains interferents at the same concentrations as well as analytes at low (1 mg/L or less) concentrations.

ICP - Inductively Coupled Plasma atomic emission spectroscopy.

ICV - Initial Calibration Verification - A standard made from a source independent from the calibration standards and with analyte concentrations different from those in the CCV; used to verify the accuracy of the instrument calibration.

IDL - Instrument Detection Limit - The lowest concentration of an analyte that can be determined with 95% confidence.

LCS - Laboratory Control Sample - A standard or solid reference material that has been brought through the sample preparation process.

LRS - Linear Range Standard - A high-concentration standard used to determine the upper reporting limit of the ICP calibration.

PB - Preparation Blank - Deionized water that has been brought through the sample preparation process.

PQL - Practical Quantitation Limit - The lowest concentration of an analyte that is routinely reported by the laboratory; nominally three to five times the IDL.

Matrix Spike - An aliquot of a sample to which a known amount of analyte has been added before digestion.

Serial Dilution - The dilution of a sample by a factor of five. When corrected by the dilution factor, the measured analyte concentrations of the diluted sample should agree with those of the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of, analysts experienced in ICP analysis by EPA Methods 6010A, 200.7, and 200.7 CLP-M. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Laboratory Technical Personnel Training".

It is the responsibility of all Katahdin technical personnel involved in ICP analysis by Method 6010A, 200.7, and 200.7 CLP-M to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the group supervisor or designated qualified data reviewer responsible for this data.

It is the responsibility of the Group Supervisor to oversee that members of their group follow this SOP, that their work is properly documented and to indicate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical safety procedures and the Katahdin Chemical Hygiene Plan and follow appropriate procedures such as: wearing safety glasses and gloves when working with chemicals or near an instrument; not taking food or drink into the laboratory; each analyst should possess a respirator and be trained on how to use it properly and should know the location and use of all safety equipment.

Samples, sample digestates, standards, and other reagents used in ICP analysis may contain high concentrations of acids and toxic metals. Safety glasses should be worn when changing or adjusting argon tanks.

1.4 Waste Disposal

Wastes from ICP analysis should be disposed of in a manner appropriate to the hazards they present. Further information regarding waste classification and disposal may be obtained by consulting the Katahdin Chemical Hygiene Plan and the Group Supervisor.

2.0 SUMMARY OF METHOD

The method describes a technique for the simultaneous multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission from sample atoms entrained in an argon plasma by optical spectroscopy. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where thermal excitation of entrained atoms and ions occurs. Characteristic atomic-line and ionic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emitted lines are monitored by photomultiplier tubes. Photocurrents from the photomultiplier tubes are measured by a computer system. Element concentrations of unknown samples are quantitated by comparison of sample emission intensities to emission intensities of standards of known concentration. A background correction technique is used to compensate for variable background contribution to the determination of trace elements.

Background is measured adjacent to the analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, has been determined by the complexity of the spectrum adjacent to the analytical line. The position used must be relatively free of spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength. The possibility of additional interferences (noted in section 3) must be recognized and appropriate corrections applied.

3.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as spectral interferences, physical interferences, and chemical interferences.

Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background from stray light from the line emission of high concentration elements. The first of these effects is compensated by utilizing the computer correction of raw data, requiring the monitoring and measurement of the interfering element (interelement correction). The second effect is controlled by choosing analytical wavelengths that are free from overlapping molecular emission spectra. The third and fourth effects are usually compensated by a background correction adjacent to the analyte line. Uncorrected spectral interferences may be detected through examination of serial dilution and matrix spike data.

Physical interferences are generally considered to be effects associated with sample nebulization and transport processes. Such properties as changes in viscosity and surface tension can cause significant inaccuracies especially in samples that may contain high dissolved solids and/or acid concentrations. Matrix matching of standards and samples and the use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem that can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Regular cleaning of nebulizer tips and dilution of samples with high dissolved solids contents are used to control this problem. Physical interferences may also be compensated through the use of an internal standard. Uncorrected physical interferences may be detected through examination of serial dilution and matrix spike data. Instrument drift caused by the salting up of nebulizer tips may also be detected by looking for oriented drift in calibration verification standards analyzed regularly throughout the run.

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique; however, if observed they can be minimized by careful selection of operating conditions (i.e., incident power, observation position, etc.), by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element. Uncorrected chemical interferences may be detected through examination of serial dilution data.

4.0 APPARATUS AND MATERIALS

4.1 Thermo Jarrell Ash ICAP 61 Inductively Coupled Plasma Atomic Emission Spectrometer
4.2 Thermo Jarrell Ash Model 300 Autosampler
4.3 Autosampler Tubes (13mm x 100mm polyethylene or polypropylene)
4.4 Peristaltic Pump (Gilson minipuls 2 or equivalent)
4.5 Peristaltic Pump Tubing (2-stop Tygon orange-orange and white-white)
4.6 Argon gas supply (welding grade or better)
4.7 Water recirculating system for cooling the radio frequency coil of the plasma torch

5.0 REAGENTS

5.1 Hydrochloric acid, conc. (ultra-high purity grade or equivalent).
5.2 Nitric acid, conc. (ultra-high purity grade or equivalent).
5.3 Deionized water (ASTM Type II or equivalent).
5.4 Rinse solution (matrix-matched to acid concentrations of samples).
5.5 Calibration blank (matrix-matched to acid concentrations of samples).
5.6 Single element and multielement standard stock solutions (purchased from vendors and traceable to NIST reference materials).
5.7 Calibration standards (prepared from single element and multielement standard stock solutions, matrix-matched to acid concentrations of samples).
5.8 Check standards (prepared from single element and multielement standard stock solutions, matrix-matched to acid concentrations of samples).

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples to be analyzed for trace metals by ICP should be collected and preserved as described in the following table.

Matrix	Container[1]	Collection Volume/ Weight	Preservation/ Treatment	Holding Time
Aqueous (total)	P, G	250 mL	HNO_3 to pH < 2	6 months
Aqueous (dissolved)	P, G	250 mL	Filter, HNO_3 to pH < 2	6 months
Solid	P, G	10 g	Cool, 4°C	6 months

[1] P = polyethylene or , G = glass

7.0 PROCEDURES

ICP START UP

7.1 Check that cooling water is on.
7.2 Set timer on side of torch box (controls argon flow and sample pump; instrument will automatically shut down when timer reaches zero).
7.3 Open argon regulator on wall behind instrument. Make sure pressure is set to 60 - 70 psi.
7.4 Turn on Torch, Auxiliary, and Sample argon switches (up position).
7.5 Engage pump tension, pump rinse until fog forms in spray chamber.
7.6 Set Power Control switch to Manual.
7.7 Press RF On (red button).
7.8 Adjust Power to 0.5 kW (Knob between power meters).
7.9 Turn off sample argon.
7.10 Push ignite button. Increase power until plasma forms, turn on sample argon. (If streamers form in torch, slowly decrease power until they disappear.) Turn Power Control switch to automatic, and turn power knob fully clockwise.
7.11 Allow instrument to warm up for 1-2 hours.
7.12 Check profile: aspirate 5 mg/L copper-manganese solution, select Operation, Analysis, Method Name : FEW, Profile (F5), Automatic (F3), set flush time to 30 seconds, and Run (F1).
7.13 Adjust micrometer for the entrance slit: clockwise, if peak position is > 0.1, or counter clockwise, if peak position is < -0.1. Press ESC, ENTER, Automatic (F3), and Run (F1). Repeat until peak position is between 0.1 and -0.1. Then Press F9 to accept the setting. Press ESC.
7.14 Check manganese to copper intensity ratio: select Analyze (F1) then Run (F1). Record results in instrument maintenance log.

ANALYSIS OF SAMPLES

7.15 Change Analysis Data File name to "B" plus the current date (B041596, if second run of the day use B0415A) : select Methods , Development, Method Name, type in method name, Method Info (F3), enter file name, Done/Keep (F9), Done/Keep (F9).

7.16 Create an autosampler table: select Operation, Autosampler, Filer (F8), Autosampler tables (5), select Default, Copy (F8), enter autosampler file name (usually the same as the data file name). Press ESC twice then enter autosampler table name or choose from List (F6). Select Edit Set (F1), Edit Samples (F1). Press F1 to insert new sample positions, F2 to delete sample positions, F3 to insert new QC sample positions, and F5 to insert calibration standards. When finished editing, press Done/Keep (F9) three times to save the table. Do not attempt move the cursor below the bottom of the autosampler table as this will lock up

the keyboard and require a reboot of the PC. To add additional sample or QC sample positions to the end of the table, use the ALT options. The analysis sequence specified in the autosampler table should be as follows:

7.16.1 Calibrate.
7.16.2 Analyze ICV, ICB, CRI, LRS, ICSA, ICSAB, CCV, and CCB (in order).
7.16.3 Analyze up to 10 samples.
7.16.4 Analyze CCV and CCB.
7.16.5 Repeat steps 7.16.3 and 7.16.4.
7.16.6 After 8 hours and/or at the end of the run, analyze CRI, ICSA, ICSAB, CCV, and CCB (in order).

7.17 Begin sample analyses: select Operation, Analysis, and enter method name. Select Autosampler (F9), enter autosampler table name, and Run (F1). To pause or terminate the run, select Abort Run (F1).

ICP SHUT DOWN

7.18 Press RF OFF (blue) button, turn Power knob fully counterclockwise.
7.19 Set Automatic Power Control to Manual.
7.20 Turn off sample pump and loosen pump tubing.
7.21 Turn off argon at wall regulator.

Note : The timer on the side of the torch box can be set to automatically shut down the plasma and the sample pump after analyses are complete.

MAINTENANCE

7.22 Peristaltic pump tubing should be replaced approximately weekly, or whenever tubing shows flattening or other signs of wear.
7.23 The quartz torch and spray chamber should be cleaned whenever they are noticeably dirty or when analytical performance is poor. The spray chamber is cleaned in an ultrasonic bath using a mild solution of soapy water. The torch is cleaned by soaking in aqua regia.
7.24 The printer paper supply should be checked each day before beginning analysis, and additional paper added as required.
7.25 The level of waste in the waste container should be checked each day before beginning operation, and the container should be emptied if insufficient room remains to contain the day's waste.

DATA REDUCTION AND REPORTING

Results are obtained in concentration units (mg/L) from the instrument, and little data reduction is required. Results that exceed the linear range of the instrument may not be reported - the sample

must be appropriately diluted and reanalyzed for the analytes in question. Dilution factors are entered in the autosampler table and results are corrected for dilutions by the instrument computer. Results for digestates of solid samples must be converted, through a calculation that takes into account the mass of sample digested and the solids content of the sample, to units of mg/kg dry weight. The dry weight calculation is as follows:

$$\text{Concentration (mg/kg dry wt.)} = \frac{(\text{Conc.})*(\text{Vol.})*1000}{(\text{Mass})*(\%\text{Solids})}$$

where:

Conc. = measured analyte concentration in mg/L

Vol. = final volume of digestate in Liters

Mass = mass of sample digested in grams wet weight

%Solids = percent solids of the sample, expressed as a decimal

Results of aqueous samples that were concentrated during digestion should be corrected for that concentration before reporting. The calculation is as follows:

$$\text{Concentration (mg/L)} = \frac{(\text{Conc.})*(\text{FV})}{(\text{IV})}$$

where:

Conc. = measured analyte concentration in mg/L

FV = final volume of digestate in Liters

IV = initial volume of sample digested in Liters

Results are reported downto the laboratory's practical quantitation level (PQL), unless otherwise requested. Results below the PQL should be reported as "<PQL". Sometimes a sample must be diluted prior to analysis to reduce matrix interference effects. If a result below the PQL is obtained for such a sample, the result should be reported as less than the PQL multiplied by the dilution factor - in effect, less than the elevated PQL. For example, if a sample is diluted 1:5 to reduce matrix intereference effects, and the resulting measured concentration is below the laboratory's PQL of 0.010 mg/L for that element, the result should be reported as "<0.050 mg/L" (i.e., <0.010 * 5).

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

ACCEPTANCE CRITERIA

Each of the EPA methods described in this SOP requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated by method in Table 1, QC Requirements.

QUALITY CONTROL CALCULATIONS

Duplicate sample analysis - Duplicate samples must be analyzed for each analyte analyzed in the original sample. The relative percent difference (RPD) between the original sample and its duplicate must be calculted for each analyte as follows:

$$\text{RPD (\%)} = \frac{|S - D|}{(S + D)/2} * 100\%$$

where:

S = Original sample value
D = Duplicate sample value

Sample matrix spike analysis - Sample matrix spike analysis is used to assess the effect of sample matrix on the digestion and measurement metodologies. Spikes are added to client samples before digestion, prior to the addition of other reagents. The percent recovery of the spike addition must be calculated for each analyte as follows:

$$\text{Recovery (\%)} = \frac{(P - S)}{A} * 100\%$$

where:

P = Spiked sample value
S = Original sample value
A = Spike amount

Laboratory Control Sample (LCS) - An aqueous or solid LCS must be prepared and anlyzed with each digestion batch. An aqueous LCS consists of spiked deionized water, and a solid LCS is a vendor-supplied solid reference material with vendor supplied true values and acceptance limits. The percent recovery of the LCS must be calculated for all analytes as follows:

$$\text{Recovery (\%)} = (L/TV) * 100\% \qquad \text{For aqueous LCS}$$

$$\text{Recovery (\%)} = \frac{L*(Vol.)*1000}{(Mass)*(TV)} * 100\% \qquad \text{For solid LCS}$$

where:

L = Measured LCS result in mg/L
TV = True value of the LCS in mg/L for aqueous, mg/kg for solid
Vol = Final volume of LCS digestate in Liters
Mass = Mass of solid LCS material digested in grams

Serial dilution analysis - A serial dilution is analyzed to check for chemical or physical interferences. The percent difference between the original sample and the serial dilution shuld be calculated as follows:

$$\text{Difference (\%)} = \frac{|L-S|}{S} * 100\%$$

where:

L = Serial dilution result (corrected for dilution)
S = Original sample result

9.0 METHOD PERFORMANCE

10.0 APPLICABLE DOCUMENTS/REFERENCES

ICAP 61 Operator's Manual, Thermo Jarrell Ash Corporation.

Methods for Chemical Analysis of Water and Wastes, US EPA 600 / 4-91-010, 1991, Method 200.7 Revision 3.3.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Method 6010A, p. 6010-1-17, US EPA SW 846, Third Edition, Updates I, II, IIA, and IIB, Revised January 1995.

US EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Document Number ILM03.0.

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

TABLE 1

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
6010A	Initial Calibration, minimum 1 point plus a calibration blank.	Daily prior to sample analysis.		
	Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 10% of true value.	Correct problem and repeat calibration.
	Initial Calibration Blank (ICB)	Before beginning a sample run.	Less than PQL.	Correct probem and repeat calibration.
	Low Level Standard (CRI)	Before beginning a sample run and after 8 hours and/or at the end of the run.	Recovery within ± 50% of true value.	No corrective action required at this time.
	Linear Range Standard (LRS)	Before beginning a sample run.	Recovery within ± 5% of true value.	If recovery of CCV or ICSA is within acceptance criteria, use the concentration of that standard as the upper reporting limit. Otherwise, correct problem and repeat calibration.
	Interference Check Standard A (ICSA)	Before beginning a sample run and after 8 hours and/or at the end of the run.	For Al, Ca, Fe, and Mg, recovery within ± 20% of true value. For analytes not spiked, ± PQL, or, if PQL ≤ 0.01 mg/L, ± 2x PQL.	Correct problem (recalculate IECs if necessary) and repeat calibration. Reanalyze all affected samples.
	Interference Check Standard B (ICSAB)	Before beginning a sample run and after 8 hours and/or at the end of the run	Recovery of each analyte within ± 20% of true value.	Correct problem (recalculate IECs if necessary) and repeat calibration. Reanalyze all affected samples.
	Continuing Calibration Verification (CCV)	After every 10 samples and at end of the run	Recovery within ± 10% of true value	Repeat calibration and reanalyze all samples analyzed since the last successful CCV.
	Continuing Calibration Blank (CCB)	After every 10 samples and at end of the run.	Less than PQL.	Repeat calibration and reanalyze samples if measured concentrations < 10x CCB value.

TABLE 1, cont'd

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
6010A, cont'd	Serial Dilution (L)	One per digestion batch.	If original sample result is at least 50x MDL, 5-fold dilution must agree within ± 10% of the original result.	Flag results or dilute and reanalyze sample to eliminate interference.
	Preparation Blank (PBW/PBS)	One per digestion batch.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Control Sample (LCSW/LCSS)	One per digestion batch.	Recovery within ± 20% of true value.	Redigest all affected samples.
	Duplicate Sample (D)	1 per 20 samples.	RPD ≤ 20%.	Flag results.
	Spike Sample (S)	1 per 20 samples.	Recovery ± 25% of true value, if sample > 4x spike value	Flag results
	MDL Study	Once per year	MDLs < PQLs	Repeat MDL study

TABLE 1, cont'd

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
200.7 CLP-M	Initial Calibration, minimum 1 point plus a calibration blank.	Daily prior to sample analysis		
	Initial Calibration Verification (ICV), prepared from a second source.	Immediately after initial instrument calibration.	Recovery within ± 10% of true value.	Terminate analysis, correct problem, repeat calibration, and reanalyze ICV.
	Initial Calibration Blank (ICB)	Immediately after the ICV.	≤ CRDL.	Correct problem, recalibrate, and reanalyze ICV and ICB.
	CRDL Standard for ICP (CRI)	At the beginning of a sample run, and after 8 hours and/or at the end of the run	No acceptance limit is applied at this time	No corrective action required at this time
	Linear Range Standard (LRS)	Analyze as a sample quarterly	Recovery within ± 5% of true value.	Correct problem, repeat calibration, and reanalyze.
	Interference Check Standard A (ICSA)	Before beginning a sample run and after 8 hours and/or at the end of the run	For Al, Ca, Fe, and Mg, recovery within ± 20% of true value.	Terminate analysis, correct problem, recalibrate, and reanalyze all analytical samples analyzed since last good ICS.
	Interference Check Standard B (ICSAB)	Before beginning a sample run and after 8 hours and/or at the end of the run	Each analyte ± 20% of true value	Terminate analysis, correct problem, recalibrate, and reanalyze all analytical samples analyzed since last good ICS.
	Continuing Calibration Verification (CCV)	After every 10 samples and at end of the run	Recovery within ± 10% of true value.	Terminate analysis, correct problem, repeat calibration, verify calibration, and reanalyze all samples analyzed since the last compliant calibration verification.
	Continuing Calibration Blank (CCB)	Immediately after each CCV.	Each analyte ≤ CRDL	Terminate analysis, correct problem, repeat calibration, verify calibration, and reanalyze all samples analyzed since the last compliant calibration blank.
	Serial Dilution (L)	Once per each matrix type or each SDG, whichever is more frequent.	If original sample result is at least 50x IDL, 5-fold dilution must agree within ± 10% of the original result.	Flag results for affected analytes for all associated samples with "E".

TABLE 1, cont'd

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
200.7 CLP-M, cont'd	Preparation Blank (PBW/PBS)	One per digestion batch or per SDG, whichever is more frequent.	Absolute value $\leq$ CRDL	1) If blank value >CRDL, report sample results if <CRDL or >10x the blank value; otherwise redigest. 2) If blank value less than negative CRDL, report sample results if >10x blank value, otherwise redigest.
	Laboratory Control Sample (LCSW/LCSS)	One per digestion batch or per SDG, whichever is more frequent.	Recovery within $\pm$ 20% of true value.	Redigest and reanalyze all associated samples for affected analytes (except Ag and Sb).
	Duplicate Sample (D)	Once per each matrix type or each SDG, whichever is more frequent.	RPD $\leq$ 20% if sample and duplicate $\geq$ 5x CRDL; $\pm$ CRDL if sample or duplicate < 5x CRDL.	Flag results for affected analytes for all associated samples with "*".
	Spike Sample (S)	Once per each matrix type or each SDG, whichever is more frequent	Recovery $\pm$ 25% of true value, if sample > 4x spike value.	1) Flag results for affected analytes for all associated samples with "N".
	MDL Study	Once per year	MDLs < corresponding PQLs	Repeat MDL study

TABLE 1, cont'd

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
200.7	Initial Calibration	Daily prior to sample analysis		Correct problem then repeat calibration
	Quality Control Sample (QCS), prepared from a second source (equivalent to ICV)	After preparation of fresh calibration standards or quarterly, whichever occurs first, to verify accuracy of the calibration standards.	Recovery within ± 5% of true value for mean of three replicate analyses of the QCS.	Correct problem and reanalyze the QCS.
	Instrument Performance Check Solution (IPC, equivalent to CCV)	Immediately following daily calibration, after every 10 samples, and at the end of the run.	1) For first IPC of run, recovery within ±5% of true value. 2) For subsequent IPCs, recovery within ±10% of true value.	Reanalyze IPC once. If reanalysis failes, terminate analysis, correct problem, and reanalyze all samples analyzed since last compliant IPC.
	Calibration Blank (CB, equivalent to ICB and CCB)	Immediately following daily calibration, after every 10 samples, and at the end of the run.	Less than PQL.	Reanalyze CB once. If reanalysis failes, terminate analysis, correct problem, and reanalyze all samples analyzed since last compliant CB.
	Linear Range Standard (LRS)	Every 6 months	No criteria given	No corrective action required at this time
	Spectral Interference Check Solutions (SIC)	Periodically, depending on demonstrated variability of IEC factors, to verify effectiveness of interelement correction.	Apparent concentrations of unspiked analytes less than PQL.	Recalculate interelement correction factors and recalibrate.

TABLE 1, cont'd

QC REQUIREMENTS

Method	QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
200.7, cont'd	Serial Dilution (L)	One per digestion batch.	If original sample result is at least 50x MDL, 5-fold dilution must agree within ± 10% of the original determination.	Flag results; dilute sample or analyze by method of standard additions to eliminate interference.
	Laboratory Reagent Blank (LRB, equivalent to PBW/PBS)	One per digestion batch.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Fortified Blank (LFB, equivalent to LCSW/LCSS)	One per digestion batch.	Recovery within ± 15% of true value	Redigest all affected samples.
	Duplicate Sample (D)	No required frequency at this time.	No criteria given.	No corrective action required at this time.
	Laboratory Fortified Sample (S)	1 per 10 samples	Recovery ± 15% of true value, if sample > 10x spike value	Flag results
	MDL Study	Once per year	MDLs < corresponding PQLs	Repeat MDL study

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-609-00	METHODS 6010A, 200.7 CLP-M, and 200.7
Apparatus/Materials		
Reagents		
Sample preservation/ handling		
Procedures		
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		
QC - Calibration Blanks	Acceptance criteria employed for 6010A and 200.7: ± PQL	Acceptance criteria stated in 6010A and 200.7: mean blank value ± 3 standard deviations

TITLE: **TRACE METALS ANALYSIS USING THE TJA 61 ICAP**

FIGURE 1

EXAMPLE OF LOGBOOK PAGE

BOOK 1, PAGE 0000100

KATAHDIN ANALYTICAL SERVICES, INC.
Elements Section
ICP Run Cover Sheet - TJA 61 ICAP

Run ID:_____ Date Analyzed:_____ Analyst:_____

Standard Name	*Standard ID Code*	*Standard Preparation Date*
Calibration Std #1		
Calibration Std #2		
Calibration Std #3		
ICV (Initial Cal. Ver.)		
CCV (Cont. Cal. Ver.)		
ICSA (Intf. Check Soln. A)		
ICSAB (Intf. Check Soln. AB)		
CRI (CRDL Std. for ICP)		

Reported Data Log

Katahdin Sample #	Digestion ID	Client	Analytes

Page_____of_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-610
Revision History
Cover Page
Page 1

TITLE: TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

Prepared By: Christopher J. Dodd Date: 7/24/96

Approved By:

Group Supervisor: Edward A. Morgan Date: 7-24-96

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QA Officer: Julie Rivardi Date: 07/24/96

General Manager: Dennis P. Hufford Date: 07/24/96

Revision History:

Revision	Changes	Authorization	Date

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-610-00,** titled **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY.**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-610-00,** titled **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY.**

Recipient: _____ Date: _____

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used by Katahdin Analytical Services, Inc. personnel for the analysis of mercury in aqueous samples using the Leeman Labs PS200 Automated Mercury Analyzer.

This method is applicable to the determination of mercury in drinking, surface, ground, sea, and brackish waters, industrial and domestic wastewaters, and mobility procedure extracts under EPA Methods 245.1 (Methods for Chemical Analysis of Water and Wastes, US EPA 600), 245.1 CLP-M (USEPA Contract Laboratory Program, Statement of Work for Inorganic Analyses), and 245.1 CLP-M and 7470AA (Test Methods for Evaluating Solid Waste, Physical/ Chemical Methods, US EPA SW 846).

1.1 Definitions

CB (Calibration Blank) or CCB (Continuing Calibration Blank) - An analyte-free solution consisting of acidified deionized water used to verify calibration accuracy periodically during analysis.

CCV - Continuing Calibration Verification - A midrange standard used to verify calibration accuracy periodically during analysis.

CRA - Contract Required detection limit sample for AA - A low concentration standard used to verify calibration accuracy near the low end of the calibration range.

Duplicate - A second aliquot of a sample that is prepared and analyzed in the same way as the original sample in order to determine the precision of the method.

ICB - Initial Calibration Blank - An analyte-free solution consisting of acidified deionized water used to verify calibration accuracy.

ICV - Initial Calibration Verification - A standard made from a source independent from the calibration standards and with analyte concentrations different from those in the CCV; used to verify the accuracy of the instrument calibration.

IDL - Instrument Detection Limit - The lowest concentration of an analyte that can be determined with 95% confidence by the instrument.

LFB - Laboratory Fortified Blank - An aliquot of LRB to which a known quantity of the method analyte has been added.

LRB - Laboratory Reagent Blank - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with other samples.

LFM - Laboratory Fortified Sample Matrix - An aliquot of a sample to which a known quantity of the method analyte is added in the laboratory.

LCS - Laboratory Control Sample - A standard or solid reference material that has been brought through the sample preparation process.

PB - Preparation Blank - Deionized water that has been brought through the sample preparation process.

PQL - Practical Quantitation Limit - The lowest concentration of an analyte that is routinely reported by the laboratory; nominally three to five times the IDL.

QCS - Quality Control Sample - A solution of the method analyte of known concentration that is obtained from a souce external to the laboratory and different from the source of calibration standards.

Matrix Spike - An aliquot of a sample to which a known amount of analyte has been added before digestion.

MDL - Method Detection Limit - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of mercury by EPA Methods 245.1, 245.1 CLP-M, and 7470A. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Laboratory Technical Personnel Training".

It is the responsibility of all Katahdin technical personnel involved in analysis of mercury by Methods 245.1, 245.1 CLP-M, and 7470A to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the group supervisor or designated qualified data reviewer responsible for this data.

It is the responsibility of the Group Supervisor to oversee that members of their group follow this SOP, that their work is properly documented and to indicate periodic review of the associated logbooks.

1.3 Safety

Many of the samples and reagents used in cold vapor atomic absorption are toxic or corrosive. Rubber gloves, safety glasses, lab coats, and other protective clothing should be worn whenever these materials are handled. Because of the toxic nature of mercury vapor, care must be taken to avoid its inhalation. The instrument exhaust fan must be operational whenever the instrument is in use (the fan should never be shut off).

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical safety procedures and the Katahdin Chemical Hygiene Plan and Safety Manual and follow appropriate procedures such as: wearing safety glasses and gloves when working with chemicals or near an instrument; not taking food or drink into the laboratory; each analyst should possess a respirator and be trained on how to use it properly and should know the location and use of all safety equipment.

1.4 Waste Disposal

Samples, sample digestates, standards, and other reagents used in cold vapor atomic absorption may contain high concentrations of acids, mercury, and other toxic metals. They should be disposed of in a manner appropriate to the types of hazards they present. Further information regarding waste classification and disposal may be obtained by consulting the laboratory's Chemical Hygiene Plan and Safety Manual and the Group Supervisor.

2.0 SUMMARY OF METHOD

The cold vapor atomic absorption technique is based on the absorption of radiation at 253.7 nm by mercury vapor. It relies on the volatility of elemental mercury at room temperature. During preparation, organic mercurials are oxidized and elemental mercury is ionized to Hg^{3+}. During instrumental analysis, mercuric ions are reduced to elemental mercury by the addition of stannous chloride. Elemental mercury is then aerated from solution and passes through a cell positioned in the path of a mercury spectrophotometer, where absorbance (peak height) is measured as a function of mercury concentration and recorded by the associated computer. The mercury vapor is then swept out of the instrument into an exhaust hood, where it is evacuated from the laboratory.

3.0 INTERFERENCES

In addition to inorganic forms of mercury, organic mercurials may be present in environmental samples. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. The presence of undigested organo-mercurials in samples will result in a low bias for analytical results. Certain volatile organic materials will also non-specifically absorb radiation at the 253.7 nm analytical

wavelength. The presence of such compounds may result in a high bias for analytical results. For these reasons, complete digestion using potassium permanganate and potassium persulfate is required for all environmental samples. Complete digestion is indicated by the persistence of the purple permanganate color (indicating the presence of excess permanganate) following digestion.

Sea waters, brines, and industrial effluents high in chlorides require additional permanganate to maintain a persistent purple color following digestion. During the oxidation step, chlorides are converted to free chlorine which will absorb radiation at the 253.7 nm analytical wavelength. Any free chlorine thus generated will be present in the headspace of the BOD bottles following digestion. Because samples are poured into autosampler tubes prior to analysis by the PS200, any free chlorine present in the headspace of the BOD bottles is not sampled by the instrument and the analysis is free of chlorine interference.

4.0 APPARATUS AND MATERIALS

4.1 300 mL BOD bottles

4.2 Water bath capable of maintaining a constant temperature of 95° C.

4.3 Adjustable volume pipettes - 0 to 1000 uL, 100 to 1000 uL, 1000 to 5000 uL

4.4 Leeman Labs PS200 Automated Mercury Analyzer

4.5. Peristaltic pump tubing, 2-stop: 1.52 mm ID viton tubing, yellow-blue stops (sample tubing); 0.057 in ID polyethylene tubing, gray stops (waste drain tubing); 0.020 in ID polyethylene tubing, orange-yellow stops (reductant tubing)

4.6 Disposable polystyrene or polypropylene culture tubes, 25x100 mm, for use as autosampler tubes

4.7 Disposable polystyrene or polypropylene culture tubes, 13x100 mm, for use as autosampler tubes

5.0 REAGENTS

5.1 ASTM Type II reagent water.

5.2 Concentrated sulfuric acid, trace metal grade

5.3 Concentrated nitric acid, trace metal grade

5.4 Concentrated hydrochloric acid, trace metal grade

5.5 10% hydrochloric acid solution: Add 100 mL of trace metal grade concentrated hydrochloric acid to 500 mL of ASTM Type II water and bring to a final volume of 1 L.

5.6 Potassium permanganate solution, 5% w/v: Dissolve 50 g of potassium permanganate in 1 L ASTM Type II water. Reagent should be labeled as suitable for use in mercury determination.

5.7 Potassium persulfate solution, 5% w/v: Dissolve 50g of potassium permanganate in 1L ASTM Type II water. Reagent should be labeled as suitable for use in mercury determination.

5.8 Hydroxylamine hydrochloride solution: Dissolve 120 g hydroxylamine hydrochloride in ASTM Type II water and dilute to a final volume of 1 L. Reagent should be labeled as suitable for use in mercury determination.

5.9 Stannous chloride solution: Add 100 mL concentrated hydrochloric acid to 500 mL of ASTM Type II water. Add 100 g stannous chloride and bring to a final volume of 1 L. Mix to dissolve. Heating may be necessary to effect complete dissolution. Reagent should be labeled as suitable for use in mercury determination.

5.10 Intermediate Mercury Standard A: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. This intermediate standard is used to prepare calibration standards, matrix spikes, CCVs, LCSs, and the CRI (refer to Section 8.0). The identity of the stock standard currently used to prepare this intermediate standard and instructions for its dilution may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard A must be prepared fresh daily, and disposed of appropriately after use. (Note: the concentrations of all stock standards must be certified by the vendors as traceable to NIST reference materials).

5.11 Intermediate Mercury Standard B: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. The source of the stock standard used to prepare Intermediate Mercury Standard B must be distinct from that used to prepare Intermediate Mercury Standard A (i.e. obtained from a separate vendor). Intermediate Mercury Standard B is used to prepare the ICV (refer to Section 8.0). The identity of the stock standard currently used to prepare this intermediate standard and instructions for its dilution may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard B must be prepared fresh daily, and disposed of appropriately after use.

5.12 Anhydrous magnesium perchlorate, coarse, for use as drying agent

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Aqueous samples to be analyzed for mercury should be collected and preserved as described in the following table.

Matrix	Container[1]	Collection Volume/ Weight	Preservation/ Treatment	Holding Time
Aqueous (total)	P, G	400 mL	HNO_3 to pH < 2	28 days
Aqueous (dissolved)	P, G	400 mL	HNO_3 to pH < 2	28 days

[1] P = polyethylene or , G = glass

7.0 PROCEDURES

PREPARATION OF STANDARDS, QC SAMPLES, AND BLANKS

7.1 Fill out the Mercury Preparation Logbook, listing all calibration standards, quality control samples, and client samples that are to be prepared. Refer to Figure 2 for an example Mercury Preparation Logbook page.

7.2 Use a graduated cylinder or graduated disposable sample cup to add 100 mL of ASTM Type II water to 6 BOD bottles. Using calibrated adjustable pipettes, prepare calibration standards by adding 0 uL, 20 uL, 500 uL, 1000 uL, 1500 uL, and 2000 uL of Intermediate Mercury Standard A to separate BOD bottles containing 100 mL of ASTM Type II water. The mercury concentrations of these calibration standards are, respectively, 0 ug/L (calibration blank), 0.2 ug/L, 5 ug/L, 10 ug/L, 15 ug/L, and 20 ug/L. The 0.2 ug/L standard is used during analysis as the CRA (refer to Section 8.0) as well as being used in the creation of the calibration curve.

7.3 Add 100 mL of ASTM Type II water to a BOD bottle. Using a calibrated adjustable pipette, prepare the QCS or ICV (refer to Section 8.0) by adding 1000 uL of Intermediate Mercury Standard B to the water in this bottle, and record the bottle number in the Mercury Preparation Logbook. The mercury concentration of this solution is 10 ug/L.

7.4 Prepare an appropriate number of CCVs (or IPCs) and LCSs (or LFBs) (refer to Section 8.0) by adding 1000 uL of Intermediate Mercury Standard B to BOD bottles containing 100 mL aliquots of ASTM Type II water. The mercury concentration of this solution is 10 ug/L.

7.5 Matrix spikes (or LFMs) are prepared by adding 100 uL of Intermediate Mercury Std A to 100 mL aliquots of samples. The amount of mercury added to each matrix spike is 1 ug/L.

7.6 Prepare an appropriate number of calibration blanks (ICBs/CCBs or CBs), preparation blanks (PB or LRB), and a permanganate blank (refer to Section 8.0) by adding 100 mL aliquots of ASTM Type II water to BOD bottles. Record the bottle numbers of blanks in the Mercury Preparation Logbook.

7.7 All calibration standards, QC samples, and blanks are digested in the same manner as client samples. Refer to Sample Preparation and Digestion, Steps 7.8 through 7.11, of this SOP.

SAMPLE PREPARATION AND DIGESTION

7.8 Using a graduated cylinder or a graduated disposable sample cup, transfer 100 mL of sample, or an aliquot diluted to 100 mL, to a BOD bottle. Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid, swirling to mix after each addition. Add 15 mL of potassium permanganate solution, swirl to mix, and allow to stand for at least 15 minutes. Samples that contain large amounts of organic substances may require additional 15 mL aliquots of potassium permanganate solution. This is indicated by the failure of the purple permanganate color to persist for the entire 15 minute waiting period. Add additional 15 mL aliquots to samples as necessary until the purple color persists for 15 minutes, and concurrently add additional 15 mL aliquots of potassium permanganate solution to the permanganate blank. If any of the samples require these additional aliquots of potassium permanganate solution, record the additional volume used for each sample and for the permanganate blank in the Mercury Preparation Logbook.

7.9 Add 8 mL of potassium persulfate solution to each sample, standard, and blank. Cap the bottles and place them in a preheated water bath. Monitor the temperature of the bath with a spirit thermometer throughout the digestion. The temperature of the water bath will fall below 95° C upon addition of the BOD bottles. After the temperature of the bath has risen back to 95° C, continue heating the samples at 95° C for 2 hours.

7.10 Remove bottles from the water bath and allow to cool to room temperature. If the purple permanganate color has failed to persist after digestion in any of the samples, add additional 15 mL aliquots of potassium permanganate solution as required to the samples and to the permanganate blank, and record these additions in the Mercury Preparation Logbook. Heat the samples requiring additional permanganate in the water bath at 95° C for an additional two hours. If the purple color fails to persist after the second heating step, consult the Supervisor for advice on how to proceed.

7.11 Add 6 mL of hydroxylamine hydrochloride solution to each BOD bottle and swirl to mix. This will reduce the excess permanganate, and the sample will change from purple to colorless. Wait at least 30 seconds before proceeding with analysis.

INSTRUMENTAL ANALYSIS

7.12 Digested mercury samples are analyzed using the Leeman Labs PS200 Automated Mercury Analyzer. Analysis is completely automated and is controlled by the PS200 software running on a dedicated PC. The PS200 software is menu driven, and its use is simplified through the use of macros. Each menu command appears on the computer screen with one letter highlighted in red. These letters are the "hot keys"; the menu command is executed by typing the "hot key" letter on the keyboard. In the discussion that follows, software menu items are identified in bold face type, and "hot keys" are underlined. Entries to be made from the alphanumeric keyboard are designated by underlining only. Entries to be made using single function keys are indicated by the name of the function surrounded by "less than" and "greater than" symbols, i.e. "< >".

The following discussion describes the steps that must be followed to perform mercury analysis using the PS200 mercury analyzer. For more information, refer to the PS200 Operator's Manual, the PS200 Setup and Training video, or consult the Supervisor.

7.13 The computer should always be left turned on, with the PS200 software running. If it is not, the PS200 software may be loaded by first typing CD/ICP at the DOS prompt, and then typing PS.

7.14 Instrument operating conditions are specified in "protocols". The protocol used by this laboratory is called "KATAHDIN". The name of the current protocol is listed in the status box at the top of the computer screen. If the current protocol is not "KATAHDIN", load "KATAHDIN" by typing **PROTOCOL**, **GET**, KATAHDIN, and then pressing the <ENTER> key.

7.15 Analytical data are stored in files called "folders". Folders are created by the user and can hold up to 999 analytical results. Folders are given seven-character names. The first character of the folder name is the instrument ID (e.g., "D" for the PS200). The second and third characters are the last two digits of the current year. The fourth, fifth, and sixth characters indicate the Julian date for the analytical run. The seventh character indicates sequence (e.g., "A" for the first run, "B" for the second run, etc.). For example, folder D96183A contains all data collected from the first run of July 1, 1996. It is the duty of the analyst to make sure that the correct current folder is in use. The name of the current folder is listed in the status box at the top of the screen. A new folder may be created, or an existing folder may be made current, by typing **DATA OUTPUT**, **OPEN FOLDER**, and then typing the desired folder name and pressing <ENTER>.

7.16 The instrument can run up to 88 client samples, which are placed in two autosampler racks that can each hold up to 44 samples. The analyst must now create a rack file - a list of samples in the order in which they are to be analyzed. Rack files are given 8-character names. The first two characters are the last 2 digits of the current year. The third, fourth, and fifth characters indicate the Julian date. The sixth and seventh characters indicate the run sequence (e.g. "01" for the first run of the day, "02" for the second run, etc.). The eighth character is a letter, A or B, indicating the rack position. For example, rack 9613201B is the second rack of the first run performed on the 132nd day of 1996. Type **AUTOSAMPLER, RACK ENTRY**. The software will ask for the name of a rack file. Enter the name of the rack file you wish to create and press <ENTER>. A table containing 44 rows will appear on the screen. Type the IDs of the samples into the table in the order in which they are to be analyzed. The first sample of the run must always be the CRA (refer to Section 8.0). Calibration standards, calibration verification standards, and calibration blanks need not be entered into the table - the instrument will insert them into the appropriate place in the analytical sequence during analysis. When all entries have been made, or when the rack file is full, press the yellow <MENU> key to return to the main menu. If creation of another rack file is necessary, repeat the process described above.

7.17 Print out the rack file by typing **AUTOSAMPLER, RACK ENTRY**, and then pressing the <ESCAPE> key. Then type **COPY**. The software will ask for the name of a rack file. Type the name of the rack file you wish to print, and press <ENTER>. The software will ask where you want to copy the file to. Type LPT1 and press <ENTER>. The rack file will be printed. Refer to Figure 3 for an example of a rack file printout.

7.18 The instrument may now be set up. The mercury lamp should be left turned on at all times. If it is not turned on, turn it on by pressing the blue lamp button at the bottom front of the instrument, and allow the lamp to warm up for two hours before proceeding.

7.19 Fill the drying tube with coarse magnesium perchlorite, and install it in the instrument.

7.20 Fill the rinse reservoir with 10% hydrochloric acid solution.

7.21 Inspect the peristaltic pump tubing for flattening or stretching, and replace any tubing showing signs of wear. Clamp the sample tubing, reductant tubing, and drain waste tubing into the peristaltic pump. Verify that the drain waste tubing is attached to the instrument's waste reservoir, and that there is sufficient room in the reservoir to contain the day's waste. Verify that the instrument's exhaust gas tubing is intact and is firmly attached to the instrument and to the exhaust hood. Verify that the exhaust hood fan is operational. Make sure that there is sufficient paper to allow the day's analytical results to be printed.

7.22 Press the yellow <MENU> key on the computer keyboard. Press **INSTRUMENT, OPERATION, GAS, ON, PUMPRATE, ON**. This will turn on the flow of compressed air

through the instrument, and will turn on the peristaltic pump. Verify that the pump is turning and that gas is bubbling through the liquid/gas separator. The pump rate and gas flow rate will be displayed on the screen. These should be 5 mL/min and 0.30 L/min, respectively. If the correct rates are not displayed on the screen, enter the correct rates using the menu instructions displayed on the screen.

Allow the instrument to warm up for 10 to 15 minutes while you fill the autosampler trays with samples to be run.

7.23 The standards autosampler rack has 14 holes and holds 25x100 autosampler tubes. Pour the calibration standards into 25x100 sample tubes (each tube holds approximately 45 mL) and place the tubes in the appropriately labeled holes in the standards autosampler rack. Pour the ICV, the CCV, and the ICB/CCB into 25x100 sample tubes and place the tubes in the appropriately labeled holes in the standards autosampler rack. Place the standards autosampler rack in its position on the autosampler tray.

7.24 Each of the two sample autosampler racks has 44 holes and holds 17x100 autosampler tubes. Using the rack file printout(s) and the Mercury Preparation Logbook as guides, pour digested samples into 17x100 sample tubes (each tube holds approximately 12 mL) and place the tubes in the appropriate holes in the sample autosampler rack, starting with the position labeled "1" and proceeding sequentially. It is essential that the analyst always know the order in which samples have been placed in the autosampler tray; therefore, frequent reference to the rack file printout(s) is required when preparing the tray. Place the sample autosampler racks in their positions on the autosampler tray.

7.25 Press the yellow <MENU> key to return to the main menu. Press **AUTOSAMPLER, SETUP**. Type 1 and enter the name of the rack file for the first autosampler rack to be run. Press <ENTER>. Enter the number of the first rack position to be sampled (normally position 1) and press <ENTER>. Enter the number of the last rack position to be sampled (up to position 44) and press <ENTER>. If the second autosampler rack is to be run, type 2 and enter the name of the rack file for the second autosampler rack to be run. Press <ENTER>. Enter the number of the first rack position to be sampled (normally position 1) and press <ENTER>. Enter the number of the last rack position to be sampled (up to position 44) and press <ENTER>. Press the yellow <MENU> key to return to the main menu.

7.26 The instrument's optics must now be adjusted to balance the signals for the sample optical path and the reference optical path. Follow the instructions in "Setting the Optics", which is reprinted from the PS200 Operator's Manual. Refer to Figure 4. After the optics have been set, the instrument is ready to run.

7.27 Press the yellow <MENU> key to return to the main menu. Press the yellow <MACRO> key, type ANALYZE, and press <ENTER>. The instrument will now

proceed to calibrate and run all of the samples listed in the autosampler rack files, inserting ICV, ICB, CCVs, and CCBs at the appropriate frequency. When the analysis has been completed, the macro "ANALYZE" will put the instrument into "sleep" mode, i.e., it will shut off the peristaltic pump and gas flow, but will turn them back on briefly at regular intervals to exercise the pump tubing and to purge the optical cell.

7.28 The instrument may be allowed to run in "sleep" mode for up to 24 hours. **NOTE**: Extended "sleep" mode operation will saturate the drying cell with water vapor and allow dissolved magnesium perchlorate to be carried into the optical cell. This will require disassembly of the optical cell for cleaning, resulting in unnecessary instrument down-time. Therefore, as soon as possible after the run has ended, the instrument should be shut down. To accomplish this, press the red <STOP> key to suspend operation of the "ANALYZE" macro. Press the yellow <MENU> key to return to the main menu. Disconnect the intake end of the reductant tubing from the reductant bottle, and suspend it in the 10% hydrochloric acid rinse solution. Type **INSTRUMENT, OPERATION, PUMPRATE, ON, GAS, ON**. This will turn on the peristaltic pump and the gas flow, and will purge any remaining stannous chloride from the reductant tubing and from the liquid/gas separator. Allow the instrument to run for five minutes. Then type **PUMPRATE, OFF, GAS, OFF**. Remove the clamps from the peristaltic pump, and allow the pump tubing to hang loosely from the pump. Dump the 10% hydrochloric acid rinse solution into an appropriate waste container, and rinse the reservoir thoroughly with ASTM Type II water and allow it to dry. Remove the autosampler tubes from their racks and dump them into an appropriate waste container. Remove the drying tube from the instrument and dump the spent drying agent into an appropriate waste container. The instrument has now been shut down.

DATA REDUCTION AND REPORTING

7.29 Results are obtained in concentration units (ug/L) from this instrument, and little data reduction is required. Results that exceed the calibration range of the instrument may not be reported - the sample must be appropriately diluted and reanalyzed Results for diluted samples should be multiplied by the dilution factor prior to reporting. If additional aliquots of potassium permanganate were added during digestion, the resulting dilution must be corrected for before reporting. Results should generally be converted to units of mg/L prior to reporting.

7.30 Results are reported down to the laboratory's practical quantitation level (PQL), unless otherwise requested. Results below the PQL should be reported as "<PQL".

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Each of the EPA methods described in this SOP requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated by method in Table 1, QC Requirements. A general discussion of the quality control requirements for mercury analysis appears below.

8.1 Instrument calibration - The instrument must be calibrated each time it is set up, and calibration standards must be digested each day that samples are digested. Calibration includes analysis of a calibration blank and five calibration standards with graduated concentrations in the appropriate range. The concentration of one of the calibration standards must be at the Contract Required Detection Limit (for CLP protocol analyses) or at the Practical Quantitation Level (for non-CLP protocol analyses). Because mercury may be adsorbed onto the walls of glass and plastic containers, the intermediate standard used to prepare calibration standards must be prepared fresh daily.

8.2 Calibration standards and instrument performance are verified by analyzing a standard prepared from a source other than that from which the calibration standards were prepared. This second-source standard is called the ICV (EPA Methods 245.1 CLP-M and 7470A) or the QCS (EPA Method 245.1).

8.3 The continuing accuracy of the calibration is verified and instrumental drift is monitored by periodic analyses of a midrange standard and a blank during the run. The midrange standard is called the CCV (EPA Method 245.1 CLP-M and 7470A) or the IPC (EPA Method 245.1). The blanks are called the ICB/CCB (EPA :Method 245.1 CLP-M and 7470A) or the CB (EPA Method 245.1).

8.4 A reagent blank is prepared and analyzed with each batch of 20 or fewer samples to assess laboratory and reagent contamination. This blank is called the PBW (EPA Method 245.1 CLP-M and 7470A) or the LRB (EPA Method 245.1).

8.5 A material of known mercury concentration (spiked deionized water or a solid reference material) is carried through the digestion and analysis processes with every batch of 20 or fewer samples. The recovery of mercury from this material, called the LCS (EPA Methods 245.1 CLP-M and 7470A) or the LFB (EPA Method 245.1), is used to assess laboratory and method performance.

8.6 Sample homogeneity can affect mercury recovery and the quality of the data. In every batch of 20 or fewer samples, duplicate aliquots of at least one sample are prepared and analyzed. The relative percent difference (RPD) between these aliquots is used to assess precision, and is calculated as follows:

$$RPD(\%) = \frac{|S - D|}{(S+D)/2} \times 100\%$$

where: S = Original Sample Value
D = Duplicate Sample Value.

8.7 Sample matrix can affect mercury recovery and the quality of the data. Sample matrix spike analysis is used to assess the effect of sample matrix on the digestion and measurement methodologies. Spikes are added to at least one sample per batch before digestion, prior to the addition of other reagents. Spike recovery is use to assess the affect of sample matrix on the method, and is calculated as follows:

$$\text{Recovery } (\%) = \frac{(P - S)}{A} * 100\%$$

where:
P = Spiked sample value
S = Original sample value
A = Spike amount

8.8 Permanganate blank - The permanganate blank is a blank which is made to contain as much potassium permanganate solution as is added to any client sample that requires additional potassium permanganate to effect complete digestion. This blank is used to assess mercury contamination of the potassium permanganate solution which could result in a high bias for samples that required additional aliquots of permanganate during digestion. The permanganate blank must be analyzed only if any associated samples required additional aliquots of potassium permanganate during digestion. If analysis of the permanganate blank yields a result above the PQL, it must be assumed that the results for all associated samples (i.e. all samples that required additional aliquots of potassium permanganate solution during digestion) have a high bias. If the measured mercury concentrations of such samples are below the PQL, the results may be reported without notation. If the measured mercury concentrations of such samples are greater than the PQL, the samples must be redigested and reanalyzed, adding equivalent amounts of potassium permanganate to all associated calibration standards, QC samples, and blanks.

8.9 The detection limit of the analysis is determined as a function of the standard deviation of replicate analyses of a low concentration mercury standard. The instrument detection limit (IDL) is determined quarterly by performing replicate analyses of deionized water spiked with mercury. Method detection limits are determined annually by analyzing replicate aliquots of spiked water that have been carried through the digestion process. Details of the methods used by Katahdin Analytical Services, Inc., for determining IDLs and MDLs are contained in the current revision of Katahdin SOP QA-806, MDL and IDL Studies.

9.0 METHOD PERFORMANCE

10.0 APPLICABLE DOCUMENTS/REFERENCES

USEPA Contract Laboratory Statement of Work for Inorganics Analysis - Multi-Media, Multi-Concentration (Document Number ILM03.0)

Methods for Chemical Analyses of Water and Wastes, United States Environmental Protection Agency, EPA 600/4-79-020, Method 245.1

Test Methods for Evaluation of Solid Waste, United States Environmental Protection Agency, Method 7470, SW-846, Third Edition, Updates I, II, IIA, and IIB, Revised January 1995.

Leeman Labs PS200 Automated Mercury Analyzer - Operator's Manual, Leeman Labs, Inc., 1991

PS200 Setup and Training (Videotape), Leeman Labs, Inc.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 1

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 7470A	Initial Calibration, 5 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct problem and repeat calibration.
	Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 10% of true value.	Correct problem and repeat calibration.
	Initial Calibration Blank (ICB)	Before beginning a sample run.	Less than PQL.	Correct problem and repeat calibration.
	Low Level Standard (CRA)	Before beginning a sample run.	Recovery within ± 50% of true value.	No corrective action required at this time.
	Continuing Calibration Verification (CCV)	After every 10 samples and at end of the run	Recovery within ± 20% of true value	Repeat calibration and reanalyze all samples analyzed since the last successful CCV.
	Continuing Calibration Blank (CCB)	After every 10 samples and at end of the run.	Less than PQL.	Repeat calibration and reanalyze all samples analyzed since the last successful CCB.
	Preparation Blank (PBW)	One per digestion batch of 20 or fewer samples.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Control Sample (LCSW)	One per digestion batch of 20 or fewer samples.	Recovery within ± 20% of true value.	Redigest all affected samples.
	Duplicate Sample (D)	One per digestion batch of 20 or fewer samples.	RPD ≤20%.	Flag results.
	Spike Sample (S)	One per digestion batch of 20 or fewer samples.	Recovery ±25% of true value, if sample > 4x spike value.	Flag results.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 1, cont'd

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 7470A, cont'd	Instrument Detection Limit (IDL) Study	Quarterly	IDL less than PQL	Repeat IDL study.
	Method Detection Limit (MDL) Study	Annually	MDL less than PQL	Repeat MDL study.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 1, cont'd

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 245.1 CLP-M	Initial Calibration, 5 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct problem and repeat calibration.
	Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 20% of true value.	Correct problem and repeat calibration.
	Initial Calibration Blank (ICB)	Before beginning a sample run.	Less than CRDL.	Correct problem and repeat calibration.
	Low Level Standard (CRA)	Before beginning a sample run.	No acceptance criteria at this time.	No corrective action required at this time.
	Continuing Calibration Verification (CCV)	After every 10 samples and at end of the run	Recovery within ± 20% of true value	Repeat calibration and reanalyze all samples analyzed since the last successful CCV.
	Continuing Calibration Blank (CCB)	After every 10 samples and at end of the run.	Less than CRDL.	Repeat calibration and reanalyze all samples analyzed since the last successful CCB.
	Preparation Blank (PBW)	One per SDG.	Less than CRDL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ CRDL and < 10x the blank concentration.
	Laboratory Control Sample (LCSW)	One per SDG.	Recovery within ± 20% of true value.	Redigest all affected samples.
	Duplicate Sample (D)	One per digestion batch of 20 or fewer samples.	RPD ≤20%.	Flag results.
	Spike Sample (S)	One per digestion batch of 20 or fewer samples.	Recovery ±25% of true value, if sample > 4x spike value.	Flag results.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 1, cont'd

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 245.1 CLP-M, cont'd	Instrument Detection Limit (IDL) Study	Quarterly	IDL less than CRDL.	Repeat IDL study.
	Method Detection Limit (MDL) Study	Annually	MDL less than CRDL.	Repeat MDL study.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 1, cont'd

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 245.1	Initial Calibration, 5 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct problem and repeat calibration.
	Quality Control Sample (QCS), prepared from a second source.	After preparation of fresh calibration standards or quarterly, whichever occurs first, to verify accuracy of the calibration stds.	Recovery within ±10% of true value.	Correct problem and reanalyze the QCS.
	Instrument Performance Check Solution (IPC).	Immediately following daily calibration, after every 10 samples, and at the end of the run.	1) For first run, recovery within ± 5% of true value. 2) For subsequent IPCs, recovery within ± 10% of true value.	Terminate analysis, correct problem, and reanalyze all samples analyzed since the last compliant IPC.
	Calibration Blank (CB)	Immediately following daily calibration, after every 10 samples, and at the end of the run.	Less than PQL.	Reanalyze CB once. If reanalysis fails, terminate analysis, correct problem, and reanalyze all samples analyzed since the last compliant CB.
	Laboratory Reagent Blank (LRB)	One per digestion batch of 20 or fewer samples.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Fortified Blank (LFB)	One per digestion batch.	Recovery within ± 15% of true value.	Identify and resolve source of problem before continuing analyses.
	Duplicate Sample (D)	No required frequency at this time.	No criteria stated in method.	No corrective action required.

TABLE 1, cont'd

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ 245.1, cont'd	Laboratory Fortified Matrix Sample (LFM)	One per 10 samples.	Recovery ±30% of true value.	Flag results.
	Instrument Detection Limit (IDL) Study	Quarterly	IDL less than PQL.	Repeat IDL study.
	MDL Study	Annually	MDL less than PQL.	Repeat MDL study.

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-610-00	METHODS 7470A, 245.1 CLP-M, and 245.1
Apparatus/Materials		
Reagents		
Sample preservation/ handling		
Procedures		
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		
QC - Calibration Blanks	Acceptance criteria employed for 245.1: ± PQL	Acceptance criteria stated in 245.1: ± MDL

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

FIGURE 1

EXAMPLE OF MERCURY RUNLOG PAGE

BOOK #4, PAGE 0000057

KATAHDIN ANALYTICAL SERVICES, INC.
METALS SECTION

Mercury Analysis Cover Sheet – Leeman Labs PS200

Run Date:	Analyst:	Prep. Date:
Protocol Name:	Matrix:	Method:
Folder Name:	Folder Sequence Nos.:	to

STANDARDS TRACEABILITY INFORMATION

STANDARD NAME	Hg CONC.(ug/L)	STANDARD I.D. CODE	STANDARD PREP. DATE
Calibration Standard 2			
Calibration Standard 3			
Calibration Standard 4			
Calibration Standard 5			
Calibration Standard 6			
Init. Calib. Verification (ICV)			
Cont. Calib. Verification (CCV)			
CRDL Std. for AA (CRA)			

REPORTED DATA LOG

KATAHDIN Sample Number	QC Batch ID	Client	Comments

Page ____ of ____ Review: _____

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

FIGURE 2

EXAMPLE PAGES FROM MERCURY PREPARATION LOGBOOK

Katahdin Analytical Services,Inc.
METALS PREPARATION BENCHSHEET
14:43:03 07/22/96

Method: 7470
Page: 1 of 1

Reagent information:

HNO3 : J28049
H2SO4 : J13812
HCl : NA
KMnO4 : H37703
K2S2O8 : 7076 KEP
NH2OH-HCl : J42706

Standards information:

ICV = 500ul of 1ppm 468-S to 100ml. 1ppm____ = 25ul of ____ to 25 ml
SO.2 = 20ul of 1ppm 550-S to 100ml. 1ppm____ = 25ul of ____ to 25 ml
S5 = 500ul of 1ppm____ to 100ml.
S10 = 1000ul of 1ppm____ to 100ml.
S20 = 2000ul of 1ppm____ to 100ml.
LCSW = 1000ul of 1ppm____ to 100ml.
Spike(S)= 1000ul of 1ppm____ to 100ml.
TCLPMS(M)= 2000ul of 1ppm____ to 100ml.
LCSS = Priority PollutnT/CLP Soil-Env. Resource Assoc. Lot = NA

Digestion Start Time (@95 C): 13:15 Digestion End Time (@95 C): 1515

Filename: MG22HGW1

Sample ID	QC Batch	Initial Wt/Vol	Init Units	Final Vol	Final Units	Mtrx	Meth	Anal.	Date	Initial Color	Initial Clar/Tex	Final Color	Final Clarity	Artifacts
PBWMG22HGW1	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
LCSWMG22HGW1	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1542-001	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1547-001	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1549-001	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1524-003	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1524-003D	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1524-003S	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1524-004	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1524-006	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-001	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-002	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-003	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-004	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-005	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-006	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-007	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-008	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-009	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-010	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					
WM1519-010S	MG22HGW1	0.100	L	0.100	L	AQ	HG	DJE	07/22/96					

Digestion performed by DJE on 072296

Documentation reviewed by _____ on _____

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

FIGURE 3

EXAMPLE RACK FILE PRINTOUT

Rack D96201B Range 1-44 Clear seQ Undo eXit

cup	Id	Extended id	Weight	Volume	Macro	checK	Help
1	PBW	MG18HGW1	1.0000	1.0000			
2	LCSW	MG18HGW1	1.0000	1.0000			
3	WM1500-001	T	1.0000	1.0000			
4	WM1500-002	T	1.0000	1.0000			
5	WM1500-003	T	1.0000	1.0000			
6	WM1497-001	T	1.0000	1.0000			
7	WM1515-001		1.0000	1.0000			
8	WM1515-001	S	1.0000	1.0000			
9	WM1518-001		1.0000	1.0000			
10	WM1518-001	D	1.0000	1.0000			
11	WM1518-001	S	1.0000	1.0000			
12	WM1510-001		1.0000	1.0000			
13	WM1510-002		1.0000	1.0000			
14	WM1510-003		1.0000	1.0000			
15	WM1510-004		1.0000	1.0000			

PaDn

TITLE: **TOTAL MERCURY DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES BY MANUAL COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY**

FIGURE 4

INSTRUCTIONS FOR SETTING THE OPTICS,
reprinted from the Leeman Labs PS200 Automated Mercury Analyzer - Operator's Manual

2.10 Setting the Optics {08:56}

1. Select the following options in sequence from the PS200 Main Menu: UTILITY, diaGnostics, and Aperture Test. Press [ENTER] . A display will appear on the monitor (Figure 2-4).

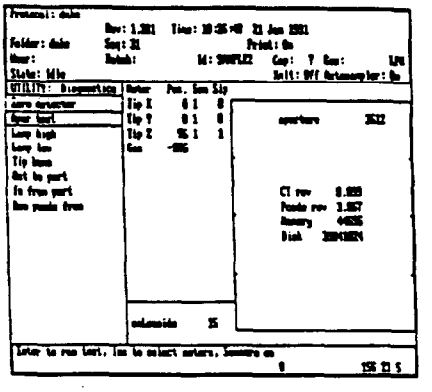

Figure 2-4
Aperture test display

2. Look at the Aperture Reading. If the value is outside +/-100, adjust the aperture. To do this:

   a. Expose the aperture adjustment screws by removing the front panel of the PS200 {09:25}. The panel is easily detached by pushing it up and pulling out. Early models require loosening two shipment screws located behind the bottom air vents of the front panel.

   b. Back-out (unscrew) the aperture screw which is threaded in the furthest with a Phillips head screwdriver {09:32}, and then press [ENTER] . Look at the Aperture Reading again on the monitor. You should note a change from the original reading. Repeat this process until the value stops changing (this indicates that neither aperture is blocking the light).

   c. Turn the appropriate aperture screw in or *clockwise* 1/8th revolution (top aperture screw if the value is positive, bottom aperture screw if the value is negative) and press [ENTER]. Check the Aperture Reading and repeat this process until the reading is within +/-100; an ideal reading is zero.

3. Replace the front panel.

Katahdin
ANALYTICAL SERVICES

October 24, 1996

Ms. Kelly A. Johnson
Brown and Root Environmental
661 Andersen Drive, Foster Plaza 7
Pittsburgh, PA 15201

Dear Ms. Johnson:

Enclosed please find a copy of Katahdin SOP CA-020-02, which describes the procedure for distillation of samples for cyanide. This SOP was inadvertently omitted from the package I sent to you earlier this week. SOP QA-5855, which you should already have received, applies only to the flow injection analysis of sample distillates for cyanide. Please note Katahdin no longer employs the spectrophotometric method described in the enclosed SOP CA-020-02. Both of the cyanide SOPs are currently under revision in order to combine the applicable portions of each into a single SOP.

Also enclosed is a revised inventory of the SOPs you should have received to date. Deborah McGrath will be contacting you next week to review the list of methods and any questions you may have. If you need additional information or have any questions prior to then please contact us at 207/874-2400.

Sincerely,

Katahdin Analytical Services, Inc.

Julie Ricardi

Julie Ricardi
Quality Assurance Officer

Enclosures

c D. McGrath

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STANDARD OPERATING PROCEDURE

Author: K. Mollison/B. Carbone
Approved by:
John C. Burton
Operations Manager

Issuing Unit: PACE-New England-ME
SOP No.: CA-020-02
Date: July 1995

TITLE: Spectrophotometric Determination of Cyanide in Domestic and Industrial Wastewater, Drinking, Surface, and Saline Waters and Sediment/Soil Samples

PURPOSE: To describe the procedures used by PACE-ME personnel for spectrophotometric determination of cyanide in aqueous and soil/sediment sample matrices.

SCOPE: A Practical Quantitation Limit (PQL) of 10 mg/L is attainable by this method with an initial aqueous sample volume of 500 mL. This limit is attainable in all drinking and surface waters and most industrial wastes not exhibiting high levels of organic compounds. For soil/sediment samples a PQL of 1 mg/kg is attainable by this method with an initial sample weight of 5 grams (dry weight). The procedures described in this SOP are applicable to the determination of cyanide in accordance with EPA Methods 335.2, 9010A, and the CLP SOW ILM03.0, provided method specified quality control samples and acceptance criteria are employed (see Procedure Section C. Quality Control).

REQUIREMENTS:

A. EQUIPMENT

1. Round Bottom Flask(s), 1000 mL, 3-necked with 24/40 ground glass joints.
2. Cold finger condenser with 24/40 ground glass joints.
3. Tygon tubing with finger clamps.
4. Heating mantles, 1000 mL flask capacity.
5. Vacuum pump.
6. Sparge tubes with absorber heads: all with 24/40 ground glass joints.
7. Vacuum grease for ground glass joints.
8. Graduated cylinders - 500 mL, 250 mL and 50 mL.
9. Boiling chips.
10. Buret, 10 mL, Class A

11. Class A Volumetric Flasks - 1000 mL, 100 mL, 250 mL

12. Class A Volumetric Pipets - 10.00 mL

13. Potassium Iodide - Starch Paper

14. pH paper

15. Lead Acetate Paper

16. Balance - capable of weighing 5 g $\pm$ 0.01 g

17. Spectrophotometer, suitable for measurements at 578 nm with a 1.0 cm cell.

B. REAGENTS

1. NaOH solution, 1.25N: Dissolve 50 g of NaOH (Reagent Grade) in laboratory Type II water and dilute to 1 liter in a volumetric flask.

2. Sodium dihydrogen phosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ (Reagent Grade) in one liter of laboratory Type II water. Store in a refrigerator (Stability - 6 months).

3. Stock KCN solution: Dissolve approximately 2.0 g KOH and 2.51 g KCN in 1 liter of laboratory Type II water. (Caution: KCN is highly toxic so avoid skin contact or inhalation.) Standardize KCN weekly against primary standard silver nitrate titrant to confirm titer. (See Step B.3 of Procedure Section.)

4. Primary standard silver nitrate titrant, 0.0192N: Purchased from an independent vendor (HACH or equivalent) and diluted to a working concentration of 0.000192N by adding 10.00 mL of the stock titrant to a 1 liter class A volumetric flask using a class A pipet and diluting to the mark with laboratory Type II water. Purchase semiannually; prepare working standard daily. Store in dark bottle.

5. Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine (Reagent Grade) in 100 mL of acetone. Prepare quarterly or as needed.

6. Chloramine-T solution: Dissolve 1.0 g white, water-soluble chloramine-T powder (Reagent Grade) in 100 mL laboratory Type II water. Prepare fresh each day of analysis.

7. Pyridine-barbituric acid reagent: Place 15 g of barbituric acid (Reagent Grade) in a 250 mL volumetric flask and add just enough laboratory Type II water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15.0 mL of concentrated HCl (sp. gr. 1.19), mix and cool to room temperature. Dilute to 250 mL with laboratory Type II water and mix. This reagent is stable for approximately six months if stored in a cool dark place.

8. Ascorbic Acid: crystals, reagent grade

9. Cyanide Check Standard: Preparation as specified by manufacturer.

10. Sulfuric Acid, concentrated

11. Magnesium Chloride Solution(2.5M): Dissolve 510 grams of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask and dilute to 1 L with Type II water.

12. Sulfamic Acid, reagent grade

13. Cadmium Carbonate, powder

14. Dilution Water (0.25N NaOH solution): Dilute 50 mL 1.25N NaOH solution to 250 mL with laboratory Type II water in a 250 mL volumetric flask and mix.

C. SAMPLE HANDLING AND PRESERVATION

1. Water samples should be collected in clean glass or plastic 1 liter bottles. Soil samples should be collected in clean glass soil jars.

2. Oxidizing agents such as chlorine which decompose most cyanides must be removed from water samples. Test a drop of the water sample with potassium iodide-starch paper; a blue color indicates the presence of chlorine or other oxidizing agents. Such samples are pre-treated with ascorbic acid until a blue color no longer is exhibited when tested with KI-starch paper (See Procedure Section B.1.b).

3. Water samples must be preserved at the time of collection to a pH>12 by adding at least 2.0 mL of 10N NaOH per liter of sample taken and stored at 4°± 2°C. Soil samples are to be stored at 4°± 2°C. If samples are received without proper preservation the project manager should be notified for discussion with the client prior to sample analysis.

4. Samples should be analyzed as soon as possible after collection. The holding time for samples analyzed by Methods 335.2 and 9010A is 14 days from date of sampling. The holding time for samples analyzed by the CLP SOW ILM03.0 is 12 days from verified time of sample receipt (VTSR).

PROCEDURE:

A. SUMMARY OF THE METHOD

Total cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The scrubber solution is placed in a volumetric container and the absorber head and body is rinsed with reagent water. A portion of this combined scrubber and absorber rinse solution is buffered then analyzed colorimetrically by converting free cyanide ions to cyanogen chloride, CNC1, with chloramine-T. The addition of the pyridine-barbituric acid reagent produces a red color

complex with cyanogen chloride that is detectable at 578 nm. The concentration of total cyanide is determined by comparing the color intensity of the sample with known cyanide standards prepared in the same salt matrix.

B. PREPARATION OF SAMPLES AND STANDARDS

1. Samples must be checked for proper preservation, the presence of chlorine, and the presence of sulfide.

   a. The water sample pH must be greater than 12 when checked with pH paper. The project manager should be notified immediately for follow up with the client if sample pH is less than 12.

   b. A blue color exhibited with potassium iodide (KI)-starch paper indicates the presence of chlorine. Test a drop of the sample with KI-starch paper. If a blue color develops treat the sample with ascorbic acid, a few crystals at a time, until a blue color is no longer exhibited when tested with KI-starch paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample.

   c. The presence of sulfide is indicated by a black color being exhibited on lead-acetate paper. If a black color appears on the lead acetate paper, treat 25 mL more of the sample than required for cyanide distillation with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Add cadmium carbonate to the sample until a drop of the treated sample does not darken the lead acetate test paper. Filter this solution through a filter paper into a beaker and use proper volume from this solution for cyanide distillation. Do not allow ample to sit in cadmium carbonate for a long period of time (less than 5 - 10 minutes). This process should be completed prior to preservation with sodium hydroxide as described in Requirements Section C.3 and Procedure Section B.1.a.

2. Sample setup and distillation. (See Figure 1 (attached) for diagram).

   a. Place 500 mL laboratory Type II water in each of two 1000 mL boiling flasks, along with 2 boiling stones per flask.

   b. To one of the flasks prepared above, add a volumetric amount of an independent cyanide check standard (either HACH or WP or equivalent) to achieve a cyanide concentration of 500 mg/L in the flask. Record the volume of check standard used in the logbook as sample volume. This flask will be the Laboratory Control Sample (LCS) for the day's run. For CLP analyses the LCS is equivalent to the initial calibration verification (ICV) standard. The other flask containing only laboratory Type II water is the method blank for the day's run (referred to as PBW or PBS, as applicable, for CLP analyses).

   c. <u>For samples analyzed by Method 335.2 or Method 9010A</u> at least two of the calibration standards (Procedure Section B.4.c), a high and a low standard, must be distilled and compared to similar values on the calibration curve to

ensure that the distillation is reliable. Corrective action must be taken before proceeding with analysis if the distilled standards do not agree within ± 10% of the undistilled standards. For samples analyzed by the CLP SOW ILM03.0 at least one of the calibration standards (B.4.c) at mid-range must be distilled and compared to a similar value on the calibration curve to ensure the distillation technique is reliable. Corrective action must be taken before proceeding with analysis if the distilled mid-range standard does not agree within ± 15% of the undistilled standard.

d. To the remaining flasks add two boiling stones and then add 500 mL aliquots of unknown samples or appropriate dilutions of samples based on the anticipated cyanide concentration present in the samples. For soil samples, add 5.0 g to 10.0 g of soil to 500 mL of Type II water in each flask (5.0 g for samples with 100% total solids). Record the sample volumes/weights used in logbook. An example logbook page is shown as Attachment C.

e. To each flask add approximately 2 g of sulfamic acid to counter nitrite/nitrate (NO_2/NO_3) interference. Mix for three minutes prior to addition of sulfuric acid (step B.2.h).

f. Place 50 mL of 1.25 N NaOH solution in each absorber body, insert sparger tube and ensure all seals are intact with stopcock grease. Record the volume of NaOH. Connect sparger to the condenser and condenser to flask making sure all seals are tight.

g. Connect absorber heads to vacuum lines and start vacuum pump.

h. Adjust air flow through the spargers to a moderate level by opening finger clamps. Start condenser water from tap. Approximately one to two bubbles of air per second should enter the boiling flask through the air inlet tube.

i. Add reagents to the boiling flask through the sidearm in the following order:

- 25 mL conc. sulfuric acid (slowly and rinse with lab Type II water)
- 20 mL magnesium chloride solution (rinse with lab Type II water)

j. Attach overflow traps to the side arm aperture and turn on heating mantles. The setting of the heating mantles should be at 90°C.

k. Bring samples to a boil while maintaining a moderate air flow through the spargers. This will require adjustment of the finger clamps as the samples start to boil to prevent boiling over.

l. Reflux for 1 hour.

m. Terminate heating and continue sparging for at least 15 minutes then seal off vacuum and turn off pump. Then turn off cooling water after seals between condenser and sparger are broken.

n. Dilute the sparger solution to 250 mL by pouring the contents of the absorber body into a 250 mL class A volumetric flask and then rinsing the absorber head and body into the flask. Record the total distillate volume in appropriate column in logbook.

3. Titration of Cyanide Standards

a. Make up a 1:100 dilution of the primary standard silver nitrate (See Reagents Section B.4) to make a working concentration of 0.000192N. This working concentration is the titrant for standardization.

b. Pipet 25 mL aliquot of working cyanide standard into a 30 mL glass beaker.

c. Add 8 to 10 drops of the rhodanine indicator (See Reagents Section B.5). Stir on a magnetic stirplate.

d. While stirring, add titrant until a pinkish/brown or peach color appears. This is the endpoint. Record volume(mL) of titrant to reach endpoint. Repeat this process a total of three times.

4. Spectrophotometric analysis

a. Set spectrophotometer (DR3000 or equivalent) to 578 nm and allow to warm up for 15 minutes or as specified in the Operator's Manual.

b. Zero instrument to 100 percent transmittance (or zero absorbance) with laboratory Type II water.

c. Prepare a six point standard curve in 250 mL volumetric flasks containing 50 mL of 1.25 N NaOH and 25.0, 10.0, 5.0, 2.0, 1.0, and 0.5 mL of standard KCN previously titrated with silver nitrate. Note one standard must be at the reporting limit (PQL for Methods 335.2 and 9010A, CRDL for CLP SOW ILM03.0). Record the standard volumes used for calibration in logbook. Bring standards up to the mark with laboratory Type II water and mix well. To analyze, withdraw 50.0 mL of each standard solution and place in 100 mL volumetric flasks. Record the analyzed volume in logbook. The calibration curve must yield a linear regression correlation coefficient of 0.995 in order to proceed with sample analysis.

d. Prepare enough fresh chloramine-T to run the standard curve and the sample distillates.

e. Add 50 mL aliquots, or appropriate dilutions brought to 50.0 mL with dilution water (0.25N NaOH), of each sample, blank, or LCS/ICV distillate to 100 mL volumetric flasks. Record analyzed distillate volume in appropriate column in logbook. Samples must be reanalyzed at a dilution if the transmittance is lower than that of the highest standard. Refer to Attachment E for typical

analytical sequences for cyanide by Methods 335.2, 9010A, and CLP SOW ILM03.0.

f. Add 15 mL sodium phosphate buffer solution with an Oxford pipet to each standard and sample distillate while mixing rigorously.

g. Add 2.0 mL chloramine-T to each standard and distillate aliquot. Swirl to mix well.

h. After 5 - 15 minutes, add 5.0 mL of the pyridine-barbituric acid solution to each standard and sample distillate, fill flask to the mark with laboratory Type II H_2O, and wait 8 - 10 minutes for color development.

i. Rinse the spectrophotometer cuvette once with the sample matrix then read and record the sample transmittance (or absorbance, as appropriate for the instrument).

j. Calculate CN in mg/L using Lotus 123 or Excel spreadsheet. (See Attachment A).

k. $$CN = mg/L = \frac{A \times 1{,}000}{B} \times \frac{250}{C}$$

where,

A = mg CN from curve
B = mL original sample for distillation
C = mL taken for colorimetric analysis

l. For soils, calculate CN in mg/kg using Lotus 123 spreadsheet (see Attachment B).

C. QUALITY CONTROL

1. The calibration curve must yield a linear regression correlation coefficient of 0.995 in order for sample analysis to proceed. Six standards (see B.4.c) and a blank are routinely analyzed for Methods 335.2, 9010A and the CLP SOW ILM03.0; a minimum of three standards and a blank are <u>required</u> for samples analyzed by the CLP SOW ILM03.0.

2. A Laboratory Control Sample (LCS) is distilled and analyzed for every batch of 20 or fewer samples as described in step B.2.b of the procedure. The LCS is equivalent to and referred to as the ICV for CLP analyses. The LCS/ICV is treated in the same manner as all other samples.

a. If the LCS/ICV exceeds the acceptance criteria, reanalyze the distillate spectrophotometrically to verify the result. Acceptance criteria for CLP-protocol samples are 85% to 115% recovery. Acceptance criteria for the LCS for non-CLP samples are statistically derived from laboratory data and are

67% to 130% recovery. However, for Method 9010A, if the LCS is to serve as the calibration verification standard for the batch (see step C.5), recovery must be 85% to 115% of the true value. If the LCS/ICV exceeds the acceptance criteria upon reanalysis, a CAR must be initiated and the section supervisor notified. Further corrective action is to be based on discussions with the section supervisor/operations manager/QA coordinator.

3. A method blank must be distilled and analyzed with each day's sample batch. The method blank is referred to as the PBW or PBS, as applicable, for CLP analyses.

   a. The acceptance criterion for the method blank is a cyanide concentration less than the reporting limit (PQL or CRDL) for the matrix. When the acceptance criteria are exceeded, a CAR must be initiated and the section supervisor notified. Reanalyze the distillate to verify the value. If blank continues to exceed the acceptance criteria, further corrective action is at the discretion of the section supervisor/operations manager/QA.

4. For samples analyzed by the CLP SOW ILM03.0 an initial calibration blank (ICB) must be analyzed immediately after the ICV and prior to the distilled mid-range standard. Acceptance criterion is a cyanide concentration less than the CRDL. If not met, analysis must be stopped and corrective action taken. The ICB is not distilled.

5. For CLP samples continuing calibration verification (CCV) standard and continuing calibration blanks (CCB) must be analyzed after every 10 samples and at the close of every analytical run. Acceptance criteria for the CCVs are percent recoveries of 85% to 115% of the true value; acceptance criterion for the CCB is a cyanide concentration less than the CRDL. If criteria are not met corrective action must be taken, including reanalysis of all samples back to the last acceptable CCV/CCB. For Method 9010A a CCV must be analyzed with every batch of 20 or fewer samples. Acceptance criteria for the CCVs are percent recoveries of 85% to 115% of the true value; the LCS (step C.2.a) may serve as the CCV for Method 9010A provided criteria of 85% - 115% are met. For Method 335.2 no CCV requirements are specified.

6. A sample duplicate is distilled and analyzed for each batch of 20 or fewer samples.

   a. Relative percent difference (RPD) for duplicate analysis should be $\leq$ 20% for aqueous and solid matrices. Reanalyze sample distillates spectrophotometrically if the duplicate RPD is outside criteria and a lab problem is suspected; notate raw data with appropriate notation if criteria are still exceeded.

7. A matrix spike is distilled and analyzed for every 10 or fewer samples. The spiking solution is the same as the independent check standard used for the LCSs and at the same concentration. These samples are distilled and analyzed in the same manner as all other samples.

   a. Acceptance criteria for the matrix spike are 75-125% recovery. Reanalyze the distillate spectrophotometrically if the spiked sample is not within criteria and

a lab problem is suspected. If matrix spike remains out of criteria, raw data must be notated with the appropriate footnote for reporting.

D. SAFETY PRECAUTIONS

Caution must be exercised when acidifying samples; vacuum must be applied when this step occurs. Equilibrium in the boiling flask must be maintained so as to prevent escape of hydrogen cyanide gas to the atmosphere.

Spectrophotometric analysis must be done in the Inorganics prep hood as pyridine is an odoriferous organic compound. It is also highly flammable (see Material Safety Data Sheet, Attachment D). If the pH of the distilled sample is not adequate (pH»8), cyanide gas could be evolved upon the addition of the pyridine. Thus, spectrophotometric analysis in a fume hood is mandatory.

E. WASTE DISPOSAL

Waste from spectrophotometric analysis of cyanide must NOT be disposed of by dilution down the drain. As pyridine is a strong reducing agent, this waste must be set aside in a waste container and labeled appropriately.

Waste cyanide standard materials are to be disposed of utilizing techniques as described in the Laboratory Chemical Hygiene Plan.

REFERENCES:

CLP Method 335.2-M, Document #ILM03.0.

"Standard Methods for the Examination of Water and Wastewater", Method #4500-CN-E, Cyanide/Colorimetric, 18th Edition, 1992.

"Test Methods for Evaluating Solid Waste: Physical/Chemical Methods," SW-846 Method 9010A, USEPA, Third Edition, July, 1992.

"Methods for Chemical Analysis of Water and Wastes," Method 335.2, US EPA EPA-600/4-79-020 , Revised March 1983.

ATTACHMENTS:

Figure 1 - Cyanide Distillation Apparatus

Attachment A - Lotus 1-2-3 Spreadsheet for Quantitation of CN^- (mg/L).

Attachment B - Lotus 1-2-3 Spreadsheet for Quantitation of CN^- (mg/kg).
Attachment C - Example Logbook Page
Attachment D - Material Safety Data Sheet for Pyridine
Attachment E - Typical Analytical Sequences for Cyanide: Methods 335.2, 9010A, and CLP SOW ILM03.0

GLOSSARY:

Total Cyanide - Cyanide ion and complex cyanides converted by refluxing with a mineral acid in the presence of magnesium ion to hydrocyanic acid (HCN).

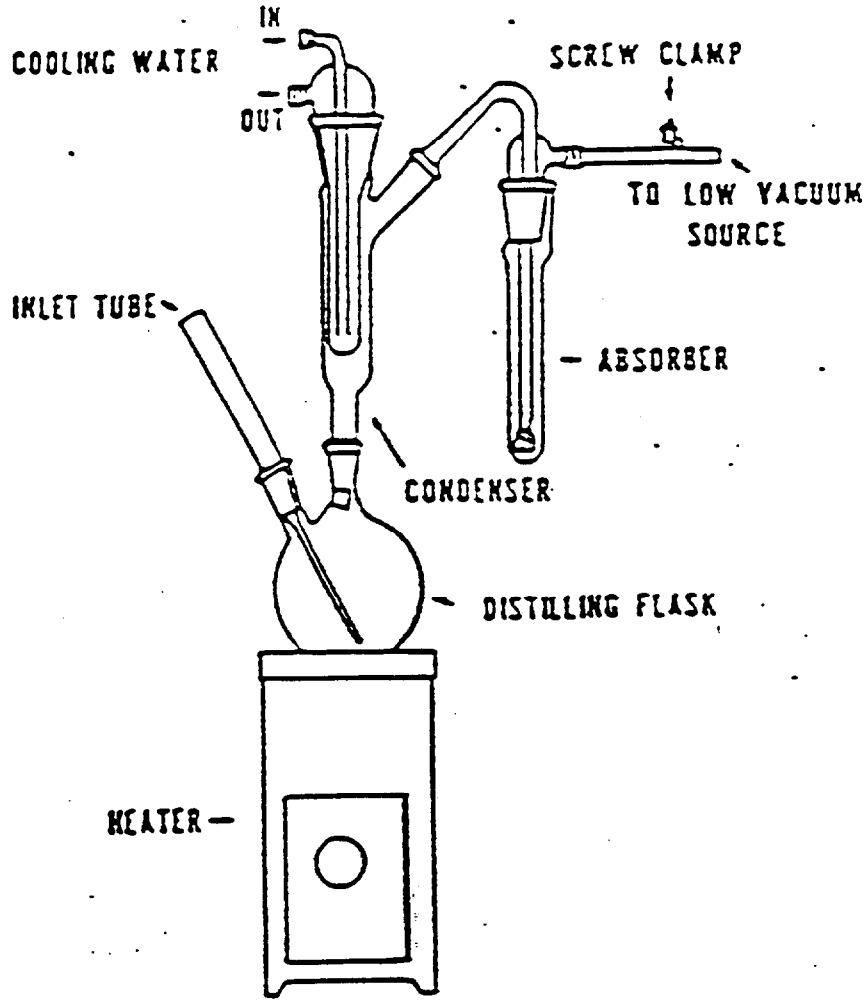

Figure 1 Cyanide distillation apparatus

ATTACHMENT A

CYANIDE, TOTAL
COLORIMETRIC-CHLORAMINE T

METHOD: CLP-M 335.2
PQL = 20 ug/L

DATE:
ANALYST:

HACH CHECK STD — CONC. = ug/ml — DATE: — BY:

CYANIDE STANDARD — CONC. = ug/mL — DATE: — BY:

STANDARD	STD VOLUME (mL)	STD (ug)	ANALYSIS VOLUME (mL)	% T @ 578 NM	ABS @ 578 NM	CORR ABS @ 578 NM	RELATIVE RESPONSE
BLANK	----	0.00	50.0		ERR	----	----
STD 1		0.00			ERR	ERR	ERR
STD 2		0.00			ERR	ERR	ERR
STD 3		0.00			ERR	ERR	ERR
STD 4		0.00			ERR	ERR	ERR
STD 5		0.00			ERR	ERR	ERR
STD 6		0.00			ERR	ERR	ERR

CLIENT	SAMPLE NO.	SAMPLE VOLUME (mL)	DISTILLATE VOLUME (mL)	ANALYSIS VOLUME (mL)	% T @ 578 NM	ABS @ 578 NM	CORR ABS @ 578 NM	CYANIDE (ug)	CALC CYANIDE (ug/L)
	METH BLANK	500.0				ERR	----	----	----
	CHECK STD					ERR	ERR	ERR	ERR % RECOVERY
						ERR	ERR	ERR	ERR
						ERR	ERR	ERR	ERR
						ERR	ERR	ERR	ERR
						ERR	ERR	ERR	ERR

CN- ug/L= ((ug CN- * 1000 ml/L)/ml sample) * (dist vol/analy vol)

ATTACHMENT B

CYANIDE SOIL CALCULATIONS

METHOD: CLP-M 335.2
PQL = 2 mg/kg

DATE:
ANALYST:

CLIENT	SAMPLE ID	WET SAMPLE WGT (g)	DEC % TS	DISTILLATE VOL (ml)	ANALYSIS VOL (ml)	CYANIDE (ug)	CYANIDE CALC.(mg/kg)
							ERR
							ERR
							ERR
							ERR
							ERR
							ERR
							ERR
							ERR

CN mg/kg= ((ug)(dist vol/analy vol)(1000g/kg))/((wet samp wgt)(dec % ts)(1000ug/mg))

ATTACHMENT C PAGE 1 OF 2
(titrimetric, spectrophotometric)

38

Notebook No. KAM 1-10-91

PROJECT Cyanide, total CLP-M 3352

Continued From Page FOLE 50ug/L Cu 2mg

STD CN 12-12-90 KAM
STOCK CN CN: 092890: F2 KAM
SULFURIC ACID Baker LOT # D26065
MgCl 12-12-90 KAM
AgNO3 0.00092N KAM 1-10-91
HACH CHK STD 1-10-91 KAM

Client	Sample ID	Std ID	Sample vol (ml)	Dist. vol (ml)	Analysis vol (ml)	% Trans at 578 nm
	Blank	RD Water	500.0	250	50.0	0.815
HACH	CHK STD	ICV	10.0			47.3
	91009037		500.0			98.2
	90365004	TS. 0.843 5.93g	500.0			98.3
	90365005	TS 0.917 5.45g	500.0			98.1
	90365006	TS. 0.797 6.27g	500.0			98.6
	90365007	TS. 0.884 5.64g	500.0			97.5
DUP	90365006		500.0			98.5
SPK	90365007		500.0 + 10.0 HACH			52.0
HACH	CHK STD	CCV	10.0			47.8

STD CURVE Vol in ml	% Trans at 578 Blank	
	99.2	
2.0	KAM 1-10 99.2	93.6
5.0	93.6	86.4
10.0	86.4	73.3
25.0	46.4	
50.0	19.2	

AgNO3 (ml)	Calculation for CN STD	AgNO3 (ml)	Calculation for HACH CHK STD
5.55	(5.55)(0.00092) = 25(x)	13.02	(12.73)(0.00092) = 25(x)
5.55	0.000042624 = x	12.62	0.000097766 = x
5.55	0.000042624/0.0192 = x	12.55	0.000097766/0.092 = x
x̄ = 5.55	2.22 ug = x	x̄ = 12.73	5.09 ug = x

Continued on Page

Read and Understood By

Karin L Wallisen — Jan 10, 1991
Distillation — Date

Karin L Wallisen — Jan 10, 1991
Analysis — Signed — Date

Signed — Date

PROJECT Cyanide, total CLP-M 335.2

Continued From Page 38

CYANIDE 1-10-91

CYANIDE, TOTAL
COLORIMETRIC-CHLORAMINE T

METHOD: CLP-M 335.2 (KAM 1-10-91)
PQL = ~~10~~ 20 ug/L

DATE: JANUARY 10, 1991
ANALYST: KAM

HACH CHECK STD — CONC. = 5.0920 ug/ml, DATE: 1-10-91, BY: KAM

CYANIDE STANDARD — CONC. = 2.22 ug/mL, DATE: 12-12-90, BY: KAM

STANDARD	STD VOLUME (mL)	STD (ug)	ANALYSIS VOLUME (mL)	% T @ 578 NM	ABS @ 578 NM	CORR ABS @ 578 NM	RELATIVE RESPONSE
BLANK	----	0.00	50.0	99.2	0.003	0.000	----
STD 1	2.0	0.89	50.0	93.6	0.029	0.025	0.0284
STD 2	5.0	2.22	50.0	86.4	0.063	0.060	0.0270
STD 3	10.0	4.44	50.0	73.3	0.135	0.131	0.0296
STD 4	25.0	11.10	50.0	46.4	0.333	0.330	0.0297
STD 5	50.0	22.20	50.0	19.2	0.717	0.713	0.0321
STD 6		0.00			ERR	ERR	ERR

Regression Output:

Constant		-0.0084
Std Err of Y Est		0.0113
R Squared		0.9986
No. of Observations		6.0000
Degrees of Freedom		4.0000
X Coefficient(s)	0.0321	
Std Err of Coef.	0.0006	

CLIENT	SAMPLE NO.	SAMPLE VOLUME (mL)	DISTILLATE VOLUME (mL)	ANALYSIS VOLUME (mL)	% T @ 578 NM	ABS @ 578 NM	CORR ABS @ 578 NM	CYANIDE (ug)	CALC CYANIDE (ug/L)
	METH BLANK	500.0	250.0	50.0	98.5	0.007	----	----	----
	CHECK STD	10.0	250.0	50.0	47.3	0.325	0.319	10.19	100.09 % RECOVERY
	91009027	500.0	250.0	50.0	98.2	0.008	0.001	0.30	3.04
	90365004	500.0	250.0	50.0	98.3	0.007	0.001	0.29	2.91 <cl was quenched
	90365005	500.0	250.0	50.0	98.1	0.008	0.002	0.32	3.18
	90365006	500.0	250.0	50.0	98.6	0.006	0.000	0.25	2.49
	90365007	500.0	250.0	50.0	97.5	0.011	0.004	0.40	4.01
	90365006	500.0	250.0	50.0	98.5	0.007	0.000	0.26	2.63
	90365007	500.0	250.0	50.0	52.0	0.284	0.277	8.91	89.11 KAM 1-10-91
	CHK STD	10.0	250.0	50.0	47.8	0.321	0.314	10.05	~~5025.32~~ / 10.18 X100 = 49%

CYANIDE SOIL 1-10-91 KAM

CYANIDE SOIL
CALCULATIONS

METHOD: CLP-M 335.2
PQL = 3 mg/kg

DATE: JANUARY 10, 1991
ANALYST: KAM

CLIENT	SAMPLE ID	WET SAMPLE WGT (g)	DEC % TS	DISTILLATE VOL (ml)	ANALYSIS VOL (ml)	CYANIDE (ug)	CYANIDE (CALC.(mg/kg)
	90365004	5.93	0.843	250.00	50.00	0.29	0.29 <cl was quenched
	90365005	5.45	0.917	250.00	50.00	0.32	0.32
	90365006	6.27	0.797	250.00	50.00	0.25	0.25
	90365007	5.64	0.886	250.00	50.00	0.40	0.40
DUP	90365006	6.27	0.797	250.00	50.00	0.26	0.26

KAM 1-10-91

Spike recovery 90365007 8.91 ug − 0.40 ug / 5.09 mg × 10.0 mg × 50 / 250 × 18 = 84%

Duplicate 90365006	x_1	x_2	$\bar{x}$	RPD
	<2.0	<2.0	<2.0	—

Continued on Page

Karen A Mellison — Jan 10, 1991 — Distillation — Date
Karen A Mellison — Jan 10, 1991 — Analysis — Signed — Date

Read and Understood By
Signed — Date 1/14/91

J.T.BAKER INC., 222 RED SCHOOL LANE, PHILLIPSBURG, NJ 08865

SECTION I - PRODUCT IDENTIFICATION

PRODUCT NAME: PYRIDINE
COMMON SYNONYMS: PYRIDIN; AZABENZENE
CHEMICAL FAMILY: HETEROCYCLIC COMPOUNDS
FORMULA: C5H5N
FORMULA WT.: 79.10
CAS NO.: 110-86-1
NIOSH/RTECS NO.: UR8400000
PRODUCT USE: LABORATORY REAGENT
PRODUCT CODES: 9391,3348,3352,9393

PRECAUTIONARY LABELING

BAKER SAF-T-DATA# SYSTEM

HEALTH	-	2	MODERATE
FLAMMABILITY	-	3	SEVERE (FLAMMABLE)
REACTIVITY	-	1	SLIGHT
CONTACT	-	2	MODERATE

LABORATORY PROTECTIVE EQUIPMENT

GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES; CLASS B EXTINGUISHER

U.S. PRECAUTIONARY LABELING

WARNING

FLAMMABLE. CAUSES IRRITATION. HARMFUL IF INHALED.
KEEP AWAY FROM HEAT, SPARKS, FLAME. AVOID CONTACT WITH EYES, SKIN, CLOTHING. AVOID BREATHING VAPOR. KEEP IN TIGHTLY CLOSED CONTAINER. USE WITH ADEQUATE VENTILATION. WASH THOROUGHLY AFTER HANDLING. IN CASE OF FIRE, USE ALCOHOL FOAM, DRY CHEMICAL, CARBON DIOXIDE - WATER MAY BE INEFFECTIVE. IN CASE OF SPILL, SOAK UP WITH SAND OR EARTH. FLUSH SPILL AREA WITH WATER.

INTERNATIONAL LABELING

HIGHLY FLAMMABLE. HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.

CONTINUED ON PAGE: 2

PRECAUTIONARY LABELING (CONTINUED)

IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE. AFTER CONTACT WITH SKIN, WASH IMMEDIATELY WITH PLENTY OF SOAP AND WATER.

SAF-T-DATA# STORAGE COLOR CODE: RED (FLAMMABLE)

SECTION II - COMPONENTS

COMPONENT	CAS NO.	WEIGHT %	OSHA/PEL	ACGIH/TLV
PYRIDINE	110-86-1	99-100	5 PPM	5 PPM

SECTION III - PHYSICAL DATA

BOILING POINT: 115 C (239 F)
(AT 760 MM HG)

VAPOR PRESSURE (MMHG): 16
(20 C)

MELTING POINT: -42 C (-43 F)
(AT 760 MM HG)

VAPOR DENSITY (AIR=1): 2.7

SPECIFIC GRAVITY: 0.98
(H2O=1)

EVAPORATION RATE: N/A

SOLUBILITY(H2O): COMPLETE (100%)

% VOLATILES BY VOLUME: 100
(21 C)

PH: N/A

ODOR THRESHOLD (P.P.M.): N/A

PHYSICAL STATE: LIQUID.

COEFFICIENT WATER/OIL DISTRIBUTION: N/A

APPEARANCE & ODOR: CLEAR, COLORLESS LIQUID. DISAGREEABLE ODOR.

CONTINUED ON PAGE: 3

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (CLOSED CUP): 19 C (66 F) NFPA 704M RATING: 2-3-0

AUTOIGNITION TEMPERATURE: 481 C (900 F)

FLAMMABLE LIMITS: UPPER - 12.4 % LOWER - 1.8 %

FIRE EXTINGUISHING MEDIA
USE ALCOHOL FOAM, DRY CHEMICAL OR CARBON DIOXIDE. (WATER MAY BE INEFFECTIVE.)

SPECIAL FIRE-FIGHTING PROCEDURES
FIREFIGHTERS SHOULD WEAR PROPER PROTECTIVE EQUIPMENT AND SELF-CONTAINED BREATHING APPARATUS WITH FULL FACEPIECE OPERATED IN POSITIVE PRESSURE MODE. MOVE CONTAINERS FROM FIRE AREA IF IT CAN BE DONE WITHOUT RISK. USE WATER TO KEEP FIRE-EXPOSED CONTAINERS COOL.

UNUSUAL FIRE & EXPLOSION HAZARDS
VAPORS MAY FLOW ALONG SURFACES TO DISTANT IGNITION SOURCES AND FLASH BACK. CLOSED CONTAINERS EXPOSED TO HEAT MAY EXPLODE. CONTACT WITH STRONG OXIDIZERS MAY CAUSE FIRE.

TOXIC GASES PRODUCED
OXIDES OF NITROGEN, CYANIDES, AMMONIA, CARBON MONOXIDE, CARBON DIOXIDE

EXPLOSION DATA-SENSITIVITY TO MECHANICAL IMPACT
NONE IDENTIFIED.

EXPLOSION DATA-SENSITIVITY TO STATIC DISCHARGE
NONE IDENTIFIED.

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE (TLV/TWA): 15 MG/M3 (5 PPM)

SHORT-TERM EXPOSURE LIMIT (STEL): NOT ESTABLISHED

PERMISSIBLE EXPOSURE LIMIT (PEL): 15 MG/M3 (5 PPM)

TOXICITY OF COMPONENTS

CONTINUED ON PAGE: 4

SECTION V - HEALTH HAZARD DATA (CONTINUED)

ORAL RAT LD50 FOR PYRIDINE	891	MG/KG
INTRAPERITONEAL RAT LD50 FOR PYRIDINE	366	MG/KG
SUBCUTANEOUS RAT LD50 FOR PYRIDINE	1000	MG/KG
SKIN RABBIT LD50 FOR PYRIDINE	1121	MG/KG

CARCINOGENICITY: NTP: NO IARC: NO Z LIST: NO OSHA REG: NO

CARCINOGENICITY
NONE IDENTIFIED.

REPRODUCTIVE EFFECTS
NONE IDENTIFIED.

EFFECTS OF OVEREXPOSURE

INHALATION: HEADACHE, NAUSEA, VOMITING, DIZZINESS, NARCOSIS, RESPIRATORY FAILURE, LOW BLOOD PRESSURE, CENTRAL NERVOUS SYSTEM DEPRESSION

SKIN CONTACT: SEVERE IRRITATION OR BURNS

EYE CONTACT: SEVERE IRRITATION OR BURNS

SKIN ABSORPTION: MAY BE HARMFUL

INGESTION: IS HARMFUL AND MAY BE FATAL, HEADACHE, NAUSEA, VOMITING, DIZZINESS, GASTROINTESTINAL IRRITATION

CHRONIC EFFECTS: KIDNEY DAMAGE, LIVER DAMAGE

TARGET ORGANS
CENTRAL NERVOUS SYSTEM, LIVER, KIDNEYS, GI TRACT, SKIN

MEDICAL CONDITIONS GENERALLY AGGRAVATED BY EXPOSURE
NONE IDENTIFIED

PRIMARY ROUTES OF ENTRY
INHALATION, ABSORPTION, INGESTION, EYE CONTACT, SKIN CONTACT

CONTINUED ON PAGE: 5

SECTION V - HEALTH HAZARD DATA (CONTINUED)

EMERGENCY AND FIRST AID PROCEDURES

INGESTION: CALL A PHYSICIAN. IF SWALLOWED, DO NOT INDUCE VOMITING. IF CONSCIOUS, GIVE LARGE AMOUNTS OF WATER.

INHALATION: IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING, GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.

SKIN CONTACT: IN CASE OF CONTACT, FLUSH SKIN WITH WATER.

EYE CONTACT: IN CASE OF EYE CONTACT, IMMEDIATELY FLUSH WITH PLENTY OF WATER FOR AT LEAST 15 MINUTES.

SARA/TITLE III HAZARD CATEGORIES AND LISTS

ACUTE: YES CHRONIC: YES FLAMMABILITY: YES PRESSURE: NO REACTIVITY: NO

TRENELY HAZARDOUS SUBSTANCE:	NO	
CERCLA HAZARDOUS SUBSTANCE:	YES	CONTAINS PYRIDINE (RQ = 1000 LBS)
TOXIC CHEMICALS:	YES	CONTAINS PYRIDINE
GENERIC CLASS:		C11
TSCA INVENTORY:	YES	

SECTION VI - REACTIVITY DATA

STABILITY: STABLE HAZARDOUS POLYMERIZATION: WILL NOT OCCUR

CONDITIONS TO AVOID: HEAT, FLAME, OTHER SOURCES OF IGNITION, LIGHT

INCOMPATIBLES: STRONG OXIDIZING AGENTS, STRONG ACIDS

DECOMPOSITION PRODUCTS: OXIDES OF NITROGEN, CYANIDES, AMMONIA, CARBON MONOXIDE, CARBON DIOXIDE

CONTINUED ON PAGE: 6

SECTION VII - SPILL & DISPOSAL PROCEDURES

STEPS TO BE TAKEN IN THE EVENT OF A SPILL OR DISCHARGE
WEAR SELF-CONTAINED BREATHING APPARATUS AND FULL PROTECTIVE CLOTHING. SHUT OFF IGNITION SOURCES; NO FLARES, SMOKING OR FLAMES IN AREA. STOP LEAK IF YOU CAN DO SO WITHOUT RISK. USE WATER SPRAY TO REDUCE VAPORS. TAKE UP WITH SAND OR OTHER NON-COMBUSTIBLE ABSORBENT MATERIAL AND PLACE INTO CONTAINER FOR LATER DISPOSAL. FLUSH AREA WITH WATER.

J. T. BAKER SOLUSORB(R) SOLVENT ADSORBENT IS RECOMMENDED FOR SPILLS OF THIS PRODUCT.

DISPOSAL PROCEDURE
DISPOSE IN ACCORDANCE WITH ALL APPLICABLE FEDERAL, STATE, AND LOCAL ENVIRONMENTAL REGULATIONS.

EPA HAZARDOUS WASTE NUMBER: U196 (TOXIC WASTE)

SECTION VIII - INDUSTRIAL PROTECTIVE EQUIPMENT

VENTILATION: USE GENERAL OR LOCAL EXHAUST VENTILATION TO MEET TLV REQUIREMENTS.

RESPIRATORY PROTECTION: RESPIRATORY PROTECTION REQUIRED IF AIRBORNE CONCENTRATION EXCEEDS TLV. AT CONCENTRATIONS UP TO 250 PPM, A CHEMICAL CARTRIDGE RESPIRATOR WITH ORGANIC VAPOR CARTRIDGE IS RECOMMENDED. ABOVE THIS LEVEL, A SELF-CONTAINED BREATHING APPARATUS IS RECOMMENDED.

EYE/SKIN PROTECTION: SAFETY GOGGLES AND FACE SHIELD, UNIFORM, PROTECTIVE SUIT, BUTYL RUBBER GLOVES ARE RECOMMENDED.

SECTION IX - STORAGE AND HANDLING PRECAUTIONS

SAF-T-DATA# STORAGE COLOR CODE: RED (FLAMMABLE)

STORAGE REQUIREMENTS
KEEP CONTAINER TIGHTLY CLOSED. STORE IN A COOL, DRY, WELL-VENTILATED, FLAMMABLE LIQUID STORAGE AREA. KEEP PRODUCT OUT OF LIGHT.

CONTINUED ON PAGE: 7

SECTION IX - STORAGE AND HANDLING PRECAUTIONS (CONTINUED)

SPECIAL PRECAUTIONS
BOND AND GROUND CONTAINERS WHEN TRANSFERRING LIQUID.

SECTION X - TRANSPORTATION DATA AND ADDITIONAL INFORMATION

DOMESTIC (D.O.T.)

PROPER SHIPPING NAME: PYRIDINE
HAZARD CLASS: FLAMMABLE LIQUID
UN/NA: UN1282 REPORTABLE QUANTITY: 1000 LBS.
LABELS: FLAMMABLE LIQUID
REGULATORY REFERENCES: 49CFR 172.101; 173.119

INTERNATIONAL (I.M.O.)

PROPER SHIPPING NAME: PYRIDINE
HAZARD CLASS: 3.2 I.M.O. PAGE: 3104
UN: UN1282 MARINE POLLUTANTS: NO PACKAGING GROUP: II
LABELS: FLAMMABLE LIQUID, POISON
REGULATORY REFERENCES: 49CFR 172.102; PART 176; IMO

AIR (I.C.A.O.)

PROPER SHIPPING NAME: PYRIDINE
HAZARD CLASS: 3.2
UN: UN1282 PACKAGING GROUP: II
LABELS: FLAMMABLE LIQUID, POISON
REGULATORY REFERENCES: 49CFR 172.101; 173.6; PART 175; ICAO/IATA

U.S. CUSTOMS HARMONIZATION NUMBER: 29333100001

N/A = NOT APPLICABLE OR NOT AVAILABLE
N/E = NOT ESTABLISHED

THE INFORMATION IN THIS MATERIAL SAFETY DATA SHEET MEETS THE REQUIREMENTS OF THE UNITED STATES OCCUPATIONAL SAFETY AND HEALTH ACT AND REGULATIONS PROMULGATED THEREUNDER (29 CFR 1910.1200 ET. SEQ.) AND THE CANADIAN WORKPLACE HAZARDOUS MATERIALS INFORMATION SYSTEM. THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONARY HANDLING OF

CONTINUED ON PAGE: 8

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THE MATERIAL BY A PERSON TRAINED IN, OR SUPERVISED BY A PERSON TRAINED IN, CHEMICAL HANDLING. THE USER IS RESPONSIBLE FOR DETERMINING THE PRECAUTIONS AND DANGERS OF THIS CHEMICAL FOR HIS OR HER PARTICULAR APPLICATION. DEPENDING ON USAGE, PROTECTIVE CLOTHING INCLUDING EYE AND FACE GUARDS AND RESPIRATORS MUST BE USED TO AVOID CONTACT WITH MATERIAL OR BREATHING CHEMICAL VAPORS/FUMES.
EXPOSURE TO THIS PRODUCT MAY HAVE SERIOUS ADVERSE HEALTH EFFECTS. THIS CHEMICAL MAY INTERACT WITH OTHER SUBSTANCES. SINCE THE POTENTIAL USES ARE SO VARIED, BAKER CANNOT WARN OF ALL OF THE POTENTIAL DANGERS OF USE OR INTERACTION WITH OTHER CHEMICALS OR MATERIALS. BAKER WARRANTS THAT THE CHEMICAL MEETS THE SPECIFICATIONS SET FORTH ON THE LABEL.
BAKER DISCLAIMS ANY OTHER WARRANTIES, EXPRESSED OR IMPLIED WITH REGARD TO THE PRODUCT SUPPLIED HEREUNDER, ITS MERCHANTABILITY OR ITS FITNESS FOR A PARTICULAR PURPOSE.
THE USER SHOULD RECOGNIZE THAT THIS PRODUCT CAN CAUSE SEVERE INJURY AND EVEN DEATH, ESPECIALLY IF IMPROPERLY HANDLED OR THE KNOWN DANGERS OF USE ARE NOT HEEDED. READ ALL PRECAUTIONARY INFORMATION. AS NEW DOCUMENTED GENERAL SAFETY INFORMATION BECOMES AVAILABLE, BAKER WILL PERIODICALLY REVISE THIS MATERIAL SAFETY DATA SHEET. IF YOU HAVE ANY QUESTIONS, PLEASE CALL CUSTOMER SERVICE (1-800-JTBAKER) FOR ASSISTANCE.

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APPROVED BY QUALITY ASSURANCE DEPARTMENT.

-- LAST PAGE --
"ISSUED 01/25/92"

ATTACHMENT E

ANALYTICAL SEQUENCE FOR CYANIDE BY EPA CLP SOW ILM03.0

Prior to analyzing the following sample sequence a calibration curve must be prepared and analyzed as specified in the current revision of PACE-New England-ME SOP No. CA-020, "Spectrophotometric Determination of Cyanide in Domestic and Industrial Wastewater, Drinking, Surface, and Saline Waters and Sediment/Soil Samples."

Note: All samples w/out ◆ are to be distilled.

	SAMPLE	SAMPLE # (count)	% RECOVERY CRITERIA
	ICV		85-115
◆	ICB		
	PBS (if soils)	1	
	PBW (if waters)	2	
	Mid Range std	3	85-115
	Sample	4	
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample	9	
	Sample	10	
◆	CCV		85-115
◆	CCB		
	Sample	1	
	Sample	2	
	Sample	3	
	Sample	4	
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample DUP	9	
	Sample MS	10	75-125

ATTACHMENT E

ANALYTICAL SEQUENCE FOR CYANIDE BY EPA METHOD 335.2

Prior to analyzing the following sample sequence a calibration curve must be prepared and analyzed as specified in the current revision of PACE-New England-ME SOP No. CA-020, "Spectrophotometric Determination of Cyanide in Domestic and Industrial Wastewater, Drinking, Surface, and Saline Waters and Sediment/Soil Samples."

Note: All samples w/out ◆ are to be distilled.

	SAMPLE	SAMPLE # (count)	% RECOVERY CRITERIA
	ICV/LCS		67-130 (1)
	PBS (if soils)	1	
	PBW (if waters)	2	
	High Range Std	3	90-110
	Low Range Std	4	90-110
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample	9	
	Sample MS	10	75-125
◆	CCV		67-130 (1)
◆	CCB		
	Sample	1	
	Sample	2	
	Sample	3	
	Sample	4	
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample DUP	9	
	Sample MS	10	75-125

(1) Laboratory statistically derived recovery criteria.

ATTACHMENT E

ANALYTICAL SEQUENCE FOR CYANIDE BY EPA METHOD 9010A

Prior to analyzing the following sample sequence a calibration curve must be prepared and analyzed as specified in the current revision of PACE-New England-ME SOP No. CA-020, "Spectrophotometric Determination of Cyanide in Domestic and Industrial Wastewater, Drinking, Surface, and Saline Waters and Sediment/Soil Samples."

Note: All samples w/out ◆ are to be distilled.

	SAMPLE	SAMPLE # (count)	% RECOVERY CRITERIA
	ICV/LCS		85-115
	PBS (if soils)	1	
	PBW (if waters)	2	
	High Range Std	3	90-110
	Low Range Std	4	90-110
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample	9	
	Sample MS	10	75-125
◆	CCV		85-115
◆	CCB		
	Sample	1	
	Sample	2	
	Sample	3	
	Sample	4	
	Sample	5	
	Sample	6	
	Sample	7	
	Sample	8	
	Sample DUP	9	
	Sample MS	10	75-125

STANDARD OPERATING PROCEDURE

Author: B. Carbone
Approved by:

Willard C. Warren, III
President, Northeastern Division

Issuing Unit: CCAS-Northeast
SOP No.: CA-040-00
Date: November 1993

TITLE: Alkalinity-Potentiometric, Titration pH 4.5

PURPOSE: To describe the procedure used by CCAS-NE to determine the concentration of CO_3, HCO_3, and OH ions in surface, groundwater and industrial wastes.

SCOPE: To determine acid-neutralizing capacity of 100 mL of sample to obtain a Practical Quantitation Level (PQL) of 20 mg/L as $CaCO_3$ in accordance with EPA Method 310.1. Sample analysis must be performed within 14 days from sample collection. Samples must be refrigerated to 4°C and stored at 4°C until analysis.

REQUIREMENTS:

A. EQUIPMENT

1. pH Meter Model 701A Orion Digital or equivalent

   a. Meter must be calibrated with buffers which bracket the end point.

2. Magnetic stir plate with 1" Teflon coated stir bars

3. Class A Buret (10 mL)

4. 150 mL beakers

5. 100 mL Class A graduated cylinder

6. Class A volumetric pipets (1.0, 5.0, 10.0 mL)

7. Hot plate (ceramic)

B. REAGENTS

1. 0.02N H_2SO_4 (Low Level, Mid Level)

   a. Prepare in accordance with EPA Method 310.1 by diluting 200 mL of 0.1N H_2SO_4 to 1 liter with ASTM Type II water in a Class A volumetric flask. Standardize following Procedure steps A.1.a through A.1.g.

2. 0.100N H_2SO_4 (High Level)

   a. Prepare in accordance with EPA Method 310.1 by diluting 3.0 mL of concentrated H_2SO_4 to 1 liter with ASTM Type II water in a Class A volumetric flask. Standardize following Procedure Steps A.2.a through A.2.c.

3. Laboratory Control Sample (LCS)

   a. Prepare by diluting 5.0 mL of 25,000 mg/L as $CaCO_3$ of HACH Check Standard to one liter with ASTM Type II water. Final concentration is equivalent to 125 mg/L.

4. Spike Solution (Mid Level)

   a. Prepare by diluting 5.0 mL of 25,000 mg/L as $CaCO_3$ HACH Check Standard to 100 mL with ASTM Type II water. Final concentration is equivalent to 1250 mg/L.

5. Sodium Carbonate (Na_2CO_3) Solution (Primary Standard Grade), 0.05N

   a. Prepare by:

      1. Drying 3-5 g Na_2CO_3 @ 250°C for four hours

      2. Cool and weigh 2.5000g $\pm$ 0.2000g and dilute to 1.0 liter with Type II water.

PROCEDURE:

A. TITRATION OF TITRANTS, STANDARDS AND SAMPLES

1. Standardization of 0.02N Titrant
   (Low Level, Mid Level)

   a. Volumetrically pipet 15 mL of Na_2CO_3 solution into three 150 ml beakers.

   b. Fill a Class A 10 mL buret with 0.02N H_2SO_4 titrant.

   c. Titrate each beaker potentiometrically to a pH of 5.00. Record titrant volume to 3 significant figures.

   d. Remove stir bars, cover with a watchglass and place on a ceramic hot plate and warm until gentle boil occurs. Gently boil under a watch glass cover for 3-5 minutes.

   e. Cool and rinse the watch glass cover into the beaker.

f. Titrate each beaker again potentiometrically to a pH of 4.50. Record titrant volume to 3 significant figures.

g. Calculate normality of titrant by the following calculation.

$$N = \frac{A \times B}{53.00 \times C}$$

where:
N = Normality of H_2SO_4
A = g Na_2CO_3 weighed into 1 L
C = mean of the total mL titrant from all titrations
B = mL Na_2CO_3 solution titrated

2. Standardization of 0.100 N titrant

a. Fill a 150 mL beaker with 40 ml Na_2CO_3 standard solution and 60 ml ASTM Type II water using a Class A 100 mL graduated cylinder.

b. Fill a Class A 10 mL buret with 0.1N H_2SO_4 titrant.

c. Calculate normality by following steps A.1.c-A.1.g.

3. Titration of standards and samples

a. Place 100 mL of sample or standard into 150 mL beaker using a 100 mL graduated cylinder.

b. Read initial pH and record.

c. Titrate with 0.02N H_2SO_4 until pH is equivalent to 4.50 +/- 0.01 units.

d. Record titration volume.

1. If titrant volume > 20 mL - Reanalyze with 0.1N H_2SO_4 titrant.
2. If desired PQL is < 20.0 mg/L proceed to step A.4.

e. Calculate total alkalinity

$$\text{Total Alkalinity} = \text{mg/L as } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{mL Sample}}$$

where: A = mL titrant to reach pH 4.50 +/- 0.01
N = normality of titrant to 3 significant figures

4. Low Level Alkalinity Measurement

   a. Perform Steps A.3.a-A.3.d.

   b. Add drop wise 0.02N H_2SO_4 titrant until pH is 0.3 units lower then endpoint recorded in Step A.3.d.

   c. Calculate total alkalinity by the following equation.

$$\text{Low Level Alkalinity} = \text{mg/L as } CaCO_3 = \frac{(2B-C) \times N \times 50{,}000}{\text{mL Sample}}$$

where: B = titrant volume (mL) to first endpoint (i.e., first recorded pH)
C = total titrant volume (mL) to 0.3 pH units lower
N = normality of titrant to 3 significant figures

B. QUALITY CONTROL

1. One blank titration of ASTM Type II water must be analyzed daily.

   a. Acceptance Criteria for Mid, High Level: <20 mg/L as $CaCO_3$
   b. Acceptance Criteria for Low Level: <5.0 mg/L as $CaCO_3$

2. One laboratory control sample (LCS) at 125 mg/L as $CaCO_3$ must be analyzed for every twenty samples or each day for mid and high level analyses.

   For low level analysis, analyze one laboratory control sample at 12.5 mg/L as $CaCO_3$ for every twenty samples or each day.

   a. Acceptance Criteria for Mid, High Level LCS: 93-106% of true value
   b. Acceptance Criteria for Low Level LCS: 90-110% of true value
   c. Corrective Action: If unacceptable, reanalysis of all samples and restandardization of titrant is required.

3. One sample duplicate is analyzed for every ten samples or each day's batch.

   a. Acceptance Criteria:

      1. 0-20% Relative Percent Difference for concentrations >60 mg/L for mid level and >15 mg/L for low level

      2. 0-100% Relative Percent Difference for concentrations <60 mg/L for mid level and <15 mg/L for low level

      3. Duplicate results not meeting RPD criteria are reported with the I-9 notation.

4. One matrix spike is analyzed for every twenty samples or each day's batch.

a. Spike is prepared by volumetrically pipetting 10 mL of spike solution into 100 mL of sample in a 150 mL beaker.

b. Acceptance Criteria

75-125% Recovery of spike True Value

c. Calculate by the following equation.

$$\frac{[(\text{Sample + Spike}) - (\text{Sample})]\ \text{mg/L Alk. as } CaCO_3}{(\text{Spike concentration})\ \text{mg/L as } CaCO_3} \times 100\%$$

C. CORRECTIVE ACTION

1. Blank Concentration Unacceptable

a. Restandardization of titrant and reanalysis of samples.

2. LCS unacceptable

a. Restandardization of titrant and reanalysis of samples to the point of acceptable LCS recovery.

3. Duplicate RPD >20%

a. Reanalysis of sample and employ Q_{90} test. Refer to section 7.2.3 of the CCAS-NE Quality Assurance Manual.

b. If all three values are acceptable by Q_{90} test, report initial sample result with I-9 notation.

c. If one value rejected, report initial result of two remaining values with I-9 notation.

4. Matrix Spike recovery outside 75-125%

If below 75% or if above 125%, report result as long as LCS is acceptable and laboratory problem is not suspected.

REFERENCES: "Methods for Chemical Analysis of Water and Wastes," Method 310.1, EPA-600/4-79-020, Revised March 1983.

"Standard Methods For The Examination of Water and Wastewater," Method 403, 16th Edition, 1985, American Public Health Association.

ATTACHMENTS: Attachment A - Example Data Page from Logbook
Attachment B - Example Lotus Spreadsheet

GLOSSARY: None.

ATTACHMENT A

Notebook No. VII

PROJECT Alkalinity - low level EPA 310.1

Continued From Page 28

Na_2CO_3 Std:

H_2SO_4 : 0.02N

PQL: 20 mg/L | 5.0 mg/L

MDL: 0.49 mg/L

Hach Check Std: 125 mg/L Alk 091693 P5W1

Hach Spike bstn: 2500 mg/L Alk 091593 P5W2

Standardization of 0.02 N H_2SO_4

Analyte	Analyte Vol	1st endpoint pH	mls H_2SO_4 added	pH after boiling	Final pH	mls H_2SO_4 added	
Na_2CO_3	15.0	5.04	33.25	7.02	4.55	0.60	33.85
↓	↓	5.00	33.25	6.27	4.47	0.40	33.65
		5.04	33.10	6.34	4.52	0.55	33.65

$\bar{X} = 33.72$

H_2SO_4 : $\frac{2.5003 g/L \cdot 15 ml}{53 g/eq \cdot 33.72 ml} = \boxed{0.0210 N}$

Client	Sample ID	Site ID	Initial pH	1st endpoint pH	2nd endpoint pH	1st mls H_2SO_4	2nd mls H_2SO_4	Δ mls H_2SO_4	Sample Vol.
	Blank		5.82	4.54	4.24	0.30	0.35	0.65	200
Hach	Check Std		10.56	4.53	4.24	24.19	0.41	24.60	↓
IP	WJ1061-4		8.75	4.54	4.24	9.65	0.40	10.05	
↓	WJ1066-4		5.99	4.53	4.23	0.35	0.35	0.70	
	WJ1090-4		6.52	4.55	4.23	1.45	0.35	1.80	↓

Continued on Page 28

Read and Understood By

Signed	Date	Signed	Date
Christa Meier	091793	D. Nadeau	9-23-93

ATTACHMENT B

PROJECT Alkalinity Low Level: EPA 310.1

Continued From Page 28

PQL: 20 mg/L / 5.0 mg/L

MDL: 0.49 mg/L

ALKALINITY, AS CaCO3
TITRIMETRIC

METHOD: EPA 310.1 - LOW LEVEL
PQL = 5.0 mg/L

DATE: 091693
ANALYST: CM

NaCO3 STANDARD CONC. = 0.2000 mg/L
DATE: 091593
BY: CM

H2SO4 SOLN TITRANT CONC. = 0.0200 NORMALITY
DATE: 091593
BY: CM

CLIENT	SAMPLE NO	SAMPLE VOLUME (mL)	INITIAL pH	1ST pH	2ND pH	INITIAL VOLUME (mL)	1ST VOLUME (mL)	2ND VOLUME (mL)	TOTAL VOLUME (mL)	ALKALINITY as CaCO3 (mg/L)
	BLANK	200	5.82	4.54	4.24	0.00	0.30	0.35	0.65	-0.25
HACH	CHECK STD	200	10.56	4.53	4.24	0.00	24.19	0.41	24.60	(118.90)(125)10^-1 =
IP	WJ1061-4	200	8.75	4.54	4.24	0.00	9.65	0.40	10.05	46.25
	WJ1066-4	200	5.99	4.53	4.23	0.00	0.35	0.35	0.70	0.00
	WJ1090-4	200	6.52	4.55	4.23	0.00	1.45	0.35	1.80	5.50

Note: No duplicate or spike sample analyzed because of limited sample volume available.

BICARBONATE AND CARBONATE IN WATER

SAMPLE NO	pH	Total Alkalinity (mg/L CaCO3)	HCO3 Alkalinity (mg/L CaCO3)	CO3 Alkalinity (mg/L CaCO3)	OH Alkalinity (mg/L CaCO3)
WJ1061-4	8.75	46.25	43.6609	2.30792	0.28117
WJ1066-4	5.99	0.00	-0.0005	0.00000	0.00049
WJ1090-4	6.52	5.50	5.4966	0.00171	0.00166

Continued on Page 29

Read and Understood By

Signed	Date	Signed	Date
Christina Miller	091693	D. Nadeau	9.23.93

DRAFT

STANDARD OPERATING PROCEDURE

Author: Lori Thompson/Julie Ricardi
Approved by:

John C. Burton
Operations Manager

Issuing Unit: Katahdin Analytical
SOP No.: CA-019-00
Date: November 1995

TITLE: Biochemical Oxygen Demand in Aqueous Sample Matrices

PURPOSE: To describe the procedures and requirements followed by Katahdin Analytical Services personnel for the analysis of biochemical oxygen demand (BOD), total and carbonaceous, in aqueous matrices utilizing the manual probe method, EPA Method 405.1.

SCOPE: This procedure is applicable to the analysis of water, wastewater, and sea water for total and carbonaceous BOD. A Practical Quantitation Level (PQL) of 6 mg/Lis attainable using an initial sample volume of 300 mL.

REQUIREMENTS:

A. EQUIPMENT

1. YSI Model 58 Dissolved Oxygen Meter (or equivalent) with bottle probe
2. Replacement membranes and probe filling solutions
3. Incubator, capable of maintaining temperature of 20 ± 1 C
4. 300 mL Wheaton BOD bottles, clear, with stoppers and caps
5. Mixing flasks, Class A
6. Graduated cylinders, 100 mL, Class A
7. Beakers, 125 mL and 400 mL, glass
8. Buret, 25 mL Class A, 0.1 mL graduations
9. Buret, 10 mL Class A, 0.01 mL graduations
10. Oxford pipettor, 5 and 10 mL
11. Disposable pipet tips, 5 and 10 mL
12. Oxford repipettor, 2-5 mL dispensing capability
13. Disposable repipet tips, 50 mL
14. Teflon magnetic stir bars
15. Stir plate
16. Multirange pH paper
17. Small scoop
18. 20 L carboys

B. REAGENTS

1. Phosphate buffer solution, Banco or equivalent
2. Magnesium sulfate solution, 22.5 g $MgSO_4.7H_2O$ diluted to 1 L with ASTM Type II water
3. Calcium chloride solution, 27.5 g $CaCl_2$ diluted to 1 L with ASTM Type II water
4. Ferric chloride solution, 0.25 g $FeCl_3.6H_2O$ diluted to 1 L with ASTM Type II water
5. Sodium Sulfite Solution, 0.025 N, 1.575 g Na_2SO_4 diluted to 1 L with ASTM Type II water
6. Glucose-Glutamic Acid solution, 150 mg dried glucose and 150 mg dried glutamic acid diluted to 1 L with ASTM Type II water. Dry reagents at 103 C for 1 hour. Transfer 5.0 mL aliquots of solution to a screw top culture tube and cap. Freeze all tubes. Material is stables for one year from date of preparation or until manufacturer expiration date is reached, whichever is sooner.
7. Nitrification Inhibitor, Hach or equivalent

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8. Sulfuric Acid, concentrated
9. Sodium Hydroxide, 10 N
10. Manganous sulfate solution, RICCA or equivalent
11. Alkaline Iodide Sodium Azide solution
12. Starch indicator, Banco or equivalent
13. Standardized sodium thiosulfate solution, Hach or equivalent
14. Potassium iodide solution, 10 g KI diluted to 100 mL with ASTM Type II water
15. Dilution water: Prepare by adding 20 mL of the calcium chloride solution, 20 mL of the ferric chloide solution, 20 mL of the magnesium sulfate solution, and 20 mL of the phosphate buffer to ASTM Type II water in a 20 L carboy precleaned and used exclusively for BOD dilution water. Fill to the 20 L mark with ASTM Type II water. Leave the carboy open to the atmosphere and allow it to equilibrate for several (2-3) days prior to use.
16. "Seeding" solution, S. Portland Water District Effluent or other appropriate source

PROCEDURE:

A. SAMPLE PRETREATMENT - pH AND INTERFERENCE CHECKS

1. Homogenize sample by rotating in a clockwise/counterclockwise agitation. Do not shake vigorously as this could super-saturate the matrix solution.

2. Check sample pH using multi-range pH test strips. The target range is 7.0 to 9.0. If the sample is outside of this range, neutralize with a solution of sulfuric acid or sodium hydroxide, as appropriate and of sufficient strength so that the quantity of solution does not dilute the sample aliquot by more than 0.5%. Record the volume of sulfuric acid or sodium hydroxide used in the BOD logbook.

3. Transfer a 50 mL aliquot of the sample to a 125 mL beaker.

4. Check for residual chlorine by adding 5 mL of a 1+50 sulfuric acid solution and 5 mL of the potassium iodide solution. If the solution remains colorless the sample has tested negative; proceed to step B.1. If the solution turns blue the sample is positive for residual chlorine; proceed to step A.5.

5. Titrate the sample using the sodium sulfite solution (0.025 N) until the solution turns clear. Record the volume of sodium sulfite used in the BOD logbook.

6. For each sample, the volume of titrant used is the volume of sodium sulfite solution that must be added per each 50 mL of the sample prior to analysis.

B. PREPARATION OF SAMPLE DILUTIONS

1. The quality control sample requirements for each analytical batch of twenty or fewer samples are as follows:

a. Unseeded Dilution Waters - two
b. Seeded Dilution Waters (for seed correction) - three
c. Laboratory Control Samples, True Value = 198 mg/L - two
d. Matrix Spike - one per ten samples
e. Sample Duplicate - one per twenty samples

The remainder of the batch consists of sample dilutions (refer to Attachment A for an example analytical run).

2. For samples with unknown analytical history, the standard sample dilution scheme consists of nine dilutions: 0.050, 0.10, 0.50, 1.0, 2.0, 5.0, 10, 50, and 100 mL of sample. The 10 to 100 mL sample

aliquots are derived by direct aliquot volumes of sample, and the 0.050 to 5.0 mL sample volumes are obtained from serial dilutions.

Serial dilutions are prepared by transferring 10 mL of sample to a 100 mL mixing flask and filling to the mark with ASTM Type II water to yield a 0.10 mL dilution. Transfer 10 mL of this dilution to another 100 mL mixing flask and fill to the mark with ASTM Type II water to yield a 0.010 mL dilution.

3. To prepare the 0.050, 0.10 and 0.50 mL dilutions, transfer 5.0, 10, and 50 mL of the 0.010 mL dilution to respective bottles. For the 1.0, 2.0, and 5.0 mL dilutions, transfer 10, 20, and 50 mL of the 0.10 mL dilution to respective bottles.

4. If analytical history is available for the site, or if an expected BOD range has been provided, prepare the sample dilution range expected with one extra dilution above and below the anticipated range. Refer to Attachment B for guidance on preparing appropriate sample dilutions for known BOD concentration ranges.

5. All samples, the two lab control samples (LCSs), and the three "Seeded Dilution Water" blanks are typically seeded with South Portland Water District Effluent (seed). Alternative seed may be used at client request; in this case guidance on the appropriate volume of seed to add should be obtained from the client (via the lab project manager).

6. If S. Portland seed is used, the "Seeded Dilution Water" bottles are seeded with 5, 10, and 25 mL of seed, respectively. The samples and LCSs are seeded with 5 mL of S. Portland seed.

7. Seed is not added to the two "Unseeded Dilution Water" bottles - these will be used to evaluate the quality of the unseeded dilution water.

C. DISSOLVED OXYGEN (DO) METER CALIBRATION AND MAINTENANCE

1. The meter should be switched to the "ZERO" position at least fifteen minutes prior to preparation of the sample dilutions.

2. Visually inspect the probe membrane for tears, oily residues, or fingerprints. Inspect for air bubbles under the membrane. If any of these are present, the membrane must be replaced.

3. Grasp the probe in your left hand such that the stirring mechanism is to the outside of your raised thumb and the probe tip is facing up.

4. Roll off the O-ring and empty the cell of any solution. Check the O-ring by placing it on the corresponding guide on the O-ring replacement packet. If it is outside of the packet guide, replace the O-ring. Rinse the cell three times with probe filling solution (PFS). After the final rinse, fill the probe with PFS until an inverted meniscus is present on the end of the probe.

5. Assure that there are no air bubbles in the probe cell solution. Remove a membrane from the packet with your right hand and place the bottom third of it against the probe.

6. Secure the membrane in place by pressing your thumb against it and the probe. In one smooth and quick motion, pull the membrane down and across the top of the probe. Secure the other side of the membrane by pinching it against the probe with your index finger.

7. Check for air bubbles. If there are none, roll the O-ring in place to secure the membrane. Be careful not to touch the top of the membrane. Remove the excess membrane by cutting away with scissors.

8. If there are air bubbles present, remove the membrane, discard it and start over.

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9. Store the probe in a bottle partially filled with dilution water. Do not submerse the probe tip in the water.

10. If the meter does not read zero, adjust it using the zero knob.

11. Fill three BOD bottles with the dilution water (each BOD bottle will contain 300 mL of water). Place the probe in one bottle and start the stirrer.

12. Add 2 mL of the manganous sulfate solution to each of the remaining two bottles. When adding the solutions, place the pipet tip below the surface of the water. Replace tips between bottles and solutions. Then add 2 mL of the alkaline iodide sodium azide solution to each. Stopper and invert ten times. Allow the brown flocculus (floc) to settle below the bottle label.

13. Switch the meter to "TEMPERATURE" and allow it to stabilize.

14. Invert the two bottles ten more times and allow the brown floc to settle.

15. Record the temperature reading from the meter in the BOD logbook under "YSI Meter Calibration" in the space labeled "PROBE TEMP" for Day 0. The temperature should be 20 $\pm$ 1 C; if not, discard water in the bottles, adjust the temperature of the dilution water in the carboy (by running cool or warm water over the carboy in the sink) and continue with step C.11 above.

16. Add 2 mL of concentrated sulfuric acid to each bottle of the two bottles. Stopper and invert each bottle until the floc dissolves. Transfer to two beakers and add a stir bar to each.

17. Using the 25 mL buret, keep the tip below the surface; while stirring at a constant rate, titrate with the standardized sodium thiosufate solution until the solution turns a pale straw color.

18. Add a few drops of the starch indicator solution and continue titration, slowly, until the solution becomes colorless. Record the volume (in mL) of titrant used in the BOD logbook under "YSI Meter Calibration" in the space labeled "DO #1" for Day 0; the titrant volume is equivalent to the dissolved oxygen (DO) in mg/L in the dilution water. Repeat for the other beaker and record the volume of titrant used in the space labeled "DO #2" (Day 0).

19. Determine the average value and record in the space labeled "X" for Day 0. The average DO for the dilution water should be between 8.5 - 8.8 mg/L to allow sufficient initial DO for the method, without reaching the supersaturation point (>8.8 mg/L at 20 C) for DO in water. If the DO is outside this range consult with the supervisor for guidance on how to proceed.

20. Switch the meter to read DO to two decimal places (0.00). Using the "CALIB" knob, adjust the readout to the average value determined from the titration. The meter is now calibrated to read DO readings for samples, blanks, and LCSs (proceed to section D).

D. MEASUREMENT OF INITIAL DISSOLVED OXYGEN (DO)

1. Fill all the bottles, carefully, to the bottom of the bottle neck; the total volume in each bottle will be approximately 300 mL. While filling the bottles it is very important that the rate of filling does not aerate the sample, i.e., there should not be any bubbles formed during the filling process.

2. Starting with the"Unseeded Dilution Water", insert the probe into each bottle; turn the stirrer on and record the stabilized readings in the BOD logbook.

3. If the sample is being analyzed for carbonaceous BOD, add one scoop of the Nitrification Inhibitor, rinse with dilution water; stopper and cap the bottle.

4. If the sample is being analyzed for total BOD, bring the level of water in the bottle to the mid-point of the neck; stopper and cap the bottle.

5. Transfer the bottles to the incubator. Record the incubator temperature twice daily on the temperature log posted on the incubator, with readings a minimum of 4 hours apart, and allow the samples to incubate for five days. The incubator temperature should be 20 ± 1 C as required by the method.

E. MEASUREMENT OF FINAL DISSOLVED OXYGEN

1. On the fifth day, prepare and calibrate the instrument as described in steps C.1 through C.20.

2. Remove the caps for all the bottles. Unstopper each bottle just prior to reading the DO for the bottle (i.e., do not remove the stoppers all at once or oxygen exchange between the samples and the atmosphere may occur). Record the DO reading for each sample, blank, and LCS in the BOD logbook.

F. CALCULATIONS AND REPORTING OF RESULTS

1. Transfer all raw data to the calculation spreadsheet.

2. Evaluate the spreadsheet results for the criteria specified in steps F.3 through F.6 and report results as described.

3. The "Unseeded Dilution Water" must not have a final "DO consumed" greater than 0.20 mg/L. If either of the unseeded dilution water blanks have >0.20 mg/L DO consumed, check the probe and recalibrate the meter. If the DO change is still >0.20 mg/L, the accuracy of the sample results will be biased high; therefore, a lab Corrective Action Report (CAR) must be initiated and the report will need to be notated. (In some cases, e.g., permit compliance monitoring, "no reported value" may be reported rather than qualifying the data as having a positive bias; therefore, it is important to notify the project manager for guidance on how to proceed.) If values are to be reported, refer to the laboratory's standard notations list for the appropriate notation (refer to Attachment D).

4. To determine the "Seed Correction Factor" (SCF), the DO consumed for each or all of the "Seeded Dilution Water" samples must be >2.0 mg/L with a final DO >1.0 mg/L. If more than one of the "Seeded Dilution Waters" meet these criteria, determine the average of the calculated BOD values and determine the SCF using the following equation:

SCF = BOD (or average BOD) * 5 mL (or seed volume used for actual samples)/300 mL

If none of the seeded dilution water samples meet the criteria, use the BOD value from the bottle that contained 25 mL of seed.

5. Calculate LCS recoveries. LCS results must be within the method specified criteria of 198 ± 30.5 mg/L (85 - 115% recovery) for the run to be acceptable. If one or both LCS recoveries are outside the acceptance criteria, a CAR must be initiated and the report will need to be notated. . (In some cases, e.g., permit compliance monitoring, "no reported value" may be reported rather than qualifying the data as having a potential bias; therefore, it is important to notify the project manager for guidance on how to proceed.) If values are to be reported, refer to the laboratory's standard notations list for the appropriate notation (Attachment D).

6. Evaluate the data for samples using the following criteria and report results as described below:

a. The "Corrected DO Consumed" must be >2.0 mg/L and the final DO must be >1.0 mg/L.

b. If only one dilution for a given sample meets the criteria, report the calculated BOD for that dilution. If more than one dilution for a given sample meets these criteria, determine the mean calculated BOD for the dilutions and report it.

c. If the DO consumed for the 100 mL dilution is not >2.0 mg/L, a value of <6.0 mg/L is reported for the sample.

d. If a 100 mL dilution was not performed and the DO consumed is less than 2.0 mg/L for the lowest dilution (i.e., largest sample volume), assume an oxygen depletion of 2.0 mg/L using the lowest dilution and report the calculated result as "less than _____" with the appropriate notation from the lab's standard notations list (Attachment D).

e. If the final DO is <1.0 mg/L for all the dilutions for a given sample, a reported value is calculated from the greatest dilution (i.e., smallest sample volume) assuming the final DO is 1.0 mg/L, and the result is notated with the appropriate notation from the standard notations list (Attachment D).

f. If the calculated BOD decreases with an increase in sample volume analyzed, a matrix interference may be present and inhibition of the seed may have occurred. In this case the reported result is notated as such (refer to Attachment D for example of notation).

7. Calculation formula for BOD appears at the bottom of each quantitation spreadsheet, as shown on the attached spreadsheet example (Attachment C).

REFERENCES:

Standard Methods for the Examination of Water and Wastewater, "5-Day BOD Test," Method 5210 B, 18th Edition, 1992.

Methods for Chemical Analysis of Water and Wastes, "Biochemical Oxygen Demand," Method 405.1, EPA-600/4-79-020, Revised March 1983.

STANDARD OPERATING PROCEDURE

Author: D. Conley/B. Carbone
Approved by:

Kyle F. Gross
Technical Director

Issuing Unit: PACE-ME
SOP No.: CA-030-00
Date: September 1994

TITLE: Analysis of Total Organic Carbon, Dissolved Organic Carbon and Total Inorganic Carbon in Aqueous Samples Using the Dohrman Carbon Analyzer

PURPOSE: To describe the PACE-ME procedures and requirements for analyzing TOC, DOC, and TIC in aqueous samples using the Dohrman Carbon Analyzer.

SCOPE: This method applies to drinking and surface waters, domestic and industrial waste waters. The Practical Quantitation Level (PQL) is 1 mg/L.

REQUIREMENTS:

A. EQUIPMENT

1. Syringes - gas tight 250 uL and 1000 uL syringes
2. Sample cups -10 mL glass vials
3. Class A volumetric flasks and pipets (1000 mL, 50 mL, 5.00 mL)
4. Dohrman Carbon Analyzer Model DC-80

B. REAGENTS

NOTE: All standards and reagents should be prepared monthly.

1. Potassium persulfate solution, 2%: Dissolve 20 g of reagent grade potassium persulfate in one liter of ASTM Type II water. Add one mL of concentrated reagent grade phosphoric acid and mix well. Store in an amber bottle in the refrigerator.

2. Potassium persulfate-mercuric salt solution: This solution is used with samples containing high concentrations of chloride salts. Dissolve 8.2 g of mercuric chloride and 9.6 g of mercuric nitrate in 400 mL ASTM Type II water. Add 20 g of potassium persulfate and 5 mL of concentrated nitric acid. Dilute to one liter and mix well. Store in an amber bottle in the refrigerator.

3. Organic carbon standards: All standards should be primary standard grade. Prepare a 2000 mg/L standard by weighing 0.4250 g of potassium

hydrogen phthalate dried to a constant weight at 120° C for 4 hours and dissolving in 100 mLs of ASTM Type II water. Add 0.10 mL of concentrated phosphoric acid. Store in an amber bottle in the refrigerator.

a. Prepare a 400 mg/L standard by diluting 20.00 mL of the 2000 mg/L standard to 100 mL with ASTM Type II water. Store in an amber bottle in the refrigerator.

b. Prepare a 10 mg/L standard by diluting a 0.50 mL of the 2000 mg/L standard to 100 mL of ASTM Type II water. This standard should be prepared fresh daily.

A. ANALYZER START-UP PROCEDURE

1. Turn the detector on by pressing the power button at least one half-hour before use.

   a. When using the autosampler, turn on the detector and the autosampler by pressing the two power buttons simultaneously.

2. Fill the reactor vessel with potassium persulfate solution (or potassium persulfate-mercuric salt solution if samples are expected to contain high concentrations of salts) by lifting the lamp assembly up and pouring the reagent into the reactor. Fill to about one inch below the recycle port. Please the reactor intake line into the bottle of reagent and the out take line into a 500 mL waste beaker.

3. Turn up the nitrogen gas flow to 40 psi.

4. Press the main power button on the electronics module.

5. Press the power button on the reaction module, then the pump button and then the lamp button in that order.

B. CALIBRATION

1. Switch the range selector to one (1) mL. Using a syringe, inject 1000 uL 10 mg/L standard through the injection port and press the start button.

2. When the ready light comes on, lift the cover over the calibration button and press it quickly.

3. Switch the range selector to 200 uL and inject 200 uL of 400 mg/L standard. Press the start button.

4. When the ready light comes on press the calibration button.

5. If the print out value is less than 9.950 or the instrument indicates an error due to high bias for the 10 mg/L standard then recalibrate.

C. SAMPLE ANALYSIS

1. Choose the appropriate volume of sample to inject and switch the TOC measurement range knob to that volume.

   a. The operating range for 1000 uL is 0.1-160 mg/L.

   b. The operating range for 200 uL is 10 - 800 mg/L.

2. Analyze an independent check standard (LCS) before each run of samples, after every 10 samples, and at the end of each run. Recovery must be between 91 -121% for manual injections and between 93 -140% for autosampler injections. If not, recalibrate the instrument, and begin sample analysis sequence again.

3. Analyze one blank consisting of water and 5-7 drops of 1:1 sulfuric acid before each run of samples. The concentration of TOC in the blank must be less than the PQL of 1.0 mg/L. If the blank is greater than 1.0 mg/L start with fresh blank cup and try again. If blank is still out recalibration will be necessary.

4. To check for purging efficiency, analyze an alkalinity check standard, acidified with 5- 7 drops of 1:1 sulfuric acid. The result must be less than 2.0 mg/L. If this is not the case, acidify a new alkalinity check standard and reanalize. If the standard is still greater than 2.0 mg/L then recalibration may be necessary.

5. A few minutes before injecting, sparge each acidified sample with nitrogen (N2) to remove the inorganic carbon. Rinse the syringe with ASTM Type II water after every injection.

6. Insert the syringe into the injection port, inject the sample using a smooth consistent motion, then press the start button IMMEDIATELY after the sample is out of the syringe. When the analysis is complete the instrument will make a beeping noise and then display a value in the window plus print the value on the printer tape. This is the value recorded in the logbook along with the volume of sample injected and the range that the instrument is set to read (1000 uL or 200 uL).

   a. When using the autosampler make sure the switch behind the autosampler coming from the nitrogen tank is flipped upwards to allow nitrogen into the autosampler.

b. Press the "AUTO" button on the autosampler after the sample tubes have been filled and the wheel is appropriately aligned with the uptake tube and the sparging tubes. The starting place is the position to the right of the gray ring when the gray ring is under the sample uptake tube.

D. QUALITY CONTROL

1. A method blank and LCS samples must be analyzed and evaluated as described in sections C.2 and C.3.

   a. If acceptance criteria are not met, the method blank, LCSs and associated samples must be reanalyzed. If for any reason sample results are to be reported from an analytical run containing an unacceptable blank or LCS, a Corrective Action Report must be initiated immediately and the project manager, section supervisor, and QAC consulted.

2. A duplicate sample must be analyzed every ten samples. For every duplicate sample tested find the mean (x) and calculate the relative percent difference (%RPD).

   a. The acceptance criteria for %RPD is <20%. Duplicates not within 20% RPD should be notated in the raw data. If a laboratory problem is suspected the duplicates and all affected samples must be reanalyzed.

3. A spiked sample must be run every 20 samples. For sample spikes use 900 uL of sample with 100 uL of the 400 mg/L standard and run on the 1000 uL range.

   a. The acceptance criteria for matrix spike recovery is 75 - 125%. Any matrix spike recovery outside of the criteria must be notated on the raw data with an I - 1 or I - 2 notation. If a laboratory problem is suspected the matrix spike and all affected samples must be reanalyzed.

E. SHUT-DOWN PROCEDURE

1. Press the lamp button on the reaction module, then the pump button, and then the power button in that order.

2. Press the main power buttons on the electronics module and autosampler if in use.

3. Turn down the nitrogen gas flow to 10 psi.

4. Remove the intake line from the bottle of potassium persulfate reagent.

5. Rinse all syringes and sample cups with ASTM Type II.

6. Discard the waste beaker contents appropriately:

   a. High salt reagent must be disposed into an acid/metal waste drum.

   b. Normal reagent may be diluted and disposed down a laboratory drain equipped with a dilution/neutralization trap.

F. MAINTENANCE

1. Change the pump tubes semi-annually or as needed.

2. Change the injection port septum as needed or anytime leakage is obvious.

3. The tin and copper scrubbers should be replaced when over half of either one is discolored.

G. TOTAL INORGANIC CARBON ANALYSIS

1. TIC is the carbon that is purged from the acidified sample as carbon dioxide before it is analyzed for TOC. To measure TIC, inject the unpurged sample to get a value for total carbon. Purge the sample and analyze it for the TOC value. The difference between the total carbon and the total organic carbon is total inorganic carbon.

REFERENCES: Dohrman Operations Manual, Edition 11, July 1986. EPA Method 415.2 " Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, Revised March, 1983.

ATTACHMENTS: Attachment A - Example of logbook entry for a standard TOC analytical run

Attachment B - Example printout from DC -80 carbon analyzer

Attachment C - Material Safety Data Sheets.

GLOSSARY: Total Organic Carbon (TOC) - Organic carbon analyzed from an unfiltered sample.

Dissolved Organic Carbon (DOC) - Organic carbon analyzed from a filtered sample.

Total Inorganic Carbon (TIC) - Carbonate species which are dissociable by acidic sparging with an inert carrier gas.

SAFETY PRECAUTIONS:

Gloves should be worn at all times during standard preparation and disposal. Follow documented safety procedures for good laboratory practices. Also note the cautions on the Material Safety Data Sheets.

WASTE DISPOSAL PROCEDURES:

Discard the waste beaker contents appropriately:

a. High salt reagent waste must be disposed of by emptying it into an Acid/Metal waste drum.

b. Normal reagent waste may be diluted down a laboratory drain equipped with a dilution/neutralization trap.

ATTACHMENT A

Notebook No. _____

PROJECT Total Organic Carbon 415.1

Continued From Page _____

TOC Reagent 12/20/91 BAC | 10ppm std 12/24/91 BAC | 400 ppm std 12/11/91 BAC
Check Std TV = 45.36 mg/L 12/23/91 BAC | Air Check (<2.0 mg/L) 10/5/91 BAC | Baseline -.0106
PQL = 1.0 mg/L

Client	Sample ID	Site ID	Range, ~~mg/L~~ µg/L	Volume, µL	TOC mg/L	Reported TOC
	10ppm std		1000	1000	12.67 set →	9.997
	Check Std		1000	1000	48.41	107%
	400 ppm std		200	200	378.2 set →	399.7
	Check Std		200	200	39.44	87%
	Blank		1000	1000	0.330	<1.0
	Air Check		1000	1000	0.572	<1.0
Etheron	91357014	Boise eff	1000	1000	80.64	81
↓	91357015	Boise dil	1000	1000	4.381	4.4
SDW	91352005	Leachate	200	200	405.3	400
	91352006	Running Hill	1000	1000	6.058	6.0
	91352007	Rte 22	1000	1000	22.75	23
	91352008	Woods	1000	1000	4.849	4.8
	91352009	mw-B35	1000	1000	6.489	6.5
	91352010	MW-B36	1000	1000	3.866	3.9
	91352011	mw-B37	1000	1000	4.538	4.5
↓	91352012	mw-C1	1000	1000	9.868	9.9
dup	91352008	Woods	1000	1000	4.978	5.0
	Check Std		1000	1000	51.29	113%
	91352013	mw-C2	1000	1000	6.061	6.1
	91352014	mw-C3	1000	1000	5.426	5.4
	91352015	mw-C4	1000	1000	7.011	7.0
	91352016	mw-HA	1000	1000	8.860	8.9
	91352017	mw-W1	1000	1000	5.734	5.7
	91352018	mw-W3	1000	1000	4.389	4.4
	91352019	mw-W4	1000	1000	3.925	3.9
	91352020	mw-W5	1000	1000	7.327	7.3
dup	91352018	mw-W3	1000	1000	4.884	4.9
Spk	91352018	MW-W3	1000	900 + 100 µL 400 ppm std	40.63	
	Check Std		1000	1000	50.69	112%

Continued on Page

Read and Understood By

Betsy A Carbone — Signed — Dec 24, 1991 — Date

Karen A. Way — Signed — Dec 30, 1991 — Date

ATTACHMENT B

Notebook No. _____

PROJECT Total Organic Carbon 415.1

Continued From Page _____

1 TOC 12.67

CAL -- 1 ML
CAL ADJ 9.997

1 TOC 48.41

2 TOC 378.2

CAL -- 200 UL
CAL ADJ 399.7

1 TOC 39.44

2 TOC 0.330

3 TOC 0.572

4 TOC 80.64

5 TOC 4.381

6 CANCELLED
DET SATURATED

7 TOC 87.44

8 TOC 405.3

9 TOC 6.058

10 TOC 22.75

11 TOC 4.849

12 TOC 6.489

13 TOC 3.866

14 TOC 4.538

15 TOC 9.868

16 TOC 4.978

17 TOC 51.29

18 TOC 6.061

19 TOC 5.426

20 TOC 7.011

21 TOC 8.860

22 TOC 5.734

23 TOC 4.389

24 TOC 3.925

25 TOC 7.327

26 TOC 4.884

27 TOC 42.63

28 TOC 50.69

Replicate	x_1 (mg/L)	x_2 (mg/L)	$\bar{x}$ (mg/L)	% RPD
91352008	4.849	4.978	4.9135	2.6%
91352018	4.389	4.884	4.6365	11%

Spike Recovery
91352018

$$\frac{42.63\ mg/L - 4.6365\ mg/L\ (900/1000)}{400\ mg/L\ (100/1000)} \times 100\% = 96\%$$

Continued on Page

Read and Understood By

Betsy A Carbone — Signed — Dec 24, 1991 — Date

Karen A. Way — Signed — Dec 30, 1991 — Date

ATTACHMENT C. P. 1

MATERIAL SAFETY DATA SHEET

J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, N.J. 08865

SECTION I . IDENTIFICATION OF PRODUCT

CHEMICAL NAME	FORMULA
Mercuric Chloride	$HgCl_2$
SYNONYM OR CROSS REFERENCE Mercury Bichloride Corrosive Sublimate Mercury Perchloride	CAS NO: 7487-94-7

SECTION II . HAZARDOUS INGREDIENTS

MATERIAL	NATURE OF HAZARD

SECTION III . PHYSICAL DATA

BOILING POINT	MELTING POINT
303°C.	277°C.
VAPOR PRESSURE	SPECIFIC GRAVITY 5.44
VAPOR DENSITY (AIR=1)	PERCENT VOLATILE BY VOLUME (%)
WATER SOLUBILITY 69 g/100 g H_2O @ 20°C.	EVAPORATION RATE (_____ = 1)

APPEARANCE
White crystal, granules or powder

SECTION IV . FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (method used)	FLAMMABLE LIMITS	Lower	Upper

FIRE EXTINGUISHING MEDIA

SPECIAL FIRE-FIGHTING PROCEDURES
Wear self-contained breathing apparatus

UNUSUAL FIRE AND EXPLOSION HAZARD

SECTION V . HEALTH HAZARD

THRESHOLD LIMIT VALUE
orl-rat LD_{50}: 37 mg/kg ipr-mus LD_{50}: 5 mg/kg HIGHLY TOXIC!!!

HEALTH HAZARDS Violent Poison!! May be fatal if swallowed. 1 or 2 grams is frequently fatal. Corrosive to mucous membranes. Ingestion may cause severe nausea, vomiting, hematemesis, abdominal pain. Toxic by skin absorption.

FIRST AID PROCEDURES Call a physician. Antidote: Dimercaprol (BAl). If swallowed, wash stomach first with 5% Formaldehyde Sodium Sulfoxylate solution; then with 2% Sodium Carbonate solution, followed by ingestion of 250cc of Formaldehyde Sodium Sulfoxylate solution. Administer dimercaprol at a dose of 4 mg/kg of body weight (not to exceed 300 mg) every four hours first day, every six hours the second day and then every eight hours for one week.

CHEMICAL NAME

SECTION VI . REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	Heat, friction or impact

INCOMPATABILITY (materials to avoid) Formates, sulfites, hypophosphites, phosphates, sulfides albumin, gelatin, alkalies, alkaloid, ammonia, lime water, antimony & arsenic, bromides, borax, carbonates, reduced iron, copper, iron, lead, silver salts, tannic acid, vegetable astringents

HAZARDOUS DECOMPOSITION PRODUCTS
Mercury

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII . SPILL AND DISPOSAL PROCEDURES

SPILLS

Dissolve in water. Convert other contaminated compounds to the soluble nitrates. Adjust the acidity and precipitate as mercuric sulfide.

DISPOSAL

Contact a professional disposal service

SECTION VIII . PROTECTION INFORMATION

RESPIRATORY PROTECTION (specify type)
Self-contained breathing apparatus

VENTILATION	LOCAL X	SPECIAL
	MECHANICAL (general)	OTHER

PROTECTIVE GLOVES	EYE PROTECTION
Rubber gloves	Safety goggles

OTHER PROTECTIVE EQUIPMENT
Approved working clothes; eyebath

SECTION IX . HANDLING AND STORAGE PRECAUTIONS

STORAGE & HANDLING

Keep in tightly closed container. Store in well-ventilated place. Polyethylene containers are suitable for small quantities. Store in a cool, dry place.

SECTION X . MISCELLANEOUS INFORMATION

Do not breathe dust. Keep away from feed or food products. Wash hands before eating or smoking. The toxicity of mercury is such that the element and its compounds should not be allowed to contaminate air or water.

Date Issued: 3/84 Revision: _____ Approved by R. M. Mitchell
Manager, Quality Assurance

The information provided in this Material Safety Data Sheet has been compiled from our experience and data presented in various technical publications. It is the users responsibility to determine the suitability of this information for the adoption of safety precautions as may be necessary. We reserve the right to revise Material Safety Data Sheets from time to time as new technical information becomes available. The user has the responsibility to contact the company to make sure that the sheet is the latest one issued.

ATTACHMENT C p.3

MATERIAL SAFETY DATA SHEET

J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, N.J. 08865

SECTION I. IDENTIFICATION OF PRODUCT

CHEMICAL NAME	FORMULA
Mercuric Nitrate	$Hg(NO_3)_2$
SYNONYM OR CROSS REFERENCE Mercury Nitrate Mercury Pernitrate	CAS NO: 10045-94-0

SECTION II. HAZARDOUS INGREDIENTS

MATERIAL	NATURE OF HAZARD

SECTION III. PHYSICAL DATA

BOILING POINT	MELTING POINT
Decomposes	79°C.
VAPOR PRESSURE	SPECIFIC GRAVITY
VAPOR DENSITY (AIR=1)	PERCENT VOLATILE BY VOLUME (%)
WATER SOLUBILITY	EVAPORATION RATE (_____ = 1)

APPEARANCE
White-yellowish, deliquescent powder

SECTION IV. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (method used)	FLAMMABLE LIMITS	Lower	Upper

FIRE EXTINGUISHING MEDIA Water spray

SPECIAL FIRE-FIGHTING PROCEDURES

UNUSUAL FIRE AND EXPLOSION HAZARD

SECTION V. HEALTH HAZARD

THRESHOLD LIMIT VALUE
ipr-mus LD_{50}: 8 mg/kg

HEALTH HAZARDS
POISON!!

FIRST AID PROCEDURES
If swallowed, if conscious, immediately induce vomiting. Call a physician. In case of contact, remove and wash contaminated clothing promptly. Wash thoroughly after handling.

CHEMICAL NAME

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (materials to avoid)

Acetylene, ethyl alcohol, hypophosphoric acid, phosphine sulfur

HAZARDOUS DECOMPOSITION PRODUCTS

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL AND DISPOSAL PROCEDURES

SPILLS

Carefully sweep up and remove. Flush spill area with water.

DISPOSAL

Contact a professional disposal service.

SECTION VIII - PROTECTION INFORMATION

RESPIRATORY PROTECTION (specify type)

Self-contained breathing apparatus

VENTILATION	LOCAL X	SPECIAL
	MECHANICAL (general) X	OTHER

PROTECTIVE GLOVES	EYE PROTECTION
Rubber gloves	

OTHER PROTECTIVE EQUIPMENT

Approved working clothes

SECTION IX - HANDLING AND STORAGE PRECAUTIONS

STORAGE & HANDLING

Do not store near combustible materials. Keep in tightly closed container in a cool, dry area. Wash thoroughly after handling.

SECTION X - MISCELLANEOUS INFORMATION

Avoid breathing dust. Avoid contact with eyes, skin, clothing.

Date issued:_____ Revision:_____ Approved by R. M. Mitchell

Manager, Quality Assurance

The information provided in this Material Safety Data Sheet has been compiled from our experience and data presented in various technical publications. It is the users responsibility to determine the suitability of this information for the adoption of safety precautions as may be necessary. We reserve the right to revise Material Safety Data Sheets from time to time as new technical information becomes available. The user has the responsibility to contact the company to make sure that the sheet is the latest one issued.

STANDARD OPERATING PROCEDURE

Author: D. Conley
Approved By:

Julie Piccardi for
Willard C. Warren, III
President, Northeast Division

Issuing Unit: CCAS-Northeast
SOP No.: CA-055-00
Date: July 1994

TITLE: Hydrogen Ion Concentration Measurements (pH) in Aqueous Samples and Solutions

PURPOSE: To describe the procedure by which all pH calibrations and measurements are performed within the CCAS-NE laboratory for buffer solutions and aqueous sample determinations.

SCOPE: This procedure is applicable for all pH measurements within the laboratory for sample analyses, as well as any buffer solution preparations or sample pH adjustments necessary for preservation, distillation or titration.

REQUIREMENTS:

A. EQUIPMENT

1. pH Meter (Orion 701A or 901 Ionanalyzer or equivalent)
2. Glass beakers (25 mL)
3. Teflon-coated stir bars
4. Stir bar retriever
5. Magnetic stir plate

B. REAGENTS

1. Buffer solutions (pH 4.0, 5.0, 7.0, 8.0, 10.0, 12.0), traceable to NIST reference material
2. ASTM Type II Water

PROCEDURE:

A. pH METER CALIBRATION

1. Normal Range Calibration (pH 2.5 - 8.5)

a. Applications:

- Buffer Preparation
- Sample Aliquot Neutralizations
- pH Sample Measurements

b. Set slope to 100 percent.
c. Set temperature setting to ambient room temperature.
d. Read 7.0 buffer and adjust to 7.00 with standardization knob.
e. Read 4.0 buffer and adjust to 4.00 with temperature knob.
f. Turn slope adjustment back to ambient temperature setting.
g. Record percent slope on calibration log.
h. Read pH buffer 5.0 and record reading on calibration log.

1. Acceptance range 4.95 - 5.05
2. If criteria are not met, drain filling solution from probe, using a Pasteur pipet. Rinse inside of probe several times with filling solution. Fill probe, to level just below filling hole, with filling solution. Submerse probe tip in pH 7.0 buffer for 15 minutes to equilibrate. Re-calibrate probe using fresh buffers.

2. High Range Calibration (pH 5.5 - 11.5)

a. Applications:

- Buffer Preparation
- Sample Aliquot Neutralizations
- pH Sample Measurements

b. Repeat steps 1.b through 1.d using pH 7 buffer.
c. Read 10.0 buffer and adjust to 10.00 with temperature knob.
d. Turn slope adjustment back to ambient temperature setting.
e. Record percent slope on calibration log.
f. Read pH buffer 8.0 and record reading on calibration log.

1. Acceptance range 7.95 - 8.05
2. If criteria are not met, drain filling solution from probe, using a Pasteur pipet. Rinse inside of probe several times with filling solution. Fill probe, to level just below filling hole, with filling

solution. Submerse probe tip in pH 7.0 buffer for 15 minutes to equilibrate. Re-calibrate probe using fresh buffers.

3. Caustic Range Calibration (pH > 11.5)

   a. Applications:

      - Buffer Preparation
      - Sample Aliquot Neutralizations
      - Soil pH Sample Measurements

   b. Repeat steps 1.b through 1.d using pH 7 buffer.
   c. Prepare pH 12.0 buffer, read and adjust to 12.00 with temperature knob.
   d. Turn slope adjustment back to ambient temperature setting.
   e. Record percent slope on calibration log.
   f. Read pH buffer 10.00 and record reading on calibration log.

      1. Acceptance range 9.95 - 10.05.
      2. If criteria are not met, drain filling solution from probe, using a Pasteur pipet. Rinse inside of probe several times with filling solution. Fill probe, to level just below filling hole, with filling solution. Submerse probe tip in pH 7.0 buffer for 15 minutes to equilibrate. Re-calibrate probe using fresh buffers.

B. pH MEASUREMENT OF SAMPLES AND BUFFERS

1. Start with the mid-range calibration. If sample pH is outside of that range, re-calibrate instrument for sample range and analyze sample.

2. Samples and buffers are analyzed by filling a 25 mL beaker, pre-rinsed with the sample/buffer.

3. Add a stir bar and place on the stir plate. Stirring speed should be moderate but consistent for all samples and buffers.

4. Submerse the probe so that the ceramic frit is below the sample/buffer level.

5. Switch the instrument to read pH at the pH/:01 setting.

6. After reading stabilization, record the pH in the appropriate column of the logbook.

7. Logbook entries should include:

   a. The day's calibration data.
   b. The client ID.
   c. The sample number and site ID
   d. The instrument pH (to 2 decimal places) and the reported pH (to one decimal place).

C. QUALITY CONTROL

1. One sample duplicate is to be analyzed per batch or every 10 sample analyses.

   a. Acceptance criteria for duplicates is relative percent difference (RPD) of $\leq$ 20 % between sample and duplicate results.
   b. If criterion is not met, check calibration and reanalyze sample in duplicate.
   c. RPD is calculated as follows:

$$RPD = \frac{|R_1 - R_2|}{(R_1 + R_2)/2} * 100$$

where R1 = Result for sample
R2 = Result for duplicate

REFERENCES: "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, Method 150.1, Revised March 1983.

ATTACHMENTS: Attachment A - Example Logbook Page

GLOSSARY: None.

SAFETY PRECAUTIONS: 'R' level protection

WASTE DISPOSAL PROCEDURES: All reagents are buffers and can be disposed of down the sink.

ATTACHMENT A

PROJECT PH ELECTROMETRIC EPA 150.1

Notebook No. XI

Continued From Page 36

CALIBRATION STD	CALIBRATED TO	CAT #
PH 7.00	7.00	34170-115
4.00	4.00	34170-106
5.00	4.95	34170-109

CLIENT	SAMPLE ID	SITE ID	PH	REPT'D PH
	PH 5.00	CALIBRATION STD	4.95/5.00 x 100 = 99%	
OLIN-CAMERON	WK0967-1	GW-11	7.70	7.7
DUPE	WK0967-1	↓	7.68	7.7
	WK0967-2	GW-10S	4.74	4.7
	WK0967-3	GW-19S	6.58	6.6
	WK0967-4	GW-24	7.82	7.8
	WK0967-5	GW-25	6.60	6.6
	WK0967-6	GW-26	6.06	6.1
	WK0967-7	GW-35S	6.59	6.6
	WK0967-8	GW-39	6.37	6.4
	WK0967-9	GW-42S	5.16	5.2
	WK0967-10	GW-55S	6.15	6.2
DUPE	WK0967-10	↓	6.16	6.2

REPLICATES:	X_1	X_2	$\bar{X}$	%RPD
WK0967-1	7.70	7.68	7.69	0.26%
WK0967-10	6.15	6.16	6.155	0.16%

Continued on Page 36

Read and Understood By

Signed	Date	Signed	Date
[illegible]	7-21-94	[illegible]	7-25-94

STANDARD OPERATING PROCEDURE

Author: W. D. Calicchio
Approved by:

Kyle F. Gross
Technical Director

Issuing Unit: PACE-Maine
SOP No.: CA-026-00
Date: November 1994

TITLE: Spectrophotometric Determination of Total Recoverable Phenolics

PURPOSE: To describe the procedures used by PACE-ME personnel for the spectrophotometric determination of total recoverable phenolics as defined by EPA method 420.1.

SCOPE: This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes. A Practical Quantitation Limit (PQL) of 5.0 μg/L is attainable for an initial sample volume of 500 mL.

The method as outlined is applicable to the measurement of a variety of phenolic compounds. Color response of phenolic materials with 4-aminoantipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present within the sample.

REQUIREMENTS:

A. EQUIPMENT

1. 1-liter Pyrex distillation flask
2. Graham condenser
3. 1-liter class "A" graduated cylinder
4. 25 mL class "A" graduated cylinder
5. 150 mL Pyrex beakers
6. 400 mL Pyrex beakers
7. Watch glasses
8. 1-liter class "A" volumetric flasks
9. 250 mL class "A" volumetric flasks
10. Separatory funnels, 500 mL
11. Funnels
12. Test tubes with caps
13. Test tube rack
14. Eppendorf Repeat Pipette 4780, 50 mL tips
15. Oxford Macro-Set pipettor, 10 mL with tips
16. Oxford Macro-Set pipettor, 5 mL with tips
17. Class "A" pipettes

18. Hengar boiling chips
19. pH Meter
20. Hach DR3000 Spectrophotometer
21. 1-cm cell
22. Whatman #40 filter paper (15 cm diameter)
23. Timer
24. Pasteur pipets
25. 500 mL Erlenmeyer flasks
26. 0.45 u Membrane filters
27. Ring stands and clamps
28. Wire gauze

B. REAGENTS

1. Chloroform, spectrophotometric grade
2. ASTM Type II Water
3. Copper sulfate solution: Dissolve 100 g $CuSO_4.5H_2O$ in ASTM Type II water and dilute to 1.0 liter. Prepare every six months
4. Buffer solution: Dissolve 16.9 g NH_4Cl in 143 mL concentrated NH_4OH an dilute to 250 mL with ASTM Type II water. Two mL should adjust 100 mL of distillate to pH 10. Prepare monthly.
5. Aminoantipyrine (4-AAP) solution: Dissolve 2.0 g of 4AAP in ASTM Type II water and dilute to 100 mL. Prepare fresh for each analytical batch.
6. Potassium ferricyanide solution: Dissolve 8.0 g of $K_3Fe(CN)_6$ in ASTM Type II water and dilute to 100 mL. Prepare fresh for each analytical batch.
7. Stock phenol solution: Dissolve 1.0000 g of reagent grade phenol in freshly boiled and cooled ASTM Type II water and dilute to 1.0 liter. 1.0 mL = 1.0 mg phenol. Prepare every six months.
8. Working solution A: Dilute 5.0 mL stock phenol solution to 500 mL with lab water. 1.0 mL = 10 μg phenol. Prepare fresh for each analytical batch.
9. Working solution B: Dilute 50 mL of working solution A to 500 mL with lab water. 1.0 mL = 1.0 μg phenol. Prepare fresh for each analytical batch.
10. 1:4 sulfuric acid solution
11. 1:2 sodium hydroxide solution
12. Sodium sulfate, granular; reagent grade

PROCEDURE:

A. DISTILLATION

1. Using a graduated cylinder, transfer a 500 mL aliquot of the sample into a 1-liter distillation flask.

2. Using pH paper, adjust the aliquot pH to approximately 4.0 by adding 1:4 sulfuric acid or 1:2 sodium hydroxide, as appropriate. If the sample pH was not originally <2.0, record in the lab notebook.

3. Add 5.0 mL of $CuSO_4$ solution and two boiling chips.

4. Begin distillation, and collect 450 mL of distillate in a 500 mL Erlenmeyer flask; stop the distillation, and when boiling ceases add 50 mL of warm ASTM Type II water to the distillation flask.

5. Continue distillation until 500 mL of distillate have been collected. Shut off heat source.

6. If the distillate is turbid, filter through a pre-washed membrane filter.

B. EXTRACTION DETERMINATION

1. Using working solution B, prepare the following standards. Preparation is made by directly pipetting the required volumes into 500 mL separatory funnels and diluting to 400 mL with lab water.

mL of working solution B	Conc. µg	Conc. µg/L
0.0	0.0	0.0
2.0	2.0	5.0
5.0	5.0	12.5
10.0	10.0	25.0
25.0	25.0	62.5
50.0	50.0	125.0

2. Using a graduated cylinder, determine the volume of distillate, record the volume in the notebook.

3. Transfer 400 mL of distillate or an aliquot diluted to 400 mL into a 500 mL separatory funnel. The remaining distillate volume should be reserved in the event further dilution is required.

4. To sample and standards, add 8.0 mL of the buffer solution. The pH should be 10 ± 0.2. Swirl to mix.

5. Add 3.0 mL aminoantipyrine solution. Swirl to mix.

6. Add 3.0 mL potassium ferricyanide solution. Swirl to mix.

7. Allow the color to develop for three (3) minutes.

8. In a fume hood, add 25 mL of chloroform to the separatory funnel. Stopper and shake at least ten times. Vent and allow the $CHCl_3$ to settle. Shake again, ten times. Vent and allow the $CHCl_3$ to settle. Chloroform should be handled in a fume hood to avoid breathing the vapors.

9. Filter the chloroform extract through filter paper containing sodium sulfate. Collect the extract into a test tube. Carry out filtration in a fume hood.

10. Set the DR3000 spectrophotometer wavelength to 460 nm. Zero the instrument (set the scale on the spectrophotometer to 100%) using chloroform in the sample cell. Read and record the % transmittance of the chloroform blank, method blank, standards and sample extracts at 460 nm.

11. If the sample transmittance is less than the transmittance of the most concentrated standard, there are two ways dilutions can be performed. First, if previous sample history indicates high levels of phenols, the volume used for the distillation can be reduced; or, second, a re-extraction using a reduced volume (<400 mL) of the original distillate can be performed. The actual sample volume and volume of distillation used for extraction ("extract volume") should be recorded in the logbook and used for calculations.

C. CALCULATIONS

1. Enter the required information and % transmittance values for the respective standards and samples into the PHENOL.wk1 Lotus spreadsheet as follows:

   a. Refer to the Lotus 123 Spreadsheet, PHENOL.wkl.
   b. Enter Standard Solution preparation data (concentration and prep dates).
   c. Enter Standard Curve data (volumes and % transmittance) and perform data regression.
   d. Enter sample data requested in spreadsheet (sample and distillate volumes, % transmittance).

2. After entering the sample, distillate and extract (volume of distillate extracted) volumes, the spreadsheet will calculate the final concentrations based upon the following calculation:

$$\text{Phenol } \mu g/L = (A/B) * (C/D) * 1000 \text{ mL/L}$$

where:

A = Phenol conc. μg as determined from curve
B = Extract volume mL
C = Distillate volume mL
D = Sample volume mL

An example spreadsheet for performing Total Recoverable Phenol calculations is included as Attachment A.

3. If the Lotus Spreadsheet is not available, perform calculations as follows:

a. Determine the calibration standard concentration (μg) by multiplying the stock solution B concentration by the standard volume. Refer to calculation A below.

b. Determine the calibration standard absorbance by taking the log of 100 divided by the percent transmittance. Refer to calculation calculation B below.

c. Determine the corrected calibration standard by subtracting the blank absorbance from the calculated absorbance. Refer to calculation C below.

d. Plot the curve and perform a linear regression on the data. The correlation coefficient (R) must be > 0.995 for the curve to be acceptable.

e. To determine the absolute concentration of phenol (μg) in the sample, take the blank corrected sample absorbance value and subtract the y-constant value obtained from the regression equation; divide this value by the x-coefficient of the regression. Refer to calculation D below.

f. To determine the concentration of phenol in the sample(μg/L), calculate the volume correction factor by dividing the distillate volume by the total initial sample volume. Refer to calculation E below. Take the absolute concentration in μg and divide it by the extract volume in mL. Refer to calculation F. Multiply this value (μg/mL) by the volume correction factor (E) and multiply it by 1000 mL/L. This will give you the phenol concentration of the sample in μg/L. Refer to calculation G below.

A: (stock solution B μg/mL) * (standard volume mL) = μg
B: log (100/ % transmittance) = absorbance
C: (calculated absorbance) - (blank absorbance) = corrected absorbance

D: (corrected absorbance - y constant value) / x-coeff. = μg in sample extracted

E: (distillate volume mL / initial sample volume mL) = volume correction factor

F: (absolute concentration μg/extract volume mL) = μg/mL in sample distillate

G: (E * F * 1000 mL/L) = μg/L

D. QUALITY CONTROL

1. Acceptance criteria for the calibration curve is an "R" (correlation coefficient) of 0.995.

2. One method blank is required per batch of samples distilled each day. The method blank consists of 500 mL of ASTM Type II water carried through the entire sample sequence.

   If the concentration of phenolics in the method blank exceeds the PQL, then contamination is likely and all samples for that batch must be redistilled for verification. This occurrence must be documented with a Corrective Action Report (CAR). The client may need to be notified so that resampling can be performed. Under some circumstances "qualified" data may be reported. This decision will be reached in conjunction with discussions by the QA Coordinator, Section Supervisor and Project Manager.

3. One Laboratory Control Sample (LCS) is required per batch of 20 samples distilled each day. The LCS is prepared from a standard independent of the calibration standards and at a concentration of approximately 60 μg/L.

   The acceptance criteria for the LCS recovery are 67-127% based on statistically derived limits from laboratory experimental data. Whenever laboratory derived control limits are in use, the most current limits will be applicable.

   The LCS recovery is calculated from the formula:

$$R = \frac{\text{calculated conc. } (\mu g/L)}{\text{true conc. } (\mu g/L)} * 100$$

   If the LCS recovery is outside the acceptance limits, the accuracy of the analysis is uncertain and samples must be redistilled if possible. This occurrence should be documented with a CAR. If hold times have expired or if insufficient sample is available for redistillation, the client

may need to be notified so that resampling can be performed. Under some circumstances "qualified" data may be reported. This decision will be reached in conjunction with discussions by the QA Coordinator, Section Supervisor and Project Manager.

4. Duplicate analyses should be performed for 10% of daily distillation batch. The precision of duplicate analyses should be interpreted as follows:

		acceptable RPD
a.	R1 & R2 $\geq$ 3x PQL	0 - 20%
b.	R1 & R2 < PQL	do not calculate
c.	R1 & R2 > PQL but < 3x PQL or R1 $\geq$ 3x PQL and R2 <3x PQL	< 100%
d.	R1 < PQL & R2 > PQL	< 100%

$$RPD = \frac{/R1 - R2/}{(R1 + R2)/2} * 100$$

where:

R1 = result 1
R2 = result 2

If the duplicate RPD falls outside of this criteria the data result must be flagged on the raw data and client sponsor checklist with an "I-9" notation indicating duplicate sample results were not within expected range, possibly due to sample non-homogeneity.

5. Matrix spikes should be performed on 5% of the daily distillation batch. The matrix spike recovery must be calculated to determine efficiency of distillation for that particular matrix distillation. The matrix spike recovery is determined as follows:

$$\text{Matrix Spike Recovery (\%)} = \frac{/A - B/}{C} * 100$$

where:

A = result (μg/L) for spiked sample
B = result (μg/L) for unspiked sample

C = true value (μg/L) of spike

If matrix spike recovery is outside the acceptance criteria of 75-125%, the data result should be notated in the raw data and on the client sponsor checklist if no laboratory problem is suspected. If a laboratory problem is suspected the sample should be redistilled and reanalyzed for confirmation

Currently, matrix spike recoveries are being utilized for internal tracking unless otherwise requested by the client.

E. SAFETY PRECAUTIONS

1. Thoroughly review MSDS for chloroform before performing this procedure.

2. Thoroughly review MSDS for ammonium hydroxide before performing this procedure.

3. Chloroform is carcinogenic. Considerable caution must be taken in handling this reagent. All extraction and final analysis steps must be performed inside of a fume hood.

4. Considerable pressure in the separatory funnel may be generated by the chloroform during the extraction procedure. Frequent and careful venting of the separatory funnel into the fume hood and away from the analyst and others in the work area is necessary.

5. General laboratory safety policies and procedures should be followed for performing this analysis. A lab coat, safety glasses and solvent resistant gloves should be worn while performing this procedure.

6. All glassware used to handle chloroform and the sample extracts should be thoroughly aired and dried in the fume hood prior to being sent to the glassware prep area for cleaning.

F. WASTE DISPOSAL

1. Spent chloroform from the extraction procedure should be collected in a 4-liter secondary container clearly marked as "Spent Chloroform". At the end of the daily extraction/analysis, the contents of the secondary container must be transferred to the waste solvent drum located in the hazardous waste disposal area for removal off-site.

2. Any distillates determined to contain phenolics must transferred to a secondary container clearly marked "Aqueous Phenolics from

Distillation". At the end of the daily extraction/analysis, the contents of the secondary container must be transferred to the waste solvent drum located in the hazardous waste disposal area for removal off-site.

3. If a disposal drum is not available the Hazard Waste coordinator must be immediately notified.

REFERENCES: Standard Methods for the Examination of Water and Wastewater, Method 5530C, American Public Health Association, 18th edition, 1992.

Methods for the Chemical Analysis of Water and Wastes, Method 420.1, US EPA 600/4-79-020 Revised March 1983.

ATTACHMENTS: Attachment A - Example of Calculation Spreadsheet

GLOSSARY: None.

CCAS
62

ATTACHMENT A

Notebook No. II

PROJECT Phenolics, TR, EPA 420.1

Continued From Page (62)

Std A = 10 µg/ml : CSG 5-18-94 PQL = 5.0 µg/L

Std B = 1.0 µg/ml : CSG 5-18-94

Phenol Stock Std : 1000 mg/L , PF01294P12W

LCS/Spike Stock Std = 3000 mg/ml (CSG : PF01294P12W)

LCS/Spike = (1.0 ml × 30.0 µg/ml) / 0.5 ml = 60 µg/L
Calibration / Curve

Std ID	Vol. of Std B	Calibrant Wt. (g)	Extract Vol. (ml)	%T @ 460 nm
Blank	Ø	—	400	90.3
#1	2.0	2.0		84.5
#2	5.0	5.0		78.3
#3	10.0	10.0		69.5
#4	25.0	25.0		46.4
#5	50.0	50.0		25.1

Client	Sample ID	Site ID	Sample Vol (ml)	Distillate Vol (ml)	Extract Vol. (ml)	%T @ 460 nm	D.F.
		Method Blank	500	526	400	89.8	1.0
		ICV	500	494	400	50.7	1.0
Pioneer	WK0477-1	End of Pipe	500	480	400	73.2	1.0
	WK0485-1		500	516	400	76.2	1.0
	WK0482-1		500	508	400	73.7	1.0
dup	WK0477-1		500	540	400	67.6	1.0
spike	WK0482-1		500	CS 1 56.0 ml 500	400	42.4	1.0
	WK0491-6						
	WK0491-7						
SDW	WK0591-6	Upstream	500	512	400	90.0	1.0
SDW	WK0591-7	Dn Stream	500	514	400	89.4	1.0

Distillation : May 18, 1994

Completion : May 18, 1994

Continued on Page (63)

Read and Understood By

Signed: [illegible] Date: May 18, 1994 Signed: [illegible] Date: [illegible]

PROJECT Phenolics, TR EPA 420.1

Continued From Page 62

PQL: 5.0 ug/L

PHENOLICS, TOTAL RECOVERABLE
COLORIMETRIC (MANUAL 4-AAP)

METHOD: EPA 420.1
PQL = 5.0 ug/L

DATE: MAY 18,1994
ANALYST: CSG

PHENOL STOCK SOLN — CONC. = 1000.00 mg/mL; DATE: PE011294P12W1; BY: CSG

PHENOL STANDARD B — CONC. = 1.00 ug/mL; DATE: 5-15-94; BY: CSG

PHENOL STANDARD A — CONC. = 10.00 ug/mL; DATE: 5-15-94; BY: CSG

STANDARD	STD VOLUME (mL)	STD (ug)	EXTRACT VOLUME (mL)	% T @ 460 NM	ABS @ 460 NM	CORR ABS @ 460 NM	RELATIVE RESPONSE FACTOR
BLANK	----	0.0	400.0	90.3	0.044	0.000	----
STD 1	2.0	2.0	400.0	84.5	0.073	0.029	0.0144
STD 2	5.0	5.0	400.0	78.3	0.106	0.062	0.0124
STD 3	10.0	10.0	400.0	69.5	0.158	0.114	0.0114
STD 4	25.0	25.0	400.0	46.4	0.333	0.289	0.0116
STD 5	50.0	50.0	400.0	25.1	0.600	0.556	0.0111
STD 6	60.0	60.0	400.0		ERR	ERR	ERR

Regression Output:

Constant	0.0049
Std Err of Y Est	0.0049
R Squared	0.9996
No. of Observations	6.0000
Degrees of Freedom	4.0000
X Coefficient(s)	0.0111
Std Err of Coef.	0.0001

CLIENT	SAMPLE NO.	SAMPLE VOLUME (mL)	DISTILLATE VOLUME (mL)	EXTRACT VOLUME (mL)	% T @ 460 NM	ABS @ 460 NM	CORR ABS @ 460 NM	PHENOL in extract (ug)	CALC PHENOL (ug/L)	%RECOVERY
	METH BLANK	500.0	525.0	400.0	89.8	0.047	0.000	-0.44	-1.16	
	CHECK STD	500.0	494.0	400.0	50.9	0.293	0.247	21.79	53.83	89.71
PIONEER	WK0477-1	500.0	480.0	400.0	73.2	0.135	0.089	7.56	18.15	
PIONEER	WK0485-1	500.0	516.0	400.0	76.2	0.118	0.071	5.99	15.45	
PIONEER	WK0492-1	500.0	508.0	400.0	73.7	0.133	0.086	7.30	18.53	
PIONEER	WK0477-1D	500.0	526.0	400.0	67.6	0.170	0.123	10.68	28.09	
PIONEER	WK0492-1S	500.0	562.0	400.0	42.4	0.373	0.326	28.95	81.34	
SDW	WK0591-6	500.0	512.0	400.0	90.0	0.046	-0.001	-0.53	-1.36 <	
SDW	WK0591-7	500.0	516.0	400.0	89.4	0.049	0.002	-0.27	-0.69 <	

ug phenol/L = (ug phenol/extract vol. mL)*(dist. vol. mL/sample vol mL)* 1000

Distillation: May 18, 1994

Continued on Page 64

Completion:

Read and Understood By

Signed — Date May 18, 1994 — Signed — Date 5.20.94

STANDARD OPERATING PROCEDURE

Author: K.A. Mollison /B. Carbone
Approved by:

John C. Burton
Operations Manager

Issuing Unit: PACE-New England-ME
SOP No.: CA-051-01
Date: July 1995

TITLE: Turbidimetric Determination of Sulfate

PURPOSE: To describe the procedures utilized by PACE-New England-ME in the analysis of dissolved and total sulfates by turbidimetry.

SCOPE: This method is applicable to surface and saline waters, domestic and industrial wastes, as well as aqueous soil extracts.

REQUIREMENTS:

A. EQUIPMENT

1. Hach 2100A turbidimeter or equivalent
2. Hach Formazin Standard, 4000 NTU or equivalent
3. Hach Gelex Secondary Standards or equivalent
4. Magnetic stir plate
5. Stir bar, Teflon
6. Stir bar retriever
7. Timer with second hand
8. Scoopula[R]
9. Volumetric flask, Class A, 1000 mL, 100 mL
10. Class A volumetric pipets 1mL, 2mL, 5mL, 10mL, 20mL
11. Beakers, 250 mL - polypropylene or glass beakers are acceptable
12. 1-5 mL Oxford pipet with extra tips
13. Sample cell for Hach turbidimeter
14. Beaker, glass - 600 mL or larger
15. Class A 100 mL graduated mixing flasks

B. REAGENTS

1. Type II ASTM Water.
2. Hydrochloric Acid (HCl) - Concentrated - only Baker analyzed high purity acid or equivalent is acceptable.
3. Isopropyl Alcohol (2-propanol) - Baker analyzed or equivalent is acceptable.
4. Sodium Chloride (NaCl) - Baker analyzed reagent grade or equivalent is acceptable.
5. Barium Chloride ($BaCl_2$) - Baker analyzed reagent for PARR turbidimeter or equivalent is acceptable. This reagent <u>must</u> be correct mesh size for the reaction to occur properly.

6. Sodium Sulfate (Na_2SO_4) - Anhydrous-Baker analyzed standard grade or equivalent is acceptable.
7. Glycerol - Baker analyzed or EM Science reagent grade or equivalent is acceptable.
8. Conditioning Reagent - Place 30mL of concentrated HCl, 300 ml of ASTM Type II Water, 100 mL of isopropyl alcohol and 75.0g of sodium chloride (NaCl) in a 600 mL glass beaker. Add 50.0 mL of glycerol and stir until NaCl is dissolved.
9. Standard Sulfate Solution - Dissolve 0.1479 g of anhydrous Na_2SO_4 in a 1 liter volumetric flask partially filled with ASTM Type II water. Dilute to mark with ASTM Type II water. Final concentration of the Standard Sulfate Solution is 100 mg/L.
10. Check Standard -- 1000 mg/L as SO_4. Dilute 25.0 mL of standard to 100 mL in a class A volumetric flask. Bring volume to mark with ASTM Type II water. Use 5.0 mL of this standard diluted to 100.0 mL for analysis as the Laboratory Control Sample (LCS) and Initial and Continuing Calibration Verification (ICV/CCV) standards. Final concentration of the LCS/ICV/CCV is 12.5 mg/L.

PROCEDURE:

A. CALIBRATION

1. A standard curve must be analyzed for each day's analysis. The curve includes a reagent blank and 4 standards. The values of all are used in the calculation of the regression line.

   The following volumes of the Standard Sulfate Solution (100 mg/L) are diluted to 100 mL with ASTM Type II water and used for analysis of the calibration curve.

Standard Volume	Conc. of SO_4 in mg	Conc. Of SO_4 in mg/L
1.0 mL	0.10 mg	1.0 mg/L
5.0 mL	0.50 mg	0.50 mg/L
10.0 mL	1.0 mg	10.0 mg/L
20.0 mL	2.0 mg	20.0 mg/L

   The standard curve is analyzed in the same manner as the samples.

2. Calibration Curve Acceptance Criteria

   a. Correlation Coefficient

      Acceptance Criteria: R > 0.995; n=3
      Corrective Action for Non-Conformance : Recalibration.

   b. Relative Response Factors (RRF)

      Acceptance Criteria: +/- 10.0 for each Regression Line Data Point

Corrective Action for Non-Conformance: Omission of Data Point, provided a minimum of three standards are used to generate the calibration curve.

B. ANALYSIS

1. Place 100 mL of sample (or portion of sample diluted to 100 mL) in a 250 mL beaker.
   NOTE: For samples with (Maximum NTU - Blank NTU) values greater than 40 NTU, a smaller aliquot of the sample must be analyzed.

2. Add 5.0 mL of conditioning reagent using the Oxford pipet.

3. Place stir bar in sample and begin spinning on stir plate at moderate speed.

4. After 3-5 minutes, read the turbidity of the sample. Record this turbidity in the BLANK NTU column.

5. Return cell contents to beaker and resume spinning.

6. Using the scoopula^R, add approximately 0.5 g of $BaCl_2$. This amount does not have to be exact as the reagent is always added in excess of what the reaction requires.

7. Begin timing immediately upon the addition of the $BaCl_2$ to the sample.

8. After 1 minute, read the turbidity of the sample again. Record this reading in the 0 NTU column. Continue to monitor the turbidity of the sample every minute for the next 4 minutes. Record each reading in the appropriate column in the logbook. If the turbidity falls below the previous reading, record the value and stop timing. Also, if three consecutive readings remain the same, timing of sample may be terminated.

9. Record the maximum NTU in the appropriate column of the logbook. This is the value which will be entered into the calculation spreadsheet.

C. DATA QUANTITATION

1. Enter data in calculation spreadsheet designated SO_4.wk1.
2. Save spreadsheet following appropriate protocol using the test name and date as the new file name (e.g., SO41295 for Jan. 2, 1995.)

3. Print spreadsheet following appropriate protocol and place in logbook.

4. Calculate relative percent difference for duplicate analyses using the following equation:

$$RPD = \frac{|\text{result 1 - result 2}|}{[(\text{result 1 + result 2})/2]} \times 100$$

5. Calculate spike recoveries using the following equation:

   ([(sample+spike)-(sample)]/spike concentration(mg))x100=% recovery
   (mg) (mg) (true value)

6. Percent recoveries of the laboratory control sample, initial calibration verification and continuing calibration verification standards are calculated by the following equation:

   (test result/true value) x 100 = % recovery
   (mg/L) (mg/L)

D. QUALITY CONTROL

1. A laboratory control sample (LCS) must be analyzed with each batch. The percent recovery must be calculated and recorded in the logbook. The LCS can be used as the initial calibration verification (ICV). The same standard material is used for both the LCS and the ICV. The standard should should be analyzed immediately following the calibration standards.

   Acceptance Criteria: 75 - 110% Recovery (statistically derived from lab data)
   Corrective Action: Recalibration and reanalysis of sample batch.

2. A duplicate must be analyzed for every 20 samples so as to verify precision for the method. The duplicate is treated in the same manner as the original sample.

   Acceptance Criteria: 0 - 20% Relative Percent Difference (RPD)
   Corrective Action: Notation of Sample Result in raw data.

3. A continuing calibration verification (CCV) must be analyzed for every batch of 10 samples. It is analyzed at the same concentration as the LCS and ICV. Percent recovery must be calculated and recorded.

   Acceptance Criteria: 75 - 110% Recovery (statitically derived from lab data).
   Corrective Action: Reanalysis of all samples back to last acceptable CCV recovery.

4. A matrix spike must be analyzed for every set of 10 samples. Using half of the original sample volume diluted to 98 mL, add to that 2.0 mL of the CCV solution. This gives a final volume of 100 mL. Analyze and record data as outlined previously. Calculated spike recovery and record in logbook.

   Acceptance Criteria: 75 - 125% Recovery
   Corrective Action: Notation of Sample Result in raw data with Notation I-1.

REFERENCES: "Methods for Chemical Analysis of Water and Wastes," Method 375.4, Sulfate, Turbidimetric, EPA-600/4-79-020, Revised March, 1983.

ATTACHMENTS: Attachment A - Example of Logbook Entry
Attachment B - Example of Quantitation Spreadsheet

SAFETY PRECAUTIONS: Gloves, safety glasses, and a labcoat are required (standard level "R" protection).

WASTE DISPOSAL PROCEDURES:

Combine all analyzed samples and standards, and rinsings, in a 4 liter beaker; neutralize and dispose down a sink drain with a neutralization trap.

ATTACHMENT A

PACE, INC.

BOOK# 14
PAGE# 23

SULFATE: EPA 375.4 PQL: 1.0 mg/l

SO4 STD: S0406209 5P38W1
GELEX STD: calibrated 050895
CONDITIONING REAGENT: 061595
CHECK STD: S0406159 5P37W1
BaCL2: Baker Lot #H34731

CLIENT	SAMPLE #	SITE ID	VOL (ml)	SEC 0	60	120	180	240	MAX NTU	BLK NTU
QC	Blank	ROH_2O	100	0.49	0.38	–	–	–	0.49	0.49
↓	0.1	Na_2SO_4	1.0	5.3	5.2	–	–	–	5.3	↓
↓	0.5	↓	5.0	14	14	13	–	–	14	↓
↓	1.0	↓	10	28	28	27	–	–	28	↓
↓	2.0	↓	20	59	58	–	–	–	59	↓
HACH	Check Std	LCS	5.0	36	36	35	–	–	36	↓
WWL	WL0921-1	Leach-1	1.0	13	13	13	–	–	13	0.17
↓	↓ -2	Leach-2	5.0	36	34	–	–	–	36	2.4
↓	↓ -3	GW-1	25	32	32	30	–	–	32	0.36
↓	↓ -4	GW-2	25	12	11	–	–	–	12	0.21
↓	↓ -5	Leach-3	2.5	17	17	16	–	–	17	0.20
↓	↓ -6	TP-10	5.0	19	18	–	–	–	19	0.48
SDL-West	WL0943-1	upstream	100	24	23	–	–	–	24	1.3
↓	↓ -2	downstream	100	28	28	26	–	–	28	1.4
dup	WL0921-1	Leach-1	1.0	12	13	13	13	–	13	0.18
Spike	WL0921-1	Leach-1	0.5 + 2.0 mL HACH	20	18	–	–	–	20	0.13
HACH	Check Std	LCS	5.0	35	35	33	–	–	35	0.20
* Price-ME	WL0724-5		10	51	49	–	–	–	51	1.8

NOTES: * Run just as a test.

ANALYST: Joe A. Thompson DATE: 06.29.95
REVIEWED BY: [illegible] DATE: 6.30.95

CONT. ON PAGE# 24

SULFATE
TURBIDIMETRIC

METHOD: EPA 375.4
PQL = 1 mg/L

DATE: 062995
ANALYST: LAT

SULFATE
STD SOLN

CONC. = 0.10 mg/mL
DATE: S04062095P38W1
BY: CLM

CHECK STD
MANUF/

CONC: 250.00 mg/L
LOT NO: S04061595P37W1
DATE: 061595
BY: CLM

STANDARD	STD VOLUME (mL)	STD (mg)	MAX NTU	BLANK NTU	CORR NTU	RELATIVE RESPONSE
BLANK	----	0.00	0.49		0.00	----
STD 1	1.0	0.10	5.30	0.49	4.81	48.10
STD 2	5.0	0.50	14.00	0.49	13.51	27.02
STD 3	10.0	1.00	28.00	0.49	27.51	27.51
STD 4	20.0	2.00	59.00	0.49	58.51	29.26

Regression Output:

Constant	0.1852
Std Err of Y Est	1.5174
R Squared	0.9969
No. of Observations	5.0000
Degrees of Freedom	3.0000
X Coefficient(s)	28.7261
Std Err of Coef.	0.9290

CLIENT	SAMPLE NO.	SAMPLE VOLUME (mL)	MAX NTU	BLANK NTU	CORR NTU	SULFATE (mg)	CALC SULFATE (mg/L)
HACH	CHECK STD	5.000	36.00	0.49	35.5	1.23	98.38
W&C	WL0921-1	1.000	13.00	0.17	12.8	0.44	440.18
	WL0921-2	5.000	36.00	2.40	33.6	1.16	232.64
	WL0921-3	25.000	32.00	0.36	31.6	1.09	43.80
	WL0921-4	25.000	12.00	0.21	11.8	0.40	16.16
	WL0921-5	2.500	17.00	0.20	16.8	0.58	231.35
	WL0921-6	5.000	19.00	0.48	18.5	0.64	127.65
SDW-WEST	WL0943-1	100.000	24.00	1.30	22.7	0.78	7.84
	WL0943-2	100.000	28.00	1.40	26.6	0.92	9.20
DUP	WL0921-1	1.000	13.00	0.18	12.8	0.44	439.84
SPIKE	WL0921-1	0.500	20.00	0.13	19.9	0.69	1370.52
HACH	CHECK STD	5.000	35.00	0.20	34.8	1.20	(241.00/250)10² = 96% ✓

% RECOVERY 245.94/250

$$\text{mg/L SO4} = \frac{\text{mg SO4} * 1000}{\text{ml sample used}}$$

Replicate	x_1	x_2	$\bar{x}$	RPD%
WL0921-1	440.18	439.84	440.01	0.08 ✓

Spike Recovery: WL0921-1

$$\left\{\left[(0.69\,mg) - (0.44\,mg)\left(\frac{0.5\,mL}{1.0\,mL}\right)\right] / \left(250\,mg/L \cdot 2\,mL \cdot 1L/10^3\right)\right\} 10^2 = 94\% \checkmark$$

RESOURCE ANALYSTS, INCORPORATED
Standard Operating Procedure QA-5860

SOP Number: QA-5860
Revision History
Cover Page
Page 1

Title: Analysis of Chloride by Flow Injection Analysis

Prepared By: Pamela M. Rosengquist Date: 4/14/92

Approved By:

Group Manager: [illegible] Date: 4/14/92

QA Officer: [illegible] Date: 4-17-92

Tech. Director: [illegible] Date: 5/14/92

President: [illegible] Date: 5-14-92

Revision History: DRAFT 10/96 MANUAL EDITS TO BE INCORPORATED INTO FINAL REVISION.

Revision	Changes	Authorization	Date JR 10/22/96
1	Incorporate EPA Region 5 comments	W. Harris	11.15.94

Title: Analysis of Chloride by Flow Injection Analysis

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA department.

I acknowledge receipt of copy_____of document QA-5860, titled **Analysis of Chloride by Flow Injection Analysis**

Name_____Date_____

I acknowledge receipt of copy_____of document QA-5860, titled **Analysis of Chloride by Flow Injection Analysis**

Name_____Date_____

Title: Analysis of Chloride by Flow Injection Analysis

1.0 Purpose and Applicability

This method details the use of the Lachat automated analyzer for the analysis of Chloride. The method should be used only by those analysts familiar with the operation of the Lachat or under the supervision of someone who is.

Chloride reacts with mercuric thiocyanate to form a complex which displaces thiocyanate. The free thiocyanate so produced reacts with aqueous iron(III) to produce ferricyanide ion. This ion absorbs strongly at 480 nm. The calibration curve is non-linear. The range of the test is from 1.0 to 300 mg/L. Samples higher than this range will need dilution prior to analysis.

2.0 Definitions

Method Blank - A deionized water sample which is carried through the entire analytical procedure in the same manner as a sample.

LCS - Laboratory Control Sample. One LCS per batch is made from the same source as the initial calibration verification. LCSs determine the validity of the batch.

ICV - Initial Calibration Verification. One ICV is read at the beginning of every run. This verifies that the calibration curve is still usable. An ICV is prepared from a separate source from the CCV and calibration curve standards.

CCV - Continuing Cablibration Verification. The CCV is made from the same source as the calibration. One CCV is run every ten samples.

CCB - Continuing Calibration Blank. The CCB is deionized water with no reagents added. One CCB is run every ten samples.

Batch - Twenty (20) samples or fewer prepared on the same day.

3.0 Applicable Documents/References

Lachat QuikChem Method No. 10-117-07-1-A

Lachat QuikChem AE Software Reference Manual, Version 12

Title: Analysis of Chloride by Flow Injection Analysis

September 1991

Operating Manual for the Lachat QuikChem Auto Analyzer.

PACE NE-NH SOP QA-800, Use, Calibration and Maintenance of Equipment - Inorganics Laboratories

4.0 Materials and Apparatus

Apparatus:

Lachat Autoanalyzer and software
Chloride board 10-117-07-1-A with 20 cm sample loop

Reagents:

-Stock Mercuric Thiocyanate solution-0.42% in methanol (purchased).

-Stock Ferric Nitrate Reagent, 0.5 M: Place 202 grams of ferric nitrate($Fe(NO_3)_3.9H_2O$) in a 1 L volumetric flask with about 800 ml of DI water. Add 25 ml of concentrated nitric acid and dilute to mark with DI water, Invert 3 times.

-Combined Color Reagent: Mix 150 ml of Stock Mercuric Thiocyanate solution and 150 ml of Stock Ferric Nitrate reagent in a 1L volumetric flask and dilute to mark with DI water. Invert 3 times. Filter through a 0.45 micron membrane filter.

- Purchased Chloride Color Reagent : Filter " " " "

Standards:

-Stock Calibration Standard, 10,000 mg/l chloride: Dry primary grade sodium chloride for 4 hours in a 100°C oven. Cool in a dessicator. Weigh 4.1213 g NaCl and dilute to 250 ml with DI water in a volumetric flask.

-Stock Laboratory Control Standard, 1000 mg/l: Purchase from a separate source.

-Working Standards, 1.0 to 300 mg/l: Prepare as below:

Title: Analysis of Chloride by Flow Injection Analysis

Calibration Standards

Final Concentration (Std Dilution)	Stock Std. used	Conc of Stock used	mls of Stock Std used	Final Volume
300 mg/l	Stock Cal Std.	10000 mg/l	3.0	100 ml
250 mg/l			2.5	
150 mg/l			1.5	
100 mg/l			1.0	
50 mg/l			0.5	
25 mg/l			0.25	
15 mg/l			0.15	
5.0 mg/l			0.05	
1.0 mg/l	↓	↓	0.01	↓

Calibration Verification

~~200~~ 150 mg/l	Stock Cal Std.	10000 mg/l	~~2.0~~ 1.5	100 ml

Laboratory Control Standard

35 mg/l	Stock LCS	1000 mg/l	3.5	100 ml

* Standards are stable for at least three months

5.0 Methods/Procedures

Samples should be stored unpreserved at 4°C and should be analyzed within 28 days of sampling.

Sample Preparation

Water samples: Samples are prepared for analysis by clearing the sample of debris by syringe filtration through a 0.45 micron filter.

Soil samples: Samples are prepared by extracting an approximately 10 gm sample with 100 mLs of water. The amount of sample and the final volume of the extract are recorded

accurately in the laboratory notebook for use in future calculations. The extract is clarified before analysis by syringe filtration through a 0.45 micron filter.

CALIBRATION PROCEDURE

The instrument is calibrated with a ten point curve using the calibration standards above plus a DI water blank. Acceptance criteria for the calibration is a ~~0.9900~~ 0.995 correlation coefficient for the full curve. See QuikChem AE Software Reference Manual (Release 12 September 1991). It is important to compare curves and absorbances with those previously generated to insure quality of data. Printouts of calibratiions are filed in the Lab for approximately 3 months. Prior calibrations are archived. All are available in data base. Significant changes should be investigated. (switching to fresh standards or fresh reagents may change absorbance slightly) Check historical data. Operator discretion in approving or rejecting calibrations is encouraged. The decision and rational should be recorded in the instrument log.

ANALYSIS

Connect Chloride board and inspect. Put reagent lines in cassettes and raise tension levers to proper level. Rinse the board by placing reagent lines in DI water and pumping through for a few minutes. Then place lines in proper reagent containers and pump until stable baseline is attained. Place calibration standards in tray in descending order.(see above)

When a valid calibration is attained, load samples in tray and run.

When all samples have been run, place lines in water to flush system. Allow system to flush for 5-10 minutes then remove lines from water and allow pump to 'dry' the system. Turn off pump, release tension levers and 'pop' pump cassettes.

Method selection

Download Method "SULFATE - chloride/sulfate". The analysis described in this SOP follows the referenced Lachat method with these exceptions:

Title: Analysis of Chloride by Flow Injection Analysis

A 20 cm sample loop is used.
Cycle period: 22.00 s.
Inject to start of peak period: 9.00 s.
Standard calibration is as described above.

Analytical sequence

The sequence of analysis is as follows:

300 ppm standard
250 "
150 "
100 "
50 "
25 "
15 "
5.0 "
1.0 "
0.0 "
ICV ~~200~~ 35 ppm
ICB
10 samples
CCV ~~200~~ 150 ppm
CCB
10 samples
...
CCV
CCB

The sequence of CCV, CCB, 10 samples is repeated until a CCV or CCB fails or until sequence ends. A CCV and CCB are included at the end of the analytical sequence.

Only results falling between acceptable calibration verification/calibration blanks will be considered valid data.

6.0 Quality Control Requirements

Immediately following calibration, an Initial Calibration Verification and an Initial Calibration Blank must be run. Continuing Calibration Verifications and Blanks are run every 10 analytical samples thereafter and at the end of the analytical session. Calibration Verifications must yield 90-110% recovery for run to continue. Calibration Blanks must be below detection limit (which for chloride is ~~1.0~~ 2.0 mg/l.)

Title: Analysis of Chloride by Flow Injection Analysis

With each Batch of 20 field samples or 10 days, the following QC must be run:

Laboratory Control Sample (LCS) - yielding 80-120% recovery

Sample Duplicates - yielding a RPD of ≤20%
1/20

Matrix Spikes - using same sample as duplicate spiked with a known concentration of chloride - yielding 75-125% recovery.
1/10

Blanks - Blanks must be less than the method detection limit for the method to be considered under control. They are run at a frequency of 1 per batch of samples.

7.0 Calculations/Reporting

Water Samples

$$\text{Reported Conc Cl- mg/l} = \text{Obs. Conc.} \times \frac{\text{final vol}}{\text{init. vol}} \times \text{Dilution Factor}$$

Where: "Dilution Factor" is the dilution factor at the instrument

"Obs Conc" is the concentration of the diluted extract.

Soil Samples

Soil Samples which have been extracted with water and the aqueous extract analyzed are reported in ug/g extractable Chloride using the following formula

$$Cl^- \text{ mg/L} = \frac{(DF)*(\text{Obs Conc})/(\text{FV extract})}{(\text{Wt sample})*(\text{Dry weight})}$$

where:

"DF" is the dilution factor at the instrument,
"Obs Conc" is the concentration of the diluted extract,
"FV extract" is the final volume of the aqueous extract,

"Wt sample" is the wet weight of sample extracted,

"Dry weight" is the dry weight of the extracted sample.

Log book data includes: date, analyst, calibration file number, results file number, sample tray well number, sample number, code, dilution, instrument reading, reported concentration and comments.

Data is reported on a spreadsheet in Quattro and sent to LABUX via Network. Spreadsheet data includes: Sample, code, analysts initials, date analyzed, initial volume, final volume, dilution factor matrix, dilution factor instrument, LCS/spike level, value observed concentration, reported concentration, % recovery and % difference.

8.0 Corrective Actions

Calibration verifications falling outside of control limits stop an analytical session. All data must fall between calibration verifications and calibration blanks that are within control limits to be considered valid. If ICV/CCV'S AND/OR ICV\CCB's are out of control, the following actions may be taken:

- -Recalibrate and rerun
- -Remake standards and/or reagents and rerun
- -Troubleshoot at instrument-check for leaks or blockages-check flow

Consult with Lachat Technical Assistance as needed (Lynn Carlson or David Reese, 1-800-247-7613)

If method remains out of control consult group manager.

Laboratory Control Standards falling out of control limits negate their associated batch. See above for appropriate actions.

Sample Duplicates out of control limits do not neccessarily invalidate data. Sample should be repeated. Poor duplicate data may be a function of the sample matrix, however such a sample should be flagged with an appropriate narrative comment. Likewise, poor spike recovery does not negate data. It should be checked for proper level of spiking (50-100% of

Title: Analysis of Chloride by Flow Injection Analysis

sample concentration), and rerun. Poor spike recovery may be a function of the sample matrix. Such a sample should be flagged with an appropriate narrative comment.

If the blank passes on reanalysis the blank is acceptable and the batch need only be reanalyzed at the instrument.

~~A batch associated with a failing blank will be reprepped with the exception of samples that were below detection limit, or greater than 5 times the level in the blank.~~

9.0 Responsibilities

It is the responsibility of the analyst or technician to follow this SOP and record data accurately in log book. It is the responsibilty of the group manager to verify data before it is released to the client.

10.0 Health and Safety

It is the responsibility of the analyst to read appropriate MSDS's before running analysis. The combined color reagent contains mercuric thiocyanate and should be handled with gloves. Caution: Mercury is toxic. Do not ingest. Wear gloves when handling reagent or waste. Clean up spills. They leave dust. Don't let eluate "blow bubbles" - aerosols. Reagents and waste should be kept in the hood while in use. The Safety Officer should be consulted if any questions or problem should arise. Gloves and safety glasses should be worn at all times.

Title: **Total Nitrate/Nitrite Cadmium Reduction and Flow Injection Analysis**

Prepared By: _____ Date: _____

Approved By:

Group Supervisor: _____ Date: 11/29/94

QA Officer: Wendy E. Harris for SAB Date: 11/29/94

Lab Manager: _____ Date: 11/29/94

Regional Director: _____ Date: 11/30/94

Revision History: DRAFT 10/96 MANUAL EDITS TO BE INCORPORATE INTO FINAL REVISION JR 10/22/96

Revision	Changes	Authorization	Date

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

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Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA department.

I acknowledge receipt of copy____of document QA-5854, titled **Total Nitrate/Nitrite by Cadmium Reduction and Flow Injection Analysis**

Name_____Date_____

I acknowledge receipt of copy____of document QA-5854, titled **Total Nitrate/Nitrite by Cadmium Reduction and Flow Injection Analysis**

Name_____Date_____

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

1.0 Purpose and Applicability

Nitrite is determined on channel 1 of LACHAT Auto Analyzer by diazotizing with sulfanilamide followed by coupling with N-(1-napthyl)ethylenediamine dihydrochloride. This results in a water soluble magenta color which is read at 520 nm. Nitrate is reduced to Nitrite by passage through a copperized Cadmium column on channel 2. The resulting Nitrite is reacted as above and read at 520 nm. This yields Nitrite plus Nitrate. Nitrate alone is determined by the difference (Nitrate + Nitrite) - Nitrite. The range of the test is 0.05 to ~~10~~ 5.0 mg/L. Samples with concentrations higher than this range will require dilution prior to analysis.

This method details the use of the Lachat automated analyzer for the analysis of Nitrate/Nitrite. The method should be used only by those analysts familiar with the operation of the Lachat or under the supervision of someone who is.

2.0 Definitions

Method Blank - A deionized water sample which is carried through the entire analytical procedure in the same manner as a sample.

LCS - Laboratory Control Sample. One LCS per batch is made from the same source and may be the same aliquot as the initial calibration verification. LCSs determine the validity of the batch.

ICV - Initial Calibration Verification. One ICV is read at the beginning of every run. This verifies that the calibration curve is still usable. An ICV is prepared from a separate source from the CCV and calibration curve standards.

CCV - Continuing Cablibration Verification. The CCV is made from the same source as the calibration. One CCV is run every ten samples.

CCB - Continuing Calibration Blank. The CCB is deionized water with no reagents added. One CCB is run every ten samples.

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

Batch - Twenty (20) samples or fewer prepared on the same day.

3.0 Applicable Documents/References

EPA 600:353.2
QuikChem Method No. 10-107-04-1-A
QuikChem AE Software Reference Manual. Version 12 September 1991
Operating Manual for QuikChem AutoAnalyzer

4.0 Materials and Apparatus

Apparatus

Lachat Autoanalyzer and software
Nitrate/Nitrite board 10-107-04-1-A with 17 cm loop and Cadmium Reduction Column
Nitrite Board 10-107-04-1-A with 17 cm loop

Reagents

Ammonium Chloride, buffer, pH = 8.5
In a large beaker, dissolve 85.0 g Ammonium Chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetra acetic acid dihydrate ($Na_2EDTA \cdot 2H_2O$) in about 800 mL DI H_2O. Using pH meter, adjust pH to 8.5 with 10N NaOH. Transfer solution to 1 L volumetric flask and dilute to mark. Invert three times.

Sulfanilamide Color Reagent
Add about 600 mL DI H_2O to a 1 L volumetric flask. Add 100 mL of 85% Phosphoric Acid (concentrated), 40 g sulfanilamide and 1.0 g N-1-naphthylethylenediamine dihydrochloride (NED). Stir on stir plate until dissolved (approx. 20 minutes). This is stable for 1 month.

Cadmium Reduction Column
Prepared columns are ordered from LACHAT and sent to LACHAT to be re-packed as needed. Cadmium is very toxic and carcinogenic. Use column with care.

Carrier - DI water

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

Standard Solutions

Nitrite Stock Calibration Standard - ~~250 mg/L purchased from RICCA~~ 100mg/L HACH

Nitrate Stock Calibration Standard - ~~100 mg/L purchased from RICCA~~ 100mg/L

Nitrite Stock LCS - ~~1000 ppm~~ 250ppm Purchased from HACH - Dry $NaNO_2$ in dessicator for at least 8 hours. DO NOT HEAT. Weigh 1.2315 g Sodium Nitrite and dilute to 250 mL in DI H_2O.

Nitrate Stock LCS - ~~1000 ppm~~ 10 12ppm Purchased from HACH - Dry $NaNO_3$ for four hours in a 100°C oven. Cool in dessicator. Weigh 1.5170 g Sodium Nitrate and dilute to 250 mL in DI H_2O.

(reagents cont'd next page)

Prepare standard dilutions as follows:

Conc. of Standard Dilution (mg/L)	Stock Standard (SS) Used	Conc. of Stock Std. (mg/L)	Volume Stock Standard Used (mL)	Final Volume (mL)	Purpose
5.0 NO_2 2.5 1.0 0.5 0.05	NO_2 SS	~~250~~ 100	5.0 ~~2.0~~ 2.5 ~~1.0~~ 1.0 ~~0.4~~ 0.5 ~~0.2~~ 0.05 ~~0.02~~	100	Cal. Curve
10 ~~0.5~~ NO_2 1.0 ~~0.5~~ NO_3 2.5 ~~0.5~~ NO_2 2.5 ~~0.5~~ NO_3	NO_2 SS NO_3 SS NO_2 SS NO_3 SS	100 ~~250~~ 12 ~~100~~ 100 ~~250~~ 100 ~~100~~	NO_2 ~~0.2~~ 0.4 0.5 8.3 2.5 ~~0.2~~ 2.5 ~~0.5~~	100 100 100 100	ICV-NO_2/LCS ICV-NO_3/LCS CCV-NO_2 CCV-NO_3

5.0 Methods/Procedures

Samples should be stored at 4°C until time of analysis. Hold time is 48 hours from time of collection. Samples stored more than 48 hours may be preserved with 2 mL concentrated H_2SO_4 per liter and run as NO_2 plus NO_3 (if requested by client). CAUTION: Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

Stock Nitrite Standard (NO_2)
100 mg/L : Dissolve 0.4926g of sodium nitrite in about 600 mLs of DI H_2O. Dilute to one liter with DI H_2O and mix thoroughly.

Stock Nitrate Standard (NO_3)
100 mg/L : Dissolve 0.6068g of Sodium nitrate in about 600 mLs of DI water. Dilute to one liter with DI water and mix thoroughly.

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

Sample Preparation

Water samples: Samples are prepared for analysis by clearing the sample of debris by syringe filtration through a 0.45 micron filter.

Soil samples: Samples are prepared by extracting an approximately 10 gm sample with 100 mL of water. The amount of sample and the final volume of the extract are recorded accurately in the Extractions Logbook for use in future calculations. The extract is clarified before analysis by syringe filtration through a 0.45 micron filter.

Calibration Procedure

The instrument is calibrated with a five-point curve using the calibration standards above (see page 5) plus a DI water blank. Acceptance criterion is a 0.995 correlation coefficient or better for the full curve. (See QuikChem AE Software Manual - version 12 September 1991.) It is important to compare curves and absorbances with those previously generated to insure the quality of the data. Printouts of calibrations are filed in the lab for approximately 3 months. Prior calibrations are archived. All are available in database. Significant changes should be investigated. (Switching to fresh standards or fresh reagents may change absorbance slightly.) Check historical data. Operator discretion in approving or rejecting calibrations is encouraged. The decision and rationale should be recorded in the instrument log.

Analysis

Connect the Nitrite board on channel 1 and the Nitrite/Nitrate board on channel 2. Inspect. Put reagent lines in cassettes and raise tension levers to proper level. Prior to connecting column, rinse the boards by placing reagent lines in DI H_2O and pumping through for a few minutes. Then place lines in proper reagent containers and pump until stable baseline is attained. Turn off pump. Connect Cadmium column into NO_2/NO_3 board using care not to introduce air bubbles into the column. Re-start pump and wait for stable baseline. Place calibration standards in tray in descending order (see above, page 5). When a valid calibration is attained, load samples in tray and run. When all samples have been run, disconnect column and

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

place lines in DI water to flush system. Allow system to flush for 5 - 10 minutes, then remove lines from water and allow pump to "dry" the system. Turn off pump, release tension levers and "pop" pump cassettes.

Method Selection

Download Method "NO_ALL_1". The analysis described in this SOP follows the referenced LACHAT method with these exceptions:

- 17 cm sample loops are used on both boards
- Cycle period: 52.50 seconds
- *** Inject to start peak: NO_2 = 9.0 sec.
  NO_2/NO_3 = 19.0 sec.
- Standard calibration is as described above (page 5)

*** Subject to change. See maintenance log for current inject to start peak time.

Analytical sequence

The sequence of analysis is as follows:

5.0 ppm standard
2.5 "
1.0 "
0.5 "
0.05 "
0.0 "
ICV/LCS (Nitrite) ~~0.5~~ 1.0 ppm
ICV/LCS (Nitrate) ~~0.5~~ 1.0 ppm-checks efficiency of column
ICB
10 samples
CCV Nitrite ~~0.5~~ 2.5 ppm
CCV Nitrate ~~0.5~~ ppm
CCB 2.5
10 samples
CCV (NO_2)
CCV (NO_3)
CCB

The sequence of CCV, CCB, 10 samples continues until a CCV or CCB fails or until the end of the analytical sequence. Each sequence ends with a CCV and CCB. Only results falling

between acceptable calibration verification/ calibration blanks will be considered valid data.

6.0 Quality Control Requirements

Immediately following calibration, an Initial Calibration Verification and an Initial Calibration Blank must be run. Separate ICVs for NO_2 and NO_3 are run to verify the efficiency of the column to reduce NO_3 to NO_2. Continuing Calibration Verifications and Blanks are run every 10 analytical samples thereafter and at the end of the analytical session.

ICV/LCS/Calibration Verifications must yield 85-115% recovery for the run to continue. Calibration Blanks must be below detection limit (which for Nitrite/Nitrate is 0.05 mg/l.)

Every 20 field samples (or at a 5% frequency), the following QC must be run:

Sample Duplicates - yielding a RPD of ≤20%

Matrix Spikes - same sample as duplicate spiked with a known concentration of nitrate and nitrite - yielding 75-125% recovery.

Blanks - Blanks must be less than the method detection limit for the method to be considered under control. They are run at a frequency of 1 per batch of samples. The ICB can be the method blank.

7.0 Calculations/Reporting

<u>Water samples</u>

Reported Conc. NO_3 =

$$[(\text{Obs. Conc. } NO_2 + NO_3) - \text{Obs. conc. } NO_2] \times \frac{\text{Final Vol.}}{\text{Init. Vol.}} \times DF$$

$$\text{Reported Conc. } NO_2 = \text{Obs. Conc. } NO_2 \times \frac{\text{Final Vol.}}{\text{Init. Vol.}} \times DF$$

Title: Total Nitrate/Nitrite Cadmium Reduction And Flow Injection Analysis

Reported Conc. $NO_2 + NO_3$ =

$$(\text{Obs. Conc. } NO_2 + NO_3) \times \frac{\text{Final Vol.}}{\text{Init. Vol.}} \times DF$$

Where: "DF" is the dilution factor at the instrument
"Obs Conc" is the concentration of the diluted extract.

Soil Samples same as above except:

$$\text{Reported Conc. as above} \times \frac{1}{\%\ \text{Dry Wgt.}}$$

Log book data includes: date, analyst, calibration file number, results file number, sample tray well number, sample number, code, dilution, instrument reading, reported concentration and comments.

Data is reported on a spreadsheet in Quattro and sent to LABUX via Network. Spreadsheet data includes: Sample, code, analysts initials, date analyzed, initial volume, final volume, dilution factor matrix, dilution factor instrument, LCS/spike level, value observed concentration, reported concentration, % recovery and % difference.

8.0 Corrective Actions

Calibration verifications falling outside of control limits stop an analytical session. All data must fall between calibration verifications and calibration blanks that are within control limits to be considered valid. If ICV/CCVs/ LCSs and/or ICB/CCBs/Method Blanks are out of control, the following actions may be taken:

- -Recalibrate and rerun
- -Remake standards and/or reagents and rerun
- -Troubleshoot at instrument-check for leaks or blockages-check flow

Consult with LACHAT Technical Assistance as needed (Lynn Carlson or David Reese, 1-800-247-7613)

If method remains out of control consult group supervisor.

Sample Duplicates out of control limits do not necessarily invalidate data. Sample should be repeated. Poor duplicate data may be a function of the sample matrix, however such a sample should be flagged with an appropriate narrative comment. Likewise, poor spike recovery does not negate data. It should be checked for proper level of spiking (50-100% of sample concentration), and rerun. Poor spike recovery may be a function of the sample matrix. Such a sample should be flagged with an appropriate narrative comment.

A batch associated with a failing blank will be reprepped with the exception of samples that were below detection limit, or greater than 5 times the level in the blank.

9.0 Responsibilities

It is the responsibility of the analyst or technician to follow this SOP and record data accurately in log book. It is the responsibility of the group manager to verify data before it is released to the client.

10.0 Health and Safety

It is the responsibility of the analyst to read the appropriate MSDSs before running analysis. Wear gloves, lab coat and safety glasses at all times. Reagents and waste should be kept in the hood while in use. Consult the Safety Officer if any questions or problems arise.

PACE NEW ENGLAND, INCORPORATED
Standard Operating Procedure QA-5855

SOP Number: QA-5855
Revision History
Cover Page
Page 1

Title: Analysis of Cyanide Extracts by Flow Injection Analysis

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Prepared By: Christine Weir Date: 11/4/93

Approved By:

Group Supervisor: Sherri V. Fleming Date: 11/4/93

QA Officer: Wendy E. Harris Date: 11/8/94

Lab Manager: R. Wellman Date: 11/8/94

Regional Director: Dawson Kuefler Date: 12/9/94

Revision History: DRAFT 10/96 MANUAL EDITS TO BE INCORPORATED INTO FINAL REVISION JR

Revision	Changes	Authorization	Date ~~10/9/96~~ JR 10/22/96 ~~10/22/96~~

Title: Analysis of Cyanide Extracts by Flow Injection Analysis

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA department.

I acknowledge receipt of copy_____of document QA-5855, titled **Analysis of Cyanide Extracts by Flow Injection Analysis**

Name_____Date_____

I acknowledge receipt of copy_____of document QA-5855, titled **Analysis of Cyanide Extracts by Flow Injection Analysis**

Name_____Date_____

Title: Analysis of Cyanide Extracts by Flow Injection Analysis

1.0 Purpose and Applicability

Total cyanide from alkaline distillates after preparation according to SOP QA-5856 is converted to cyanogen chloride by reaction with chloramine-T at a pH lower than 8.0. The CNCl forms a red-blue dye by reaction with pyridine barbituric acid. The color is read at 570 nm. The range of the test is from 0.01 to 1.0 mg/L. Samples higher than this range will need dilution prior to analysis.

This method details the use of the Lachat automated analyzer for the analysis of Cyanide in distillates. The method should be used only by those analysts familiar with the operation of the Lachat or analysts under the supervision of someone who is.

2.0 Definitions

CCV - Continuing calibration verification
ICV - Initial calibration verification
CCB - Continuing calibration blank
ICB - Initital calibration blank

3.0 Applicable Documents/References

PACE SOP QA-5856 (Sample Prep)
QuickChem Method No. 10-204-00-1-A
QuickChem AE Software Reference Manual, Version 12-Sept. 1991

4.0 Materials and Apparatus

Apparatus

Lachat Autoanalyzer, software and autosampler operation manuals.
Cyanide board 10-204-00-1-A with 150 cm loop
QuikChem Method No. 10-204-00-1-A

Reagents

Carrier, 0.25 M Sodium Hydroxide: In a 1 L volumetric flask, dissolve 10.0 g NaOH in 1.00 L DI water. Store in a plastic bottle. Stable for 1 year.

Phosphate Buffer, 0.71 M: In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH_2PO_4) in approximately 800 mL water. Dilute to the mark and invert three times. Stable for one month.

Chloramine-T: Dissolve 2.0 g of chloramine-T hydrate in 500 mL of DI water. Prepare fresh ~~weekly~~ daily. ~~Store in refrigerator~~.

Pyridine-Barbituric Acid Reagent: In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL of water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12 M HCl) and mix. Transfer to a 1 L volumetric flask, dilute to the mark and invert three times. Stable for 2 months.

Standards

Two sources of standards are required. One source is used to prepare the working standards and CCVs. The other source is used to prepare ICVs.

Stock Calibration Standard (1000 ppm Cyanide): Dissolve 0.5 g potassium hydroxide (KOH) in DI water and add 0.6275 g potassium cyanide (KCN) and dilute to 250 mL with DI water. Check titer weekly or with each use whichever is the least frequent.

Intermediate Standard (50 mg/L Cyanide): Add 5.0 mL of 1000 ppm stock calibration standard to 100 mL of 0.25N NaOH. Stable for six months.

Working Standards (0.01 to 1.0 mg/L): Prepare fresh daily as below:

Calibration Standards

Final Conc.	Stock Std. Used	Conc. of Std. Used	mL Stock Std. Used	Final Vol. mL
1.0	Int Std.	50 ppm	1.0	50 ml
0.8	Int Std.	50 ppm	0.8	50 mL
0.6	Int Std.	50 ppm	0.6	50 mL

0.4	Int Std.	50 ppm	0.4	50 mL
0.2	Int Std.	50 ppm	0.2	50 mL
0.08	Int Std.	50 ppm	0.08	50 mL
0.04	Int Std.	50 ppm	0.04	50 mL
0.02	Int Std.	50 ppm	0.02	50 mL
0.01	Int Std.	50 ppm	0.01	50 mL

Calibration Verifications Standards

Final Conc.	Stock Std. Used	Conc. of Std. Used	mL Stock Std. Used	Final Vol. mL
~~0.15~~ 0.40	Int. Std.	50 ppm	~~0.15~~ 0.40	50

Continuing and Initial Blank Standards

0.25 N NaOH

5.0 Methods/Procedures

Samples should be stored at 4°C and preserved to a pH of >12 with NaOH.

Samples are prepared for analysis by distillation following SOP QA-5856.

Method Selection

Download Method "TCN". The analysis described in this SOP follows the referenced LACHAT method with the following exceptions:

Inject to start peak: 26.00 sec.
Standard calibration is as described above.

Analysis Setup

Connect the cyanide board and inspect. Make sure that the heating block is connected and functioning properly. Put reagent lines in cassettes and raise tension levers to achieve

flow through the system. Rinse the board by placing reagent lines in DI water and pumping through for a few minutes. Then place lines in proper reagent containers and pump until stable baseline is attained.

Analytical Sequence

The sequence of analysis is as follows:

1.0 ppm std
0.8
0.6
0.4
0.2
0.08
0.04
0.02
0.01
0.00
ICV 0.~~15~~ 0.50 ppm
ICB
10 samples
CCV 0.~~15~~ 0.40 ppm
CCB
10 samples
...

The sequence of "CCV,CCB, 10 samples" is repeated until a CCV or CCB fails or until the sequence ends. Only results falling between acceptable calibration verification/calibration blanks will be considered valid. (CCB's are 0.25 N NaOH.)

Calibration Procedure

Prepare a calibration tray table (see Lachat manual) starting with the high standard and ending with the blank as shown above. The instrument is calibrated with a 9 point curve using the calibration standards listed above plus a 0.25 N NaOH blank. Acceptance criteria for the calibration is a 0.995 correlation coefficient for the full curve. See QuikChem AE Software Reference Manual (Release 12 September 1991). It is important to compare curves and absorbances with those previously generated to insure quality of data. Absorbance of the 0.200 mg/L standard should be in the range of 0.0400 - 0.7000. Deviation from this range must be investigated. Operator discretion in approving or rejecting

calibrations is encouraged. The decision and rational should be recorded in the instrument log.

Sample analysis

When a valid calibration is attained, load samples in tray, prepare a sample tray table (see Lachat manual) starting with the ICV as shown above and run. As samples are running, periodically review sample results, CCVs, CCBs and raw peak data for any irregularities (carryover from concentrated samples, poor recoveries, failing calibrations, air bubbles, samples requiring dilution, etc.). Samples exceeding the highest calibration point are diluted to the midpoint of the range and rerun.

System Shutdown

When valid results have been obtained for all samples, place lines in water to flush system. Allow system to flush for 5-10 minutes then remove lines from water and allow pump to 'dry' the system. Turn off pump, release tension levers and 'pop' pump cassettes.

6.0 Quality Control Requirements

Immediately following calibration, an ICV and an ICB must be run. CCVs and CCBs are run every 10 analytical samples thereafter until the end of the analytical session. Calibration Verifications must be 85 - 115% for run to continue. Results outside the range of 90-110 are unusual. The run may continue but the occurance should be reported to the supervisor. Calibration Blanks must be below detection limit (0.~~01~~ 02 mg/l.)

With each Batch of 20 field samples or 10 days, the following QC must be run:

Distilled Standard (Low)
Distilled Standard (HIGH)
~~Duplicate~~ Laboratory Control Sample~~s~~ - yielding ~~80-120%~~ 85-115% recovery ~~and RPD ≤ 20%~~.

Distilled Sample Duplicates - yielding a RPD of ≤ 20%

Matrix Spikes - using same sample as duplicate spiked with a known concentration of cyanide - yielding 75-125% recovery.

Blanks - Blanks must be less than the method detection limit for the method to be considered under control. They are run at a frequency of 1 per batch of samples. (Blanks are 0.25 N NaOH.)

7.0 Calculations/Reporting

$$\text{Reported Conc. TCN} = (\text{Obs. conc.}) \frac{\text{Final Vol.}}{\text{Initial Vol.}} (\text{Dilution Factor})$$

where: Dilution factor = the dilution factor at the instrument

Obs. Conc. = the concentration of the diluted extract

RPD

LCS, CCV, ICV percent of expected

Matrix spike recovery

Run log book data includes: date, analyst, calibration file number, results file number, sample tray well number, sample number, code, dilution, instrument reading, reported concentration and comments. (Figure 1). Printouts of calibrations are filed in the Lab for approximately 3 months. Prior calibrations are archived. All are available in the Lachat data base.

Data is reported on a spreadsheet in Quattro and sent to LABSAM via Network. Spreadsheet data includes: Sample, code, analysts initials, date analyzed, initial volume, final

volume, dilution factor matrix, dilution factor instrument, LCS/spike level, value observed concentration, reported concentration, % recovery and % difference. See Sop ( ) for Spreadsheet entry and sending.

8.0 Corrective Actions

Calibration verifications falling outside of control limits stop an analytical session. All data must fall between calibration verifications and calibration blanks that are within control limits to be considered valid. If ICV/CCV'S and/or ICB/CCB's are out of control, the following actions may be taken:

- Recalibrate and rerun.
- Remake standards and/or reagents and rerun.
- Troubleshoot at instrument: check for leaks, blockages, flow problems, bubbles, etc. If a problem is found, correct and verify calibration with a CCV/CCB before rerunning affected samples.

Consult with Lachat Technical Assistance as needed (Lynn Carlson or David Reese, 1-800-247-7613)

If method remains out of control consult group manager.

LCS's falling out of control limits negate their associated batch. See above for appropriate actions.

Sample Duplicates out of control limits do not necessarily invalidate data. Sample should be repeated. Poor duplicate data may be a function of the sample matrix, however such a sample should be flagged with an appropriate narrative comment. Likewise, poor spike recovery does not negate data. It should be checked for proper level of spiking (50-100% of sample concentration), and rerun. Poor spike recovery may be a function of the sample matrix. Such a sample should be flagged with an appropriate narrative comment.

If the blank passes on reanalysis the blank is acceptable and the batch need only be reanalyzed at the instrument.

A batch associated with a failing blank will be re-prepped with the exception of samples that were below detection limit, or greater than 5 times the level in the blank.

9.0 Responsibilities

It is the responsibility of the analyst or technician to follow this SOP and record data accurately in log book. It is the responsibility of the group manager to verify data before it is released to the client.

10.0 Health and Safety

It is the responsibility of the analyst to read the appropriate MSDS's before running this analysis. Gloves, safety glasses, and lab coat must be worn at all times. Reagents and waste should be kept in the hood while in use. Dispose of all waste in Cyanide Base waste containers. Consult the Safety Officer if questions or problems should arise.

Potassium Cyanide

Cyanide is fast acting, highly poisonous by ingestion (2250 mg, adult lethal dose). It can also enter the body through the skin or by inhilation or dust, solution mist or HCN. Cyanide inhibits cellular respiration. Over exposure caused headaches, dizziness, weakness, profuse ineffective breathing and nausea, which may be followed by weak irregular heartbeat, unconsciousness, convulsions and death. Use extreme caution! Avoid contact with Acid.

Barbituric Acid

Barbituric Acid is moderately irritating to the eyes, skin, respiratory tract and mucous membranes. If ingested it may cause gastrointestinal irritation, nausea, vomiting and diarrhea. Barbituric Acid is an allergin.

Pyridine

Pyridine is a flammable liquid which is harmful if swallowed, inhaled or absorbed through the skin. It's odor is penetrating and sickening. Pyridine is classified as an experimental carcinogen and a positive mutagen. Liver and kidney damage may occur with over exposure. Store in regridgerator and use in fume hood.

Title: Analysis of Cyanide Extracts by Flow Injection Analysis

Potassium Phosphate

May cause irritation, avoid contact with eyes, skin, clothing. Store in a tightly closed container.

Chloramine-T

May irritate eyes, skin, mucous membranes and cause allergic respiratory reactions. It may react with amino acids in the gastro intestinal tract to form toxic cyanogen compounds. Ingestion of large amounts may cause cyanosis and death. Store below 35oC.

Sodium Hydroxide

Severly corrosive to all tissue. May be fatal if swallowed. Ingestion may cause severe burns to mucous membrane. Inhalation of dust or concentrated mist may cause damage to respiratory tract. Skin contact may cause irritation or severe burns. Use extreme caution!

PACE, INCORPORATED NEW ENGLAND
Standard Operating Procedure QA-5802

SOP Number: QA-5802
Revision History
Cover Page
Page 1

Title: **Anions by IC**

Prepared By: Cynthia A. Foster Date: 07/07/92

Approved By:

Group Manager: Sharon D. Henry Date: 7/7/92

QA Officer: R. Wellman for SB Date: 9/21/94

Tech. Director: R. Wellman Date: 12/3/92

President: R. Wellman for DFM Date: 9/21/94

Revision History:

Revision	Changes	Authorization	Date
1	reformat update, renumber from # 102.1	S. Beck	12/17/92
2	incorporate EPA Region 5 comments, update LCS QC	W. Harris	11/15/94

WEH (3) 11.14.94

Title: Anions by IC

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA department.

I acknowledge receipt of copy_____of document QA-5802, titled **Anions by IC.**

Name_____Date_____

I acknowledge receipt of copy_____of document QA-5802, titled **Anions by IC.**

Name_____Date_____

Title: Anions by IC

1.0 Purpose and Applicability

This method covers the determination of the following inorganic anions by ion chromatography: Sulfate, Bromide, Chloride, Nitrate-N, Nitrite-N, and Ortho-Phosphate-P.

This test may be used to measure Sulfate in the range of 1 to 100 mg/L. Any sample reading above this must be diluted to be within range and reanalyzed.

The matrices applicable to each method are as follows: Drinking Water, Surface Water, Mixed Domestic and Industrial Wastewaters, Groundwater, Reagent Waters, Solids (after extraction), Leachates.

This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method.

When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by spiking anions of interest.

In order to use this method for solids, an extraction procedure must be performed. (See Sample Preparation, Sec. 5.0)

2.0 Definitions

Method Blank - A deionized water sample which is carried through the entire analytical procedure in the same manner as a sample.

LCS - Laboratory Control Sample. One LCS per batch is made from the same source as the initial calibration verification. LCSs determine the validity of the batch.

ICV - Initial Calibration Verification. One ICV is read at the beginning of every run. This verifies that the calibration curve is still usable. An ICV is prepared from a separate source from the CCV and calibration curve standards.

CCV - Continuing Cablibration Verification. The CCV is made from the same source as the calibration. One CCV is run every ten samples.

CCB - Continuing Calibration Blank. The CCB is deionized water with no reagents added. One CCB is run every ten samples.

Batch - Twenty (20) samples or fewer prepared on the same day.

3.0 Applicable Documents/References

Calculation and Procedure Reference Manuals
- Wisp712 Operator Manual
- Waters 510 HPLC Pump Manual
- Hewlett Packard LAS Manual
- LABUX Manual
- Dionex 200i Manual

PACE NE-NH SOP QA-800, Use, Calibration, and Maintenance of Laboratory Equipment - Inorganics Laboratories

Methods for Chemical Analysis of Water and Wastes, USEPA 600 - 4/79/020, 1979 revised 1983, Method 300.0

ASTM Method D 3987-85, "Standard Test Method for Shake Extraction of Solid Waste with Water"

4.0 Materials and Apparatus

Apparatus

Waters 712 Wisp
Waters 510 Pump
Dionex conductivity Detector Model 2000i
Ion Pac^R AG4A Guard Column
Ion Pac^R NG1 Guard Column
Ion Pac^R AS4A Separation Column
2 Liter Regenerant Bottle
Compressed Air
Dionex Micromembrane Suppressor
Hewlett Packard LAS System
Analytical Balance capable of accurately weighing to the nearest 0.0001g.
B-D 5 ml Syringes
Millex-HV$_{13}$ Filters
48 Place Carriage Drive, with 4ml sample vials and septa
96 Place Carriage Drive, with 1ml sample vials and caps

Class "A" pipets, assorted volumes
Class "A" volumetric flasks, assorted volumes

Reagents

Regenerant, 0.025N H_2SO_4: Dilute 2.8 mL conc. H_2SO_4 to the one gallon mark with ASTM type II Laboratory Pure Water(DI Water). Dionex Eluent Concentrate: Add 14.2817g (170 mm) $NaHCO_3$ and 19.0782g (180 mm) Na_2CO_3 to a one liter volumetric flask. Dilute to volume with deionized water.

Working Eluent: Dilute 15 mL of the Eluent Concentrate to 2 L in a volumetric flask with deionized water. Resulting solution contains 1.8 mm (milli-molar) Na_2CO_3 and 1.7 mm $NaHCO_3$. Working eluent is vacuum filtered through a 0.20μm or 0.45μm filter paper before use. Eluent preparation is recorded in the Dionex Eluent Log Book.

Stock Standards

All salts except $NaNO_2$ are to be dried at 103°C for four hours, cooled in a desicator then weighed. $NaNO_2$ will break down when heated, and should therefore be dried at least 24 hours in a desicator. The dried salts are stored in the small desiccator for standards.

Anstn 1 Nitrate-N stock standard, 1000 ppm: Dissolve 1.5170g $NaNO_3$ in DI water; dilute to 250.0 mL.

Anstn 2 Phosphate-P stock standard, 1000 ppm: Dissolve 1.0984g KH_2PO_4 in DI water; dilute to 250.0 mL.

Anstn 3 Nitrite-N stock standard, 1000 ppm: Dissolve 1.2315g $NaNO_2$ in DI Water; dilute to 250.0 mL.

Anstn 4 Sulfate stock standard, 1000 ppm: Dissolve 0.4536g K_2/SO_4 in DI water; dilute to 250.0 mL.

Anstn 5 Chloride stock standard, 1000 ppm: Dissolve 0.4122g NaCl in DI water; dilute to 250.0 mL.

Anstn 6 Bromide stock standard, 1000 ppm: Dissolve 0.3219g NaBR in DI water; dilute to 250.0 mL.

Anstn 7 Combined stock standard, 100 ppm SO_4 & Br, 50 PPM Cl & PO_4-P, and 25PPM NO_2-N & NO_3-N: Pipet 20.00 mL each

of Sulfate and Bromide stock standards, 10.00 mL each of Chloride and Phosphate-P stock standards and 5.00 mL each of Nitrite-N and Nitrite-N stock standards into a 200 mL volumetric flask rinse the sides of the flask between each addition with DI water. Dilute to mark. Store at 4°C. Make fresh monthly, or as needed.

Anstn 8 Daily combined standard, 20/10/5 ppm: Dilute 10.00 mL combined stock standard to 50.00 mL. Store at 4°C. Make fresh weekly, or as needed.

5.0 Methods/Procedures

Sample Collection, Preservation and Storage

Samples should be collected in clean glass or polyethylene bottles.

Sample preservation and holding times for the anions that can be determined by this method are as follow.

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
O-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Sample Preparation

Water samples are filtered through a 0.45 μ membrane filter immediately prior to analysis, with no additional preparation step. Solid samples are extracted with deionized water and the analysis performed on the extract. The extraction procedure is based on the ASTM Method D 3987-85, "Standard Test Method for Shake Extraction of Solid Waste with Water". A representative aliquot of the material to be tested is mixed with ASTM Type II Water (DI Water) and the resulting supernatant is analyzed by the appropriate method. The amounts of solid and DI water used will depend on the nature of the sample and the level of detection required. This will require some judgement on the part of the analyst.

As a general rule, 10 g of sample extracted with 100 ml of DI Water (added from a graduated cylinder) is a practical starting point and will give usable numbers for most samples. The sample should be mechanically agitated in the EPTOX extractor for approximately 30 minutes. The sample is then allowed to settle for 15 to 30 minutes and filtered through a Whatman glass fiber filter. Immediately prior to analysis by IC, sample extracts are filtered through 0.45 μ filter.

The sample is then ready for analysis.

The dry weight of the sample is determined on a separate aliquot and the concentration is determined by

$$\text{Concentration } (\mu g/g) = \frac{C \times V}{W \times S} \times 100$$

Where, C = concentration of analyte in extract (μg/ml)
V = volume used in extraction (ml)
W = weight of material (g, as received)
S = percent solids in sample

Parameters tested by the above method should always be reported as "leachable.

<u>Preparing an LAS Sequence</u>

<u>Log in</u> with designated LAS user password.

<u>F4</u> Specify Instrument {Dionex}

Pr,S Prepare Sequence {hit "P" two times}

Sequence Name	IC_04_12
Method Name	IC375
Tab to Prefix:	IC37
Tab to counter:	191

Sample Parameters: <u>Accept Screen</u>

Number of Samples: <u>Enter Number</u> {18}, Accept Screen

Type sample table, use next page to get to sample number 12. When done with all samples, Accept Screen.

Amount Specification: <u>Accept Screen</u>

Another Subsequence?: Enter {NO}

Type "A" for Assign Files
Instrument {Dionex}
Single Sample {NO}

Assign Sequence: Sequence Name {IONS30 12 02}, Accept Screen

Check the screen before starting instrument:

INSTRUMENT:	Dionex	RESULT FILE:	DIASF16725
STATUS :	READY	METHOD :	Dionex 130
LEARN MODE:	OFF	SEQUENCE :	IONS30_12_02

If you have tried to assign a result file that has already been used you get:

Rst File /Data/ION1/Result/I1ASF18016.RES
Overwrite {NO}

Hit return and modify sequence; MO,S and put in new counter and prefix. Never overwrite files!

Refer to Table 2 for example sequences.

Loading Samples

Select carriage drive for 48 or 96 samples.

Write sequence in run log, follow page format and proper sample coding. (See Table 3.)

Prepare Sequence in LAS.

Filter all samples through 0.45 um filters into the appropriate samples vials. (1 ml vials for 96 carriage drive, 4 ml sample vials for 48 carriage drive.)

Turning on Instrument

Ensure sufficient volumes of eluent and regenerant solutions.

Open valve to compressed air line and adjust pressure on regulator to 4 PSI. Regenerant flow at this time should be 1.5 to 2 ml per minute. Check discharge line for proper flow.

Turn on pump (2.0 ml per minute, pressure not to exceed 1,900 psi) blue power button must be on to turn on pump.

Turning on Detector

Local Remote button should be on "Local".

Cell should be on.

Auto offset should be off until equilibrium is reached. An acceptable conductivity reading on 30 micros range at equilibrium with auto offset off is <20 micros. When this is achieved, turn auto offset on.

Ensure wisp is programmed correctly; Injection Volume (15 ul), Sample Numbers, Run Time (12 min.).

Set up an ICV and inject to ensure separation and good chromatography.

Start run of samples by putting sample carriage in carriage drive and pressing start button.

Shut Down Procedure

Shut off blue power button.

Shut off compressed air and crack cover of regenerant bottle.

6.0 Quality Control Requirements

Analytical Run Requirements

Initialize 6 point calibration. See Table 3, Example Run Log.

Calibration standards: Anstn 8 is the initial calibration verification (ICV) and the continuing calibration verification (CCV). The ICV is the first sample analyzed in a sequence. CCVs are run in between every 10 injections throughout and at the end of a sequence. ICV's and CCV's must be within 85 - 115% recovery to accept data without flagging.

Calibration Blanks: use small water bottle; a distilled water blank is the second sample run in every sequence (ICB). Continuing calibration blanks are run in between every 10

injections and at the end of a sequence, analogous to the CCV. ICB's and CCB's must be below the detection limit.

An Laboratory Control Sample (LCS) is performed with every analytical batch. Consult Anion Standard Log Book for preparation of LCS. LCS stock standards are generally purchased from Ricca Chemical Company. LCS recovery must be between 80 - 120% Recovery.

Performance Evaluations Samples (PEs) are analyzed as required by the USEPA to remain certified.

Laboratory Duplicates: one set of duplicate samples is run in every batch of 20 analytical samples.

For samples with values at least 5 times the detection limit, Sample Precision must be 20% or less.

Matrix Spikes: add 1 ml of Anstn 8 to 5 ml of sample (spike level 10/5/20). At least one spike is run in every batch of 20 analytical samples.

Spike recovery should be between 80 and 120%.

Calibration and Standardization - See anion standards book for current 6 point calibration

Calibration Standards (4 or 6 point calibration)

Anion mg/l:

	Chloride	Nitrite-n	Bromide	Nitrate-N	O-Phosphat-P	Sulfate
Level 1	5	2.5	10	2.5	5	1
Level 2	10	5	20	5	10	5
Level 3	20	10	40	10	20	10
Level 4	50	25	100	25	50	20
Level 5						40
Level 6						100

Curve Coefficients must be 0.990000 or higher for acceptable curves. All 24 standards must be between 90 and 110% recovery for acceptable curves.

Each analyst using this method must have formal training in quality control. The minimum requirements of this training consist of an initial demonstration of method capability and the

analysis of spiked samples as a continuing check on performance. The laboratory should maintain performance records to define and document the quality of data that is generated. (See Quattro Files)

In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to make a new method in LAS.

Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method, using the protocol stated within this SOP.

Method Detection Limit

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

The MDL is determined bi-annually by injecting 7 replicate samples at a concentration three to five times the detection limit. The Standard Deviation of these numbers is multiplied by 3.14 and this number is the MDL. The current MDL for all six anions is 1 mg/l. Lower detection limits can be attained by injecting higher sample volumes.

Limit of Acceptability for Anion Analysis (mg/l)

Output Range = 30 micros:

	Chloride	Nitrite-n	Bromide	Nitrate-N	O-Phosphat-P	Sulfate
Lower Limit	1	1	1	1	1	1
Upper Limit	50	25	100	25	50	100
Cal Check	10	5	20	5	10	20
LCS Value	10	N/A	10	N/A	N/A	10
Spike Level	10	5	20	5	10	20

7.0 Calculations/Reporting

Calculations are performed by the Laboratory Automation System(LAS) using the following equation:

$R = B_o + B_1A$ where:

R = response (peak area)
B_o = y intercept
B_1 = slope
A = amount (concentration)

The final report will include information on initial and continuing calibrations and results of all quality control data. The Anion spreadsheet includes Sample no., Analyst, Prepdate, Date analyzed, Ion initial volume, Ion final volume, Dilution Factor Matrix, Dilution Factor Instrument, LCS spike level, OBS(erved) concentration, Reported concentration, % Recovery, and % Difference. (See Table 4).

8.0 Corrective Actions

If the spiked sample recovery is outside the range of 80 to 120% or if the RPD exceeds 20%, and the unspiked sample value contains less than twice the analyte concentration than was spiked, notify the supervisor and reevaluate the method for potential problems and continue to observe recoveries and ranges.

Every instance of noncompliant method quality control requires the generation of a Corrective Action Report describing the problem, suspected cause and final resolution. Corrective action reports must be signed by the initiator, section supervisor, QA officer, and lab management.

Interferences

Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

The water dip or negative peak that elutes near and can interfere with the chloride peak can usually be eliminated by the addition of the equivalent of 1 ml of eluent concentrate to 100 mL of each sample.

All samples are filtered through 0.45 micron filters.

The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

9.0 Responsibilities

The analyst or technicians responsibility is to follow this SOP and record all the data in the lab notebook. Any irregularities within the test or samples should be recorded in the lab notebook and reported to the lab manager who is responsible for reviewing the data.

10.0 Health and Safety

Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method. However, every sample in the lab should be handled as if it is hazardous waste. All technicians shall be familiar with the Chemical Hygiene Plan.

Title: Anions by IC

Table 1

Generic Analytical Sequence With Acceptance Criteria

Sample Number	Instrument Run Log	Acceptance Limit
1	ICV	± 10%
2	ICB	BDL
3	Sample 1	
4	Sample 2	
5	Sample 3	
6	Sample 4	
7	Sample 5	
8	Sample 6	
9	Sample 7	
10	Sample 8	
11	Sample 9	
12	Sample 10	
13	CCV	± 10%
14	CCB	BDL
15	Sample 11	
16	Sample 12	
17	Sample 13	
18	Sample 14	
19	Sample 15	
20	Sample 16	
21	Sample 17	
22	Sample 18	
23	Sample 19	
24	Sample 20	
25	CCV	± 10%
26	CCB	BDL

Title: Anions by IC

Table 2

Analytical Sequence With Acceptance Criteria

Example Batch Of 20 Field Samples

Sample Number	Analytical Batch	Acceptance Limit
1	ICV	± 10%
2	ICB	BDL
3	LCS	
4	Method Blank	BDL
5	Field Sample 1	
6	Sample Duplicate	≤ 20% RR
7	Matrix Spike	± 25%
8	Field Sample 2	
9	Field Sample 3	
10	Field Sample 4	
11	Field Sample 5	
12	CCV	± 10%
13	CCB	BDL
14	Field Sample 6	
15	Field Sample 7	
16	Field Sample 8	
17	Field Sample 9	
18	Field Sample 10	
19	Field Sample 11	
20	Field Sample 12	
21	Field Sample 13	
22	Field Sample 14	
23	Field Sample 15	
24	CCV	± 10%
25	CCB	BDL
26	Field Sample 16	
27	Field Sample 17	
28	Field Sample 18	
29	Field Sample 19	
30	Field Sample 20	
31	CCV	± 10%
32	CCB	BDL

Title: Anions by IC

Table 3

Example of Anion Run Log Page

DIONEX EPA 600.300.0 — PACE NE — 107

IC_03_09 cont

	SAMPLE NO	CODE	SEQ/FILE NO	SO4	DILN	
37	35272-81	S18	IC35438	dilute	L10	CF 3/9/93
38	MB442		39	1.60	—	B442 method to 353
39	LCS442	Anstu 883	40	51.4/50	—	
40	LCS442A	↓	41	51.5/50	—	
41	35224-97	S1	42	16.3	L100	
42	-97d	S1d	43	16.8	↓	
43	CCV	Anstu 883	44	19.8/20	—	
44	CCB		45	0.83	—	
45	35224-97ap	S1ap	46	23.8	L100	0.4ml Anstu 883 → 1ml sample
46	35202-73	S2	47	79.0	—	
47	-74	S3	48	58.7	—	
48	75	S4	49	93.2	—	
49	76	S5	50	33.6	—	
50	77	S6	51	94.6	—	
51	78	S7	52	dilute	L10	
52	79	S8	53	77.1	—	
53	80	S9	54	7.27	L10	
54	81	S10	55	0.18	L10	rerun neat
55	CCV	Anstu 883	56	20.2	—	
56	CCB	5	57	0.24	—	
57	35224-89	S11	58	13.9	L10	
58	90	S12	59	15.5		
59	91	S13	60	20.4		
60	92	S14	61	45.3		
61	93	S15	62	11.3		
62	94	S16	63	38.2		
63	95	S17	64	14.2		
64	96	S18	65	52.1		
65	98	S19	66	21.6	↓	
66	99	S20	67	0	—	
67	CCV	Anstu 883	68	19.7/20	—	
68	CCB	—	69	0	—	

CF 3/10/93

Title: Anions by IC

Table 4

Example of Anion Spread Sheet

304

Sulfate

SENT TO DB

Batch 442
Method EPA-600 300.0 / SW846 9056
Det. Limit 1
Matrix WATER

IDC Sample	% Code	ANAL Inits	PREP Date Prepared	DATE Date Analyzed	IONINIT Init Vol	IONFIN Fin Vol mls	DFM Matrix DF	DFI Instr DF	% LCS/SPK LCSW Level	VAL Obs Conc.	%	% Rated Conc.	% Rec	% Diff
Y-Blank	BW	CF	03/09/93	03/09/93	1	1	1	1		1.6		1.6		
LCSW	LCS1	CF	03/09/93	03/09/93	1	1	1	1	50	51.6		51.6	103.2	
LCSS	LCS2	CF	03/09/93	03/09/93	1	1	1	1	50	51.5		51.5	103	
35224-87	S1	CF	03/09/93	03/09/93	1	1	1	100		16.3		1630		
35224-87	SD	CF	03/09/93	03/09/93	1	1	1	100		16.3		1630		3.0211
35224-87	MS	CF	03/09/93	03/09/93	1	1	1	100	1000	23.8		2380	75	
35202-73	S2	CF	03/09/93	03/09/93	1	1	1	1		79		79		
35202-74	S3	CF	03/09/93	03/09/93	1	1	1	1		58.7		58.7		
35202-75	S4	CF	03/09/93	03/09/93	1	1	1	1		93.2		93.2		
35202-76	S5	CF	03/09/93	03/09/93	1	1	1	1		33.6		33.6		
35202-77	S6	CF	03/09/93	03/09/93	1	1	1	1		94.6		94.6		
35202-78	S7	CF	03/10/93	03/10/93	1	1	1	10		7.94		79.4		
35202-79	S8	CF	03/09/93	03/09/93	1	1	1	1		77.1		77.1		
35202-80	S9	CF	03/09/93	03/09/93	1	1	1	10		7.27		72.7		
35202-81	S10	CF	03/10/93	03/10/93	1	1	1	1		0.69	<	1		
35224-89	S11	CF	03/09/93	03/09/93	1	1	1	10		17.9		179		
35224-90	S12	CF	03/09/93	03/09/93	1	1	1	10		15.5		155		
35202-91	S13	CF	03/09/93	03/09/93	1	1	1	10		20.4		204		
35224-92	S14	CF	03/09/93	03/09/93	1	1	1	10		45.3		453		
35224-93	S15	CF	03/09/93	03/09/93	1	1	1	10		11.3		113		
35224-94	S16	CF	03/09/93	03/09/93	1	1	1	10		38.2		382		
35224-95	S17	CF	03/09/93	03/09/93	1	1	1	10		14.2		142		
35224-96	S18	CF	03/09/93	03/09/93	1	1	1	10		32.1		321		
35224-98	S19	CF	03/09/93	03/09/93	1	1	1	10		21.6		216		
35224-99	S20	CF	03/09/93	03/09/93	1	1	1	1		0	<	1		
CCV	CCV										<	ERR	ERR	
CCV	CCV										<	ERR	ERR	
CCV	CCV										<	ERR	ERR	
CCV	CCV										<	ERR	ERR	

CF Verified

lr 3/16/93

APPENDIX D

DATA SUMMARIES FOR SWMUS OF CONCERN FOR GROUNDWATER

SUMMARY OF FINDINGS
SWMU #6 - DRMO STORAGE YARD (DRMO)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #6 - DRMO STORAGE YARD	
Target for Characterization	Contamination of soils and groundwater.
Objective	Delineate the nature and extent of contamination in soils and groundwater. Potential offshore impacts are being investigated under the offshore OU.
Source of Contamination	Leaching from temporarily stored refuse. The site has been in operation for more than 30 years. Refuse stored at the DRMO included lead and nickel-cadmium battery elements, motors, typewriters, paper products, and scrap metal.
Analytical Parameters	McLaren/Hart RFI (Phases I, II, III, IV, and IVA) Soils: Appendix IX Organics (volatiles, semivolatiles, pesticides/PCBs, herbicides) Priority Pollutant Metals TCL Organics (volatiles, semivolatiles, pesticides/PCBs) TAL Inorganics plus cyanide Other (pH, TOC, TPH, limited particle size analysis and sulfide) Groundwater: TCL Organics (volatiles, semivolatiles, pesticides/PCBs) Appendix IX organics (volatiles, semivolatiles, pesticides/PCBs, herbicides) TAL Inorganics plus cyanide Appendix IX Inorganics Priority Pollutant Metals RCRA 8 Metals Other (Petroleum ID) Sediments: TCL Organics (pesticides, PCBs) Priority Pollutant Metals Other (TPH) Halliburton NUS (Phase VI) Groundwater: Total Gasoline & Total Diesel (limited sampling) TCL Organics (volatiles, semivolatiles) TAL Inorganics Other (limited chloride, sulfate, alkalinity, tritium, salinity, and hexavalent chromium)

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #6 - DRMO STORAGE YARD (DRMO)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #6 - DRMO STORAGE YARD	
Nature of Contamination	A complete suite of analytes was included. Because the DRMO is outside of the CIA area, MPSs for Future Residential Land Use are applicable for soils and groundwater. For informational purposes, both Future Industrial Use and Future Residential Use are evaluated below: Soils (Future Residential Land Use): Numerous exceedences of lead (at approximately 500 times the residential MPS) occurred. Other metals occurred at lesser frequency and were of lesser concern. Similarly pesticides, PAHs, and BEHP sporadically exceeded the MPSs. TPH occurred frequently and at significant concentrations (up to 7500 mg/kg). Aroclor 1254 also occurred frequently at significant concentrations (up to 700 times the residential MPS). Volatile and semivolatile TICs were detected both inside the DRMO and at the Old Incinerator Area east of the DRMO. Soils (Future Industrial Land Use): Numerous exceedences of lead (up to 255 times the industrial MPS) and TPH (up to 7500 mg/kg in concentration) occurred with sporadic exceedences of PAHs at one location (less than 2 times the industrial MPS). TPH occurred frequently and at significant concentrations (up to 7500 mg/kg). Groundwater (Future Residential Use): The primary form of groundwater contamination is metals in the particulate (or possibly colloidal) form. Lead is the primary contaminant of concern. The measured concentration of several metals (total) exceeded residential MPSs by several orders of magnitude (lead at 3300 times the MPS, arsenic at 6 times, aluminum at 50 times, antimony at 100 times, cadmium at 11 times, chromium at 4 times, copper at 6 times, manganese at 18 times, nickel at 6 times and zinc slightly above the MPS). The maximum lead (total) concentration of 49,200 ug/l was observed at DW-02. The corresponding filtered concentration for lead of 213 ug/l was much lower. In general, total (particulate/colloidal) concentrations were higher and more prevalent than for filtered (dissolved) concentrations. Lead concentration in the bedrock well at DW-02 was present at 25.7 ug/l total (particulate/colloidal) concentration and no exceedences occurred for the corresponding filtered (dissolved) sample. In general, shallow wells were more highly contaminated and contained a greater quantity of contaminants than bedrock wells. Also of note, total lead concentrations east of the DRMO (Old Incinerator Area) are elevated (up to 440 times the MPS). An exceedence of DDD occurred once (at 10 times the residential MPS) and PCB exceedences occurred sporadically (at up to 260 times the MPS). One slight exceedence of the residential MPS for BEHP occurred in the old incinerator area. Petroleum ID fingerprinting occurred at 3 locations during the Phase IV investigation. Monitoring well DW-06 was nondetect. DW-02B indicated 1.6 mg/l of No. 6 Fuel Oil and DW-08 indicated No. 6 fuel oil (0.8 mg/l) and compressor oil (0.4 mg/l).

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #6 - DRMO STORAGE YARD (DRMO)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #6 - DRMO STORAGE YARD	
Extent of Contamination	Soils: Lead, Aroclor 1254, and TPH are the primary concerns. All of the DRMO appears to be impacted as well as areas west and east (Old Incinerator Area) of the DRMO. Lead contamination appears to decrease with depth. The vertical extent of metal contaminated soil ranges in thickness from 2 feet in the western portion of the DRMO to 38 feet by building 310 east of the DRMO. Lead concentrations in saturated soils have not been completely characterized. Groundwater: Groundwater within and surrounding the DRMO is contaminated, particularly with lead; this includes the Old Incinerator Area east of the DRMO. Monitoring wells slightly upgradient of the DRMO are contaminated as well, likely because of tidal effects.
Additional Sampling Needs	Low flow sampling techniques for groundwater is recommended to determine whether particulate metals are primarily in the particulate or colloidal form to aid in the evaluation of contaminant migration potential. Contaminant/flow modeling is also recommended. Additional sampling of saturated soils may be required depending on the selected alternative.

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GROUNDWATER SAMPLING ANALYTICAL PARAMETERS
DRMO SWMU #6
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	DW1	DW1B	DW2	DW2B	DW3	DW4	DW5	DW5 (DUP)	DW6	DW7	DW7 (DUP)	DW7B	DW7DB	DW8	DW8B	DW9	DW9 (DUP)	DW10B
Salinity	B/S	B	S	S	S	B	F/B	F/B	S	B/S	B/S	B	B	B	B	B/S	B/S	B/S
PHASE II																		
TCL Volatiles	X	NI	X	NI	X	X	X	X	X	X		NI		NI	NI	NI	NI	NI
TCL Pesticides/PCBs	X	NI	X	NI	X	X	X	X	X	X		NI		NI	NI	NI	NI	NI
Priority Pollutant Metals (Filtered)	X	NI	X	NI	X	X	X	X	X	X		NI		NI	NI	NI	NI	NI
PHASE III																		
TCL Volatiles,Semivolatiles & Pesticides/PCB					X	X	X		X					NI	NI	NI	NI	NI
TAL Inorganics plus cyanide (Total)					X	X	X		X					NI	NI	NI	NI	NI
TAL Inorganics (Filtered)					X	X	X		X					NI	NI	NI	NI	NI
Appendix IX Organics	X	X	*	X						X	X	X		NI	NI	NI	NI	NI
Appendix IX Inorganics (Total)	X	X	*	X						X	X	X		NI	NI	NI	NI	NI
Appendix IX Inorganics (Filtered)	X	X	*	X						X	X	X		NI	NI	NI	NI	NI
PHASE IV																		
TCL Volatiles,Semivolatiles & Pesticides/PCB	X	X	X	X	X	X	X		X	X		X		X	X	X	X	X
TAL Inorganics plus cyanide (Total)	X	X	X	X	X	X	X		X	X		X		X	X	X	X	X
TAL Inorganics (Filtered)	X	X	X	X	X	X	X		X	X		X		X	X	X	X	X
PHASE IVA																		
TCL Volatiles	X	X	X	X	X	X	X		X	X	X	X		X	X	X		X
TCL Pesticides/PCBs			X						X	X	X			X				
RCRA Metals (8) (Total)														X	X	X		X
RCRA Metals (8) (Filtered)	X	X	X	X	X	X	X		X	X	X	X		X	X	X		X
Petroleum ID				X					X					X				
PHASE VI																		
TCL Volatiles (plus Freon) & Semivolatiles										X		X	X					
TAL Inorganics (Total)										X		X	X					
TAL Inorganics (Filtered)										X		X	X					
Total Gasoline & Total Diesel										X		X	X					
Other (Chloride, Sulfate, Alkalinity, Tritium, Salinity, and Hexavalent Chromium)										X		X	X					

* - Not sampled due to ice blockage
NI- Not Installed. Note that wells installed in Phase I were sampled in Phase II.
Salinity Identifiers: F= Fresh; B= Brackish; S= Seawater

SUMMARY OF FINDINGS
SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)	
Target for Characterization	Contamination of soils and groundwater.
Objective	Delineate the nature and extent of contamination in soils and groundwater. Potential offshore impacts are being investigated under the offshore OU.
Source of Contamination	The landfill operated from approximately 1945 to 1978. The landfilled wastes included refuse; trash; construction rubble; incineration ash; plating sludges containing chromium, lead, and cadmium; asbestos insulation; TCE; methylene chloride; toluene; MEK; acetylene and chlorine gas cylinders; waste paints; solvents; spent sandblasting grit; reinforcing bars; chain-link fencing; and contaminated dredge spoils containing chromium, lead, small amounts of oil containing PCBs, mercury and possibly phenols.
Analytical Parameters	McLaren/Hart RFI (Phases I, II, III, IV, and IVA) Soils: Appendix IX Organics (volatiles, semivolatiles, pesticides/PCBs, herbicides) Priority Pollutant Metals TCL Organics (volatiles, semivolatiles, pesticides/PCBs) TAL Inorganics plus cyanide Other (pH, TOC, TPH, limited particle size analysis and sulfide) Groundwater: TCL Organics (volatiles, semivolatiles, pesticides/PCBs) Appendix IX organics (volatiles, semivolatiles, pesticides/PCBs, herbicides) TAL Inorganics plus cyanide Appendix IX Inorganics Priority Pollutant Metals RCRA 8 Metals Other (Petroleum ID) Sediments: Refer to Clark's Island Embayment data package Halliburton NUS (Phase VI) Groundwater: Total Gasoline & Total Diesel (limited sampling) TCL Organics (volatiles, semivolatiles) TAL Inorganics Other (limited chloride, sulfate, alkalinity, tritium, salinity, and hexavalent chromium)

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)	
Nature of Contamination	A complete suite of analytes was included. Because the JILF is outside of the CIA area, MPSs for Future Residential Land Use are applicable for soils and groundwater. For informational purposes, both Future Industrial Use and Future Residential Use are evaluated below: Soils (Future Residential Land Use): Contaminants exceeding MPSs included metals (lead at 12 times the residential MPS, mercury less than 2 times, beryllium at 4 times, zinc at 14 times, cadmium at 5 times, antimony at 4 times, copper at 16 times, and nickel at 2 times the residential MPS. PAHs (at up to 16 times the residential MPS) and Aroclor 1254 (at approximately 200 times the MPS) are also of concern. Volatile and semivolatile TICs were also present. Soils (Future Industrial Land Use): Several exceedences of lead (at approximately 6 times the industrial MPS). One slight exceedence of benzo(a)anthracene occurred. Groundwater (Future Residential Use): The primary form of groundwater contamination is metals in the particulate (or possibly colloidal) form. The measured concentration of several metals (total) exceeded residential MPSs by several orders of magnitude (lead at approximately 1200 times the MPS, arsenic at 8 times, aluminum at 125 times, antimony at 23 times, beryllium at 3 times, cadmium at 22 times, chromium at 20 times, copper at 86 times, manganese at 44 times, nickel at 18 times and zinc at 5 times the residential MPS). In general, total (particulate/colloidal) concentrations were higher and more prevalent than for filtered (dissolved) concentrations. Also, in general, shallow wells were more highly contaminated and contained a greater quantity of contaminants than bedrock wells. Of note, arsenic and manganese in soils did not exceed the soils MPS; other inorganics were present in both soils and groundwater. Mercury was present in SWMU #8 groundwater but an MPS was not developed for this analyte. Organics were sporadically detected: BEHP (up to 2 times the residential MPS), methylene chloride (up to 3 times the MPS), and benzene (up to 2 times the MPS), 4,4'-DDD (at 7.5 times the MPS) and Aroclor-1254 (at approximately 200 times the MPS). Organic contamination was generally present associated with SWMU #11 (Former Waste Oil Tanks) and the west corner of the JILF near Mercury Burial Site II. Petroleum hydrocarbon fingerprinting was conducted at 8 locations during the Phase IV investigation. Monitoring wells JW-07B, JW-12S, and JW13D indicated nondetects. No. 5 fuel oil (1.9 mg/l) was present at JW-14; No. 4 fuel oil existed at JW-15 and JW-16 (8.2 mg/l and 5.3 mg/l respectively); No. 6 fuel oil was also present at JW16 (14.0 mg/l); lube oil (1.2 mg/l) and compressor oil (1.8 mg/l) were present at JW-18; and gasoline (6.3 mg/l) occurred at JW-19. Of note, soil borings were limited. Based on known disposal of solvents, paints, etc., organics are expected to be present throughout the landfill, although not reflected by the previous investigations.

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #8 - JAMAICA ISLAND LANDFILL (JILF)	
Extent of Contamination	Soils: The entire landfill appears to be contaminated. Lateral extent of contamination is generally known but needs to be refined. Although soil borings were somewhat limited in quantity, the entire landfill appears to be contaminated based on the presence of groundwater contamination and the contents of fill material. Groundwater: Contaminants within the entire JILF, as well as areas upgradient and side-gradient of the JILF, have exceeded the residential MPSs.
Additional Sampling Needs	Low flow sampling techniques for groundwater is recommended to determine whether particulate metals are primarily in the particulate or colloidal form to aid in the evaluation of contaminant migration potential. Contaminant/flow modeling is also recommended. Additional recommended predesign work includes refinement of the lateral extent of contamination and predesign support for the cutoff wall (if selected), and pump testing, etc.

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GROUNDWATER SAMPLING ANALYTICAL PARAMETERS
JILF SWMU #8
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	JW3	JW4	JW4 DUP	JW5	JW6	JW7	JW7 DUP	JW7B	JW8	JW8B	JW9	JW9 DUP	JW9B	JW10	JW12S	JW12D	JW12B	JW13S	JW13B	JW13D	JW13DB
Salinity	F	F	F	B	F	F/B	F/B	F/B	F	F	B/S	B/S	F/B	S	S	S	B	S	B	S	B
PHASE II																					
TCL Volatiles, Semivolatiles and Pesticides/PCBs	X	X	-	X	X	X	-	NI	X	NI	X	X	NI	X	NI	NI	NI	NI	NI	NI	NI
TAL Inorganics (Filtered)	X	X	-	X	X	X	-	NI	X	NI	X	X	NI	X	NI	NI	NI	NI	NI	NI	NI
PHASE III																					
TCL Volatiles, Semivolatiles and Pesticides/PCBs	X*	X	X	X	X						X	-	NI	X*							
TAL Inorganics (Total)	X	X	X	X	X						X	-	NI	X							
TAL Inorganics (Filtered)	X	X	X	X	X						X	-	NI	X							
Appendix IX Volatiles, Semivolatiles, Herbicides & Pesticides/PCBs						X	-	X	X	X					X	X**	NI	X	NI	X**	NI
Appendix IX Inorganics (Total)						X	-	X	X	X					X		NI	X	NI		NI
Appendix IX Inorganics (Filtered)						X	-	X	X	X					X		NI	X	NI		NI
PHASE IV																					
TCL Volatiles, Semivolatiles & Pesticides/PCBs	X	X	-	X	X	X	-	X	X	X	X	-	X	X	X	X	X	X	X	X	NI
TAL Inorganics (Total)	X	X	-	X	X	X	-	X	X	X	X	-	X	X	X	X	X	X	X	X	NI
TAL Inorganics (Filtered)	X	X	-	X	X	X	-	X	X	X	X	-	X	X	X	X	X	X	X	X	NI
PHASE IVA																					
TCL Volatiles	X	X	-	X	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X	X	NI
RCRA Metals (8) (Total)													X		X				X	X	NI
RCRA Metals (8) (Filtered)				X	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X	X	NI
TCL Semivolatiles and Pesticides/PCBs	X	X	-																		
TAL Inorganics (Total)	X	X	-																		

Parameter	JW3	JW4	JW4 DUP	JW5	JW6	JW7	JW7 DUP	JW7B	JW8	JW8B	JW9	JW9 DUP	JW9B	JW10	JW12S	JW12D	JW12B	JW13S	JW13B	JW13D	JW13DB
Salinity	F	F	F	B	F	F/B	F/B	F/B	F	F	B/S	B/S	F/B	S	S	S	B	S	B	S	B
TAL Inorganics (Filtered)	X	X	-																		
Petroleum ID								X													
PHASE VI																					
TCL Volatiles (plus Freon) & Semivolatiles																		X	X	X	X
Total Gasoline & Total Diesel																		X	X	X	X
Other (Chloride, Sulfate, Alkalinity, Tritium, Salinity, and Hexavalent Chromium)																		X	X	X	X

GROUNDWATER SAMPLING ANALYTICAL PARAMETERS
JILF SWMU #8
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	JW14	JW14B	JW14B DUP	JW15	JW15 DUP	JW15B	JW16	JW16 DUP	JW16B	JW17B	JW17B DUP	JW18	JW18B	JW19	JW19B	GW1
Salinity	B	B	B	S	S	S	NTB	NT	F/B	B	B	B	B	B	B	NT
PHASE II																
TCL Volatiles Semivolatiles & Pesticides/PCBs	NI	-	NI	NI	-	NI	NI		NI	NI	-	NI	NI	NI	NI	NI
TAL Inorganics (Filtered)	NI	-	NI	NI	-	NI	NI		NI	NI	-	NI	NI	NI	NI	NI
PHASE III																
TCL Volatiles Semivolatiles & Pesticides/PCBs																
TAL Inorganics (Total)																
TAL Inorganics (Filtered)																
Appendix IX Volatiles Semivolatiles Herbicides & Pesticides/PCBs	X	X	X	X	X	X	NI	-	NI	NI	-	NI	NI	NI	NI	NI
Appendix IX Inorganics (Total)	X	X	X	X	X	X	NI	-	NI	NI	-	NI	NI	NI	NI	NI
Appendix IX Inorganics (Filtered)	X	X	X	X	X	X	NI	-	NI	NI	-	NI	NI	NI	NI	NI
PHASE IV																
TCL Volatiles Semivolatiles Pesticides/PCBs	X	-	X	X	-	X	X	X	X	X	-	X	NI	X	NI	X
TAL Inorganics (Total)	X	-	X	X	-	X	X	X	X	X	-	X	NI	X	NI	X
TAL Inorganics (Filtered)	X	-	X	X	-	X	X	X	X	X	-	X	NI	X	NI	X
PHASE IVA																
TCL Volatiles	X	-	X	X	-	X	X	-	X	X	X	X	X	X	X	X
RCRA Metals (8) (Total)							X	-	X	X	X	X		X		X
RCRA Metals (8) (Filtered)	X	-	X	X	-	X	X	-	X	X	X	X		X		X
TCL Semivolatiles & Pesticides/PCBs													X		X	
TAL Inorganics (Total)													X		X	

Parameter	JW14	JW14B	JW14B DUP	JW15	JW15 DUP	JW15B	JW16	JW16 DUP	JW16B	JW17B	JW17B DUP	JW18	JW18B	JW19	JW19B	GW1
Salinity	B	B	B	S	S	S	NTB	NT	F/B	B	B	B	B	B	B	NT
TAL Inorganics (Filtered)													X		X	
Petroleum ID				X			X					X		X		
PHASE VI																
TCL Volatiles (plus Freon) & Semivolatiles																
Total Gasoline & Total Diesel																
Other (Chloride, Sulfate, Alkalinity, Tritium, Salinity, and Hexavalent Chromium)																

NI - Not Installed

Salinity Identifiers F= Fresh B= Brackish S= Seawater NT= Not Tested

* - Analyzed for all TCL organics except for pesticides/PCBs

** - Analyzed for all Appendix IX parameters except herbicides and pesticides/PCBs

Monitoring wells installed in Phase I were analyzed in Phase II

SUMMARY OF FINDINGS
SWMU #9 - MERCURY BURIAL SITES (MBI AND MBII)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #9 - MERCURY BURIAL SITES (MBI AND MBII)	
Target for Characterization	Potential soils and groundwater contamination.
Objective	Determine whether mercury contaminated waste has escaped from the buried poured concrete blocks.
Source of Contamination	Poured concrete blocks and precast concrete pipes containing mercury contaminated wastes which were reportedly buried between 1973 and 1975 at two locations (MBI and MBII) in the JILF. The wastes at MBI include three concrete blocks and a concrete pipe containing mercury contaminated materials; reportedly such as rags and thermometers. The sealed concrete pipe was removed intact during the Phase VI investigation and is awaiting offsite disposal. The reported location of MBII is in the western portion of the JILF. However, MBII was not located during the either the McLaren/Hart RFI investigation or the Phase VI Halliburton NUS RFI Data Gap Field Work. Also, because several TICs were of concern near/upgradient of MBII, a direct push soil gas program was conducted during the HNUS RFI Data Gap Investigation (Phase VI). A plume was not indicated and so no additional monitoring wells were warranted.
Analytical Parameters	McLaren/Hart RFI (Phases I, II, III, IV and IVA) RFI Soils: Phase I - RCRA metals Phase II - TCL organics (volatiles, semivolatiles, pesticides/PCBs) TAL inorganics and cyanide Other (pH, TOC, selected particle size analysis & Atterberg limits) Groundwater: Phase I - RCRA Metals [filtered only] Phase II - TCL organics (volatiles, semivolatiles, pesticides/PCBs) TAL inorganics & cyanide [filtered only] Phase III and Phase IV - TCL organics (volatiles, semivolatiles, pesticides/PCBs) TAL inorganics [total & filtered] TAL cyanide [total only] Phase IVA - TCL organics (volatiles) RCRA Metals [filtered only] Other [petroleum ID for selected samples] HNUS RFI Data Gap (Phase VI) Phase VI - TAL mercury

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #9 - MERCURY BURIAL SITES (MBI AND MBII)
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #9 - MERCURY BURIAL SITES (MBI AND MBII)	
Nature of Contamination	A complete suite of analytes was included. Several volatile and semivolatile TICs are present in both soils and groundwater. Because SWMU #9 is outside of the CIA area, Media Protection Standards for Future Residential Use is applicable to soils and groundwater. For informational purposes, both Future Industrial Use and Future Residential Use are evaluated below: Soils (Future Residential Land Use): Mercury did not exceed the residential MPS at either MBI or MBII. MBI: Lead, beryllium and copper (at less than 2 times the residential MPS) were encountered. MBII: PAHs (at concentrations about 10 times the residential MPS) were encountered. Soils (Future Industrial Land Use): Mercury did not exceed the residential MPS at either MBI or MBII. MBII: PAHs (at less than 2 times the industrial MPS) were encountered. Groundwater (Future Residential Use): No MPS was developed for mercury. However, the maximum detection of total mercury was 1.5 ug/l at MW-02 (MBII), with a corresponding nondetect concentration for the filtered sample. This maximum concentration is below the final MCL for mercury of 2 ug/l. Petroleum ID results identified gasoline (49.4 mg/l) and lube oil (1.0 mg/l) in MW-3 and No. 4 fuel oil (1.1 mg/l) and No. 6 fuel oil (4.1 mg/l) in MW-7, which is consistent with the volatile and semivolatile compounds detected in the wells. MBI: Primary exceedences in all 3 wells were comprised of numerous inorganics (up to several orders of magnitude exceedences of residential MPSs). Inorganics were primarily present in the unfiltered form. Only single exceedences of benzo(a)anthracene, chrysene, benzene, and methylene chloride occurred and were of low concentrations. MBII: Primary exceedences in all 3 wells were comprised of numerous inorganics (up to several orders of magnitude exceedences of residential MPSs). Inorganics were primarily present in the unfiltered form. Benzene (at the MPS concentration); pesticides (4,4'-DDD and 4,4'-DDE at 1 order of magnitude above the MPS); PCBs (at up to 2 orders of magnitude exceedences of MPSs); and PAHs and BEHP (up to 30 times the MPS) were also present. Contamination is attributed to SWMU #8 rather than SWMU #9. No releases to date have occurred from the buried concrete blocks and the concrete pipe that were found at MBI. Although the soil sampling in the vicinity of MBI and MBII did not indicate mercury contamination, inorganic and organic contamination indicative of contamination found at the JILF was noted.
Extent of Contamination	Soils: Since the contamination appears to be related to JILF activities and not to the mercury burial sites, the extent of contamination is delineated as part of the SWMU #8 investigation. Groundwater: The contamination is delineated as part of the SWMU #8 investigation.
Additional Sampling Needs	No additional sampling is recommended.

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GROUNDWATER SAMPLING AND ANALYSIS SUMMARY (a)
SWMU #9 - MERCURY BURIAL SITES (MBI AND MBII)
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	MW2	MW2(DUP)	MW3	MW4	MW5	MW6	MW7
Salinity	F	F	F	F/B	F/B	F/B	F/B
Phase I							
RCRA Metals (8) (Filtered)	X	X	X	X	X	NI	NI
Phase II							
TCL Volatiles	X	X	X	X	X	NI	NI
TCL Semivolatiles	X	X	X	X	X	NI	NI
TCL Pesticides/PCBs	X	X	X	X	X	NI	NI
TAL Inorganics (Filtered)	X	X	X	X	X	NI	NI
Phase III							
TCL Volatiles	X		X	X	X	X	X
TCL Semivolatiles	X		X	X	X	X	X
TCL Pesticides/PCBs	X		X	X	X	X	X
TAL Inorganics (Total)	X		X	X	X	X	X
TAL Inorganics (Filtered)	X		X	X	X	X	X
Phase IV							
TCL Volatiles	X	X	X	X	X	X	X
TCL Semivolatiles	X	X	X	X	X	X	X
TCL Pesticides/PCBs	X	X	X	X	X	X	X
TAL Inorganics (Total)	X	X	X	X	X	X	X
TAL Inorganics (Filtered)	X	X	X	X	X	X	X
Phase IVA							
TCL Volatiles	X		X	X	X	X	X
RCRA Metals (8) (Filtered)	X		X	X	X	X	X
Petroleum ID			X				X

(a) Monitoring wells MW-4, MW-5, and MW-7 are associated with MBI
Monitoring wells MW-2, MW-3, and MW-6 are associated with MBII
NI Not Installed
Salinity Identifiers: F= Fresh; B= Brackish; S= Seawater

SUMMARY OF FINDINGS
SWMU #11 - FORMER WASTE OIL TANKS
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #11 - FORMER WASTE OIL TANKS	
Target for Characterization	Contamination of soils and groundwater.
Objective	Delineate the nature and extent of contamination in soils and groundwater.
Source of Contamination	Two former 8000 gallon underground steel tanks located at the northeastern end of the JILF were in operation from 1943 to 1989. Waste oils from facility shops including cooling, cutting oils, motor oils and transmission oils were stored in the tanks prior to offsite disposal. Degreaser solvents were also suspected to be stored in these tanks. In 1986 the tanks were tightness tested and found to be sound. The tanks were excavated and removed in 1989 according to state regulations and inspections. Soil contamination is believed to have occurred by occasional spillage during filling. Following tank removal, sampling was conducted by NSY Portsmouth and MEDEP. The main contaminant of concern at that time in soils was lead. As a result of the elevated levels of lead and other contaminants, 332 tons of soils were excavated and disposed in an offsite RCRA permitted land disposal facility. The soils excavation effort was terminated due to proximity to the JILF.
Analytical Parameters	McLaren/Hart RFI (Phase IV and IVA) Soils: Soil boring JSB-16 (from the source area) was sampled during Phase IV of the SWMU #8 investigation. Samples were collected from 2-4 foot depth and 7-9 foot depth and analyzed for TCL Organics (volatiles, semivolatiles, pesticides/PCBs), TAL Inorganics plus cyanide, and other parameters (pH and TOC). Groundwater: Monitoring wells JW-16 and JW-16B were sampled during Phase IV and IVA of the SWMU #8 investigation. Groundwater samples were analyzed for TCL Organics (volatiles, semivolatiles, pesticides/PCBs), TAL Inorganics plus cyanide (total and filtered), and RCRA 8 metals (total and filtered), and petroleum ID. HNUS RFI Data Gap (Phase VI) Soils: TCL Organics (volatiles plus Freon, semivolatiles, pesticides/PCBs) TAL Inorganics Groundwater: The new monitoring wells WOT-01 through WOT-06 were analyzed for: TCL Organics (volatiles plus Freon, semivolatiles, pesticides/PCBs) TAL Inorganics Other (Total Gasoline and Total Diesel)

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #11 - FORMER WASTE OIL TANKS
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #11 - FORMER WASTE OIL TANKS	
Nature of Contamination	A complete suite of analytes was included. Because SWMU #11 is outside of the CIA area, the Future Residential Use Media Protection Standards apply for both soils and groundwater. For informational purposes, evaluations for both Future Residential Use and Future Industrial Use are provided below: Soils (Future Residential Land Use): Exceedences of residential MPSs occurred for PAHs (present at up to 100 times the residential MPSs). In order of descending concentrations of PAHs were WOT-15, WOT-05, WOT-13, and WOT-09 which were in and around the source area. Sporadic exceedences occurred for inorganics (lead at less than 2 times the residential MPS, copper at up to 2 times, zinc at up to 4 times, and beryllium at up to 10 times the residential MPSs). TICs were present also, particularly for sample locations WOT-2, WOT-5, WOT-10, WOT-11, WOT-13, and WOT-15. In the area of the new Hazardous Waste Consolidation and Storage Facility, beryllium slightly exceeded the residential MPS; no detections of petroleum hydrocarbons were reported from the petroleum hydrocarbon scan. Soils (Future Industrial Land Use): Exceedences occurred only for PAHs at locations WOT-05 and WOT-15 (at concentrations up to 6 times the industrial MPS). Groundwater (Future Residential Use): Benzene was present at location JW-16 (at a concentration approximately 2 times the residential MPS). Manganese exceedences occurred consistently (at up to 13 times the residential MPS). Other inorganics were sporadically present at concentrations of concern (cadmium slightly above the residential MPS, lead up to 15 times, and aluminum at 4 times the residential MPS). Of note, the maximum detection of manganese occurred upgradient of SWMU #11. TICs were present predominantly in monitoring wells WOT-02, WOT-03, WOT-04, and WOT-05. Although diesel fuel (dissolved) was detected in groundwater at significant concentrations, free product was not encountered.
Extent of Contamination	Soils: The extent of soil contamination has been defined. The subsurface soil investigation of the Hazardous Waste Consolidation and Storage Facility, conducted by C.T. Male Associates in June of 1994, indicates that subsurface soils are not at concentrations of concern in this area. Groundwater: The extent of groundwater contamination, except for potential upgradient contributions, has been defined. Note that PAH contamination in groundwater is limited to WOT-02 and WOT-03, with no exceedences of groundwater MPSs at these locations. This indicates that PAHs are adsorbing to soils and not significantly impacting groundwater.
Additional Sampling Needs	No additional sampling is recommended.

ROUGH DRAFT

GROUNDWATER SAMPLING AND ANALYSIS SUMMARY (a)
SWMU #11 - FORMER WASTE OIL STORAGE TANKS
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	WOT-01	WOT-02	WOT-03	WOT-04	WOT-05	WOT-O6
Salinity	F	F	F	F	F	F
Phase VI (a)						
TCL Volatile Organics (plus Freon)	X	X	X	X	X	X
TCL Semivolatile Organics	X	X	X	X	X	X
TCL Pesticides/PCBs	X	X	X	X	X	X
TAL Inorganics (Total)	X	X	X	X	X	X
TAL Inorganics (Filtered)	X	X	X	X	X	X
Total Gasoline	X	X	X	X	X	X
Total Diesel	X	X	X	X	X	X

(a) In addition to the described sampling program, monitoring JW-16 and JW-16B were installed during Phase IV of the McLaren/Hart RFI investigation of SWMU #8 (JILF). Samples from these two wells were analyzed for TCL volatiles, semivolatiles, pesticides/PCBs, TAL inorganics (total and filtered), and RCRA Metals (8).

Salinity Identifiers: F= Fresh; B= Brackish; S= Seawater

SUMMARY OF FINDINGS
SWMU #27 - FUEL OIL SPILLAGE AREA
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #27 - FUEL OIL SPILLAGE AREA	
Target for Characterization	Fuel oil contamination of soils and groundwater
Objective for Investigation Effort	Delineate the nature and extent of contamination in soils and groundwater.
Source of Contamination	Release from a ruptured underground pipeline (reportedly located 6 ft below ground surface parallel to and along Berth 6) containing No. 6 Fuel Oil. The leak was detected in 1978.
Analytical Parameters	McLaren/Hart RFI Soils: TCL Organics (PAHs, volatiles, semivolatiles, pesticides/PCBs) TAL Inorganics and cyanide Other (limited TPH, TOC, hydrocarbon fingerprinting, particle size analysis, Atterberg limits) Groundwater: TCL Organics (volatiles, semivolatiles, pesticides/PCBs) TAL Inorganics plus cyanide RCRA Metals (8) Other (limited Petroleum ID) Sediments: TCL Pesticides/PCBs Other (TPH, TOC) Outfalls: TCL Organics (volatiles, semivolatiles, pesticides/PCBs) TAL Inorganics plus cyanide

ROUGH DRAFT

SUMMARY OF FINDINGS
SWMU #27 - FUEL OIL SPILLAGE AREA
NSY PORTSMOUTH, KITTERY, MAINE

SWMU #27 - FUEL OIL SPILLAGE AREA	
Nature of Contamination	A sufficient suite of analytes was included. Because SWMU #27 is inside the CIA area, MPSs for Future Industrial Land Use are applicable for soils; groundwater would not be used for industrial purposes. For groundwater, MPSs are only available for future residential use. For informational purposes, both Future Industrial Use and Future Residential Use are evaluated below: Soils (Future Residential Land Use): There were sporadic, slight exceedences (less than 2 times) of MPSs for lead, zinc, cadmium, and benzo(a)anthracene. Elevated TPH concentrations exceeding 100 mg/kg were detected at several sampling locations, with the maximum TPH concentration at approximately 40 times the guidance level. Finger Printing of two soil samples (FSB-5 and FSB-6) classified petroleum hydrocarbons as partly weathered diesel fuel oil. Soils (Future Industrial Land Use): There were no exceedances of industrial MPSs. Refer to the TPH discussion above on Future Residential Land Use. Groundwater (Future Residential Use): McLaren/Hart RFI - There were isolated exceedances of MPSs for numerous metals including arsenic, aluminum, cadmium, chromium, lead, manganese, copper, and beryllium. Inorganics were primarily detected in the particulate, or possibly colloidal, form. It is uncertain whether these constituents are site related since SWMU #27 soils were not of significant concern associated with metals. Also, the maximum concentrations of metals were consistently located in monitoring wells FW-05 and FW-06 which are cross-gradient of the site. No TPH analysis was performed. GC Fingerprinting (For FW-06 only) indicated the presence of No. 4 fuel oil (4.8 mg/l) and lube oil (2.9 mg/l). In support of the GC Fingerprinting, semivolatile TICs were encountered in FW-06. Free product, depth not identified, was observed in monitoring wells FW-02 and FW-06. Sterns & Wheler - TPH analysis was performed for samples in wells FW-04 (non detect) and FW-06 (5.0 mg/l).
Extent of Contamination	Soils: The saturated zone is present at 5 to 6 feet below the ground surface. Full lateral and vertical extent of contamination (i.e., TPH exceeding 100 mg/kg) was not delineated. The entire area of Berth 6 is suspected to be contaminated with TPH. Groundwater: The source of the contamination was not identified but is not believed to solely be from the SWMU #27 fuel spill. Lateral and vertical extent of TPH groundwater contamination was not delineated during RFI but was further refined during the Oil Terminal Investigation by Sterns & Wheler.
Additional Sampling Needs	Source of metals contamination in groundwater, which probably is not site-related, needs to be determined.

ROUGH DRAFT

GROUNDWATER SAMPLING ANALYTICAL PARAMETERS
FUEL OIL SPILLAGE AREA (SWMU #27)
NSY PORTSMOUTH, KITTERY, MAINE

Parameter	Groundwater							Outfalls
	FW1	FW2	FW3	FW4	FW5	FW6	FW6 (DUP)	OF-1 OF-2
Salinity	B/S	S	S	S	S	NA	NA	—
PHASE I								
No Analysis	NI	NI	NI	NI	NI	NI	NI	
PHASE II								
No Analysis	NI	NI	NI	NI	NI	NI	NI	
PHASE III								
No Analysis	NI	NI	NI	NI	NI	NI	NI	
PHASE IV								
TCL Volatile Organics	X	X	X	X	X	X	X	X
TCL Semivolatile Organics	X	X	X	X	X	X	X	X
TCL Pesticides/PCBs	X	X	X	X	X	X	X	X
TAL Inorganics (Total) plus cyanide	X	X	X	X	X	X	X	X
TAL Inorganics (Dissolved)	X	X	X	X	X			
PHASE IVA								
TCL Volatiles	X	X	X	X	X	X		
RCRA Metals (8) (Total)	X	X	X	X	X	X		
RCRA Metals (8) (Dissolved)	X	X	X	X	X	X		
Petroleum ID						X		

NI - Not Installed
Salinity Identifiers: F= Fresh; B= Brackish; S= Seawater

APPENDIX E

HEALTH AND SAFETY PLAN

TO: Linda Klink (PM CTO 0148)

cc: Mark Perry
Mark Mengel
Stan Conti
Tim Evans

FROM: Matt Soltis (CLEAN Health and Safety Manager)

SUBJECT: CTO 0148 Health and Safety Plan Addendum Portsmouth Naval Shipyard - Safe Work Permits

The addition of a Safe Work Permit is intended to incorporate safe work requirements/restrictions for exclusion zone, contamination reduction zone, and general support activities has been added to the Draft HASP of CTO 0148. The catalyst for this action was based on the fact that the Rough Draft HASP had no reference, hazard assessment, safety controls for the activities including well pad demolition, reconstruction, and the conversion of stick-up wells to flush mounts. The inclusion of the Safe Work Permit will allow us to address suitable safety control measures to ensure the safety of those individuals performing those tasks and also to document our actions.

10.5 SAFE WORK PERMITS

In order to incorporate site-specific conditions into the PPE selections and safety control measures identified by this HASP, the use of a Safe Work Permit has been included for use as part of this HASP. This action will incorporate all Exclusion Zone, Contaminated Reduction Zone, and general support activities conducted in support of this project. This HASP will serve as a reference guide for completing the permit and the Safe Work Permits will serve to direct and guide field crews concerning PPE selections and safety control measures on a task-by-task basis. An example of the Safe Work Permit as it is to be used is illustrated in Figure 10-1.

All permits will be issued by the SSO or his/her on-site representative in the morning prior to the commencement of on-site activities.

All personnel identified on the permit as participating in the identified task will be made aware of the contents of the Safe Work Permit by the supervisor accepting the permit. Any problems which occurred throughout the completion of the task regarding the contents of the permit will be documented on the permit.

All permits will be returned to the SSO or his/her on-site representative at the end of each day.

FIGURE 10-1
SAFE WORK PERMIT

Permit No. _____ Date: _____ Time: From _____ to _____

SECTION I: General Job Scope (To be filled in by person performing work)

I. Work limited to the following (description, area, equipment used): Monitoring well repair to include demolition of existing concrete pads, the conversion of several stick-up type wells to flush mount vault boxes, replacing the pads with new concrete.

II. Names: _____

III. Onsite Inspection conducted ☒ Yes ☐ No Initials of Inspector _____ B&RE _____ PNS

SECTION II: General Safety Requirements (To be filled in by permit issuer)

IV. Protective equipment required

Level D ☒ Level B ☐
Level C ☐ Level A ☐
Detailed on Reverse

Respiratory equipment required

Full face APR ☐
Half face APR ☐
SKA-PAC SAR ☐
Skid Rig ☐

Escape Pack ☐
SCBA ☐
Bottle Trailer ☐
None ☒

Modifications/Exceptions: Minimum Level D requirements as stipulated in Section II, Item IV.

V.

Chemicals of Concern	Action Level(s)	Response Measures
Total Dust	5 mg/m^3	Apply water to control dust
Respirable Dust	3 mg/m^3	Apply water to control dust

VI. Additional Safety Equipment/Procedures

Hardhat	☐ Yes	☒ No	Hearing Protection (Plugs/Muffs)	☒ Yes	☐ No
Safety Glasses	☒ Yes	☐ No	Safety belt/harness	☐ Yes	☒ No
Chemical/splash goggles	☐ Yes	☒ No	Radio	☐ Yes	☒ No
Splash Shield	☐ Yes	☒ No	Barricades	☐ Yes	☒ No
Splash suite/coveralls	☐ Yes	☒ No	Gloves (Type- Leather work)	☒ Yes	☐ No
Steel toe/shank Workboots	☒ Yes	☐ No	Work/rest regimen	☐ Yes	☒ No

Modifications/Exceptions: _____

VII. Procedure review with permit acceptors

	Yes	NA		Yes	NA
Safety shower/eyewash (Location & Use)	☐	☒	Emergency alarms	☒	☐
Procedure for safe job completion per HASP	☐	☒	Evacuation routes	☒	☐
Contractor tools/equipment inspected	☒	☐	Assembly points	☒	☐

VII. Equipment Preparation

	Yes	NA
Equipment drained/depressured	☐	☒
Equipment purged/cleaned	☐	☒
Isolation checklist completed	☐	☒
Electrical lockout required/field switch tested	☐	☒
Blinds/misalignments/blocks & bleeds in place	☐	☒
Hazardous materials on walls/behind liners considered	☐	☒

VIII. Additional Permits required (Hot work, Confined Space Entry, Excavation etc.). ☐ Yes ☒ No
If yes, contact the Health Sciences Department

IX. Special instructions, precautions: Associated hazards for this task includes noise, pressurized system, flying projectiles, pinch & compression hazards, and whole body vibration. The above selected PPE and safety control measures identified within this permit are intended to protect individuals associated with this task from those hazards.

Permit Issued by: _____ Permit Accepted by: _____
Job Completed by: _____ Date: _____

GROUNDWATER MONITORING AND INVESTIGATION HEALTH AND SAFETY (HASP)

COMPREHENSIVE LONG-TERM ENVIRONMENTAL ACTION NAVY (CLEAN) PROGRAM

PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

SUBMITTED TO:
NORTHERN DIVISION, ENVIRONMENTAL BRANCH, CODE 18
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY, MAIL STOP #82
LESTER, PENNSYLVANIA 19113-2090

SUBMITTED BY:
BROWN & ROOT ENVIRONMENTAL

CONTRACT NUMBER N62472-90-D-1298

CONTRACT TASK ORDER 0148

NOVEMBER 1996

APPROVED BY:

Linda E. Klink

LINDA E. KLINK
PROJECT MANAGER
BROWN & ROOT ENVIRONMENTAL
PITTSBURGH, PENNSYLVANIA

APPROVED FOR SUBMISSION BY:

for MMS

MATTHEW M. SOLTIS, CIH, CSP
CLEAN HEALTH & SAFETY MANAGER
BROWN & ROOT ENVIRONMENTAL
PITTSBURGH, PENNSYLVANIA

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ATTACHMENT II - OSHA POSTER

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1.0 INTRODUCTION AND ORGANIZATION

1.1 PURPOSE

The purpose of this Health and Safety Plan (HASP) is to provide for the protection of personnel performing activities planned, specifically groundwater monitoring and investigation and seep sampling at the Portsmouth Naval Shipyard site. This HASP specifies personnel responsibilities and restrictions, establishes requirements (such as the use of personal protective equipment, adherence to standard work practices, etc.), and the use of evaluation techniques that will be utilized (such as the use of real-time monitoring instrumentation) throughout the planned site activities.

This HASP has been prepared to satisfy the requirements of applicable OSHA standards, most specifically standard 29 CFR §1910.120, entitled "Hazardous Waste Operations and Emergency Response". This HASP has been developed based on available information regarding potential chemical and physical hazards which may be encountered by field personnel during the performance of the planned site activities. If additional or revised information becomes available, this HASP will be modified accordingly. It is the responsibility of the Brown & Root Environmental Project Manager to communicate any such information to the CLEAN Health and Safety Manager (HSM), Matthew M. Soltis, CIH, CSP, who will determine any HASP modification needs.

1.2 KEY PROJECT PERSONNEL AND ORGANIZATION

Key project personnel and their associated project positions (responsibilities), including identifying safety and health responsibilities are identified in Figure 1-1. The Brown & Root Environmental Project Manager (PM) has overall responsibility for the direction and implementation of health and safety for this project. The Brown & Root Environmental Field Team Leader (FTL) is responsible for the implementation of this HASP, with technical assistance and support from the Site Safety Officer (SSO). The SSO is the individual assigned the responsibility of overseeing the implementation of this HASP throughout all site activities, and is a member of the onsite field team. The Project Health and Safety Officer is a member of the Brown & Root Environmental Health Sciences staff, and is the primary contact for technical health and safety support for this project. The CLEAN HSM is responsible for providing health and safety technical oversight, review and approval duties for all CLEAN projects, and for monitoring compliance with this HASP and the CLEAN Health and Safety Management Plan.

FIGURE 1-1

KEY PROJECT PERSONNEL AND RESPONSIBILITIES

NAME	RESPONSIBILITY
Mark Perry	Project Manager
TBD	Field Team Leader
Thomas Dickson, ASP	Project Health and Safety Officer (HSO)
TBD	Site Safety Officer (SSO)
TBD	Field Technicians/Geologists
Matthew M. Soltis, CIH, CSP	CLEAN Health and Safety Manager (HSM)

TBD: To be determined. Assignments have not yet been made.

1.3 SITE BACKGROUND

A detailed discussion of the history and background of the Portsmouth Naval Shipyard, and of the individual site areas where groundwater monitoring and investigation work activities are planned to be performed under this project, is presented herein in a previous section of the Work Plan, and is not repeated here. Discussion of seep sampling work activities is provided in the Technical Memorandum on Seep Sampling for Portsmouth Naval Shipyard (Brown & Root Environmental, March 1996, currently being revised April 1996).

2.0 SCOPE OF WORK

Detailed discussions on the planned activities, methods, and equipment for the groundwater monitoring and investigation effort are presented in previous sections of the Work Plan. The primary action to be carried out as part of this scope is summarized in this section. In addition, seep sampling activities, discussed in detail in the Technical Memorandum on Seep Sampling (Brown & Root Environmental, scheduled for release in May 1996) are summarized in this section.

These tasks are considered the basis for identifying potential hazards that may be posed to site personnel in their performance. The results of those considerations are presented in the Risk Assessment section (Section 3.0) of this HASP. Additionally, necessary evaluation and control efforts for those identified potential hazards are also contained in various sections of this HASP.

Groundwater Monitoring and Investigation

The purpose of this Groundwater Investigation and Monitoring Plan is to facilitate the implementation of a cost effective, long-term groundwater monitoring program for sites of concern at NSY Portsmouth. The data will be used to determine the site's impact on the quality of groundwater in the aquifer and impact on State waters.

To meet this objective, a pilot study to evaluate the effects of low-flow purging on field monitored groundwater quality parameters, followed by two rounds of sampling will initially be conducted. All 70 existing RFI and RFI Data Gap monitoring wells, plus one monitoring well from the Stearns & Wheler investigation (Stearns & Wheler 1994) will be sampled as part of this effort.

Seep water emanating from the PNS will be sampled to evaluate potential transport of contaminants to the estuary. Seeps are rivulets of water emerging from the shoreline of Seavey Island identified in Phase II of the Ecological Risk Assessment (ERA) conducted by the Navy for the PNS. Some seeps are fresh water and some are a mixture of fresh and saline water. Their sources may be fresh water that is coming through the Jamaica Island Landfill or tidal water that is forced into the landfill at high tide and drains back into the estuary at low tide. In either case, seeps represent a potential contaminant pathway to the estuary.

Seeps will be sampled to establish trends in the concentration of metals and organic contaminants in the water. Seeps will be sampled under periods of high and low seep flow in order to determine if the seeps constitute a significant pathway of contaminant transport to the estuary. If seep sampling requires the use of a small boat appropriate safety equipment and flotation devices will be employed.

3.0 RISK ASSESSMENT

This section of this HASP presents information regarding the known and suspected chemical and physical hazards which may be encountered in, or associated with, the planned activities, schedules, and work areas as described in this HASP. This assessment is based on the information available at the time of the preparation of this HASP. If new or revised information becomes available, it will be promptly reviewed to determine any needs to modify this risk assessment.

The potential hazards recognized for the planned site activities are summarized and presented (by task) in Section 3.1 of this HASP. In general, these potential hazards include personnel exposure to site contaminants via inhalation (gas/vapor form), dermal contact, and (to a much lesser extent) ingestion. Other hazards include those of a physical nature. Each of two categories, chemical hazards and physical hazards, is presented in later subsections of this risk assessment discussion.

3.1 TASK-SPECIFIC RISK ASSESSMENT

In accordance with the requirements of OSHA standard 29 CFR 1910.120 (b) (4) (A), a task-specific risk assessment for the planned activities is as follows:

Groundwater Monitoring Pilot Study and Investigations

Numerous groundwater monitoring wells, both deep and shallow, are planned to be monitored and sampled at several site areas as identified within the groundwater monitoring plan.

This task presents minimal hazard potentials as it is nonintrusive in nature.

As stated earlier, exposure to site contaminants during this activity is anticipated to be minimal. The predominant hazard for this task is associated with working near water or from small boats. All samples collected from a boat or by persons wading in water will require the use of U.S. Coast Guard approved life vest or other applicable floatation devices and life-lines. In addition, all work is to be conducted using the "buddy system". No site activities will be performed in the absence of another individual.

3.2 CHEMICAL HAZARDS

The chemical contaminants which may be present and encountered in the performance of site activities have been identified based on information such as the histories of the site areas, and the results of previous investigatory activities. Information regarding these substances is presented in Table 3-1.

The potential for worker exposure to hazardous concentrations of site chemical contaminants is generally considered to be low. This assumption is based on overall levels identified within the groundwater media and the method of extraction. It is considered that the low-flow purge and sample method is less likely to mobilize contaminants into the air presenting an inhalation threat through this less aggressive sample acquisition method.

For seep sampling, workers have the potential to come in contact with seep water that may be contaminated with various metals, PCBs, and several different insecticides and pesticides. The potential for worker exposure to hazardous concentrations is site contaminants is generally considered low.

3.3 PHYSICAL HAZARDS

Certain physical hazards may also be presented to site personnel involved with field activities. These may be intrinsic to the nature of the operation being performed, or the result of factors such as the work location or schedule. These potential risks include the following:

- Uneven or unstable terrain (Slip/trip hazards) and fall from elevated surfaces
- Strain/muscle pulls from manual lifting.
- Pinch/compression Points
- Water hazards
- Inclement weather
- Natural hazards (e.g. snakes, ticks, mosquitos, poisonous plants, etc.)

Each of the above mentioned items are further detailed below.

3.3.1 <u>Uneven/Unstable Terrain and Fall from Elevated Surfaces</u>

Planned activities described in the scope of work for this remedial action will bring field personnel into areas where this potential hazard exists. It will be the FTL's responsibility to inspect the work areas, and implement necessary controls or restrictions prior to placing heavy equipment or personnel at risk. As planned activities move from one area to another, this hazard (and others associated with that area or task) will be discussed as part of the safety briefing prior to the commencement of activities.

3.3.2 Strain/Muscle Pulls

The potential exists for workers to be injured while lifting or maneuvering cumbersome and/or heavy objects during the execution of this groundwater monitoring plan. During labor intensive activities such as loading/hanging pumps, workers have the potential to over-exert themselves. In addition, various tasks may require lifting heavy pieces of equipment. If objects are improperly lifted, debilitating back strain and/or other injuries can result. Workers shall obtain help from others when necessary, employ proper lifting techniques, and use machinery, where possible, to assist when handling heavy objects.

3.3.3 Pinch/Compression Points

Pinch and compression points of sampling equipment may result in injury. All equipment must be maintained in proper working order, with machine guarding devices in place. Any equipment found to be lacking in these areas shall be removed from service. Additionally, all personnel shall be properly trained in the use and function of all equipment used within the investigating activity.

3.3.4 Water Hazards

Several of the planned activities involve locations that are near bodies of water. To avoid potential hazards associated with working on or over water (drowning) the field team shall employ lifelines, safety harnesses, and U.S. Coast Guard approved personal flotation devices and lifeline (tie-off) procedures will be used when working within two feet of the waters edge. Due to the obvious hazards associated with working on or near waters edge during inclement weather, all field activities may be temporarily suspended or terminated at the discretion and direction of the FTL, or SSO representative.

3.3.5 Inclement Weather

As all work will be conducted outdoors, inclement weather may be encountered. As conditions may vary, it will be at the discretion of the FTL and the SSO representative to temporarily suspend or terminate activities as conditions dictate. All activities will be terminated in the advent of electrical storms.

3.3.6 Natural Hazards (ticks, snakes, and other indigenous creatures)

Natural hazards such as poisonous plants, bites from poisonous or disease carrying animals or insects (e.g. snakes, ticks, mosquitos) cannot be avoided in this type of environment. However in an effort to offset the impact of this hazard, field personnel will have access to commercially available snake bite kits

and insect repellents. Potential nesting areas in and about work areas shall be avoided to the greatest extent possible. Lastly, within recent years a marked increase in Lyme's Disease has been reported. Ticks have been shown to be the primary vector in the transmission of this disease. In an effort to control this hazard, close attention will be given during operations and decontamination with regard to personal hygiene to detect and remove any ticks from personnel. The information provided in Attachment I will be reviewed with site personnel to aid in the recognition and control of this threat.

3.4 GENERAL REQUIREMENTS

- Head protection (hard hats) will be required whenever and wherever potential overhead hazards are recognized, including when in the vicinity of any operating heavy machinery

- Loose items of clothing will be secured when working around items of moving machinery. Also, personal items such as jewelry which can become caught or entangled will be prohibited around such operations.

- Electrical cords (such as on hand tools or electrical extension cords) shall be inspected prior to being put in use, and periodically thereafter. Also, these devices will be used and stored in a manner that protects them from damage. Cords found to be defective (i.e. plug damaged, ground prong removed, insulation damaged, etc.) will be immediately removed from service and either effectively repaired or replaced.

- Eye protection will be required wherever potential eye hazards are recognized.

- Any use or storage of compressed gas cylinders on site will be will be done in a manner that complies with applicable OSHA standards and Compressed Gas Association specifications. This includes (but is not limited to) proper labeling of container contents, marking and segregating containers as "full" or "empty", securing in an upright position, placing valve end caps in place when cylinders are not in use, etc.

- Incidents of inclement weather will be evaluated by the FTL, with input from the SSO, in regard to limiting or interrupting site operations. At a minimum, however, site operations will be interrupted in the event of electrical storms.

- The "buddy system" will be required throughout all onsite operations, intrusive and nonintrusive.

TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
1,1 Dichloroethene See also vinylidene chloride	75-34-4	Ionization potential = 10.00 Relative response ratio for detection with the FID is 40%.	Air sample using a charcoal filter tube; carbon disulfide desorption; GC/FID Detection using NIOSH Method # 1015	ACGIH TLV-TWA 5 ppm, STEL 20 ppm NIOSH & OSHA have not established exposure limits	An air purifying respirator equipped with a organic vapors filter is acceptable for escape purposes only. For exposures greater than the recommended exposures limits should employ supplied air respirators. Odor threshold - 190 ppm **Recommeded glove:** Butyl, nitrile, or neoprene	**Boiling Pt:** 89°F; 32°C **Melting Pt:** -188°F;-122°C **Solubility:** Slight (0.04%) **Flash Pt:** -2°F; -19°C **LEL/LFL:** 6.5% **UEL/UFL:** 15.5% **Vapor Density:** 3.25 **Vapor Pressure:** 500 mmHg @ 68°F; 20°C **Specific Gravity:** 1.21 @ 20°F; 4°C **Incompatibilities:** Aluminum, air, copper, and heat. Polymerization may occur if exposed to oxidizers **Appearance and Odor:** Colorless liquid with a slight sweet chloroform odor.	Overexposure to this substance may result in irritation to the eyes, nose, throat, and respiratory system. Dermal contact with concentrated solutions may cause slight irritation, redness and inflammation. Systemically, headaches, dizziness, nausea, and difficulty in breathing. Chronic effects may include kidney and liver dysfunction, and pnuemonitis. This material has expressed cancer causing potential in laboratory animals including liver and kidney tumors.
Acetylene	74-86-2	Not determined; Excellent response	Air sampling not applicable	OSHA and ACGIH do not have established limits for acetylene. NIOSH has proposed a limit of 2,500 ppm for common impurities.	Warning property acceptable (for commercial grades - which are the likely grades involved).	**Boiling point:** -75°F **Specific Gravity:** 0.91 **Solubility:** 1.1 @ 15 C **Flash Point:** Gaseous at room temperature **LEL:** 2.5% (explosive) **UEL:** 81% **Appearance and odor:** Colorless, odorless gas when pure, commercial grades have a garlic-like odor from impurities.	A simple asphyxiant. Exposure to high concentrations may result in narcosis. At 20% concentration: dyspnea and headache. At 40% or higher concentrations: collapse.
Aldrin	309-00-2	I.P. Unknown PID will not detect this substance FID will not detect this substance	Sample using a glass fiber, binder free filter with a midget impinger. Analyze with Gas Chromatography - electrolytic conductivity detector in accordance with NIOSH method 5502	OSHA 0.25 mg/m^3 NIOSH 0.25 mg/m^3 (skin) ACGIH 0.25 mg/m^3 (skin)	An air purifying respirator equipped with a combination filter for organic vapors, pesticides, and High Efficiency Particulate Air (HEPA) filter is acceptble. **Recommeded glove:** Nitrile or neoprene gloves are adequate for protection against contact with the skin.	**Boiling Pt:** Decomposes **Melting Pt:** 219°F; 104°C **Solubility:** 0.003% **Flash Pt:** Not available **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** Not available **Vapor Pressure:** 0.00008 mmHg **Specific Gravity:** 1.60 **Incompatibilities:** Concentrated minieral acids, active metals, acid catalysts, acid oxidizing agents, phenol. **Appearance and Odor:** Colorless to dark-brown crystalline solid with a mild chemical odor.	Exposure to aldrin may result in the following symptoms: headache, dizziness, nausea, vomiting, tonic convulsions, myclonic jerks of the limbs, malaise (vague feeling of discomfort), hematuria (blood in the urine), and coma. Aldrin also is known to have carcinogenic properties. Target organs include. Central Nervous System (CNS), liver, kidneys, and skin.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Aroclor-1260 (Polychlorinated Biphenyl, PCB) It should be noted that this substance is representative of the more common isomers Aroclor - 1242, 1254, which may be encountered.	11096-82-5 53469-21-9 (42%) 11097-69-1 (54%)	Substance is not volatile (VP=0.00006 mmHg), no I.P. exists, therefore PID will not detect substance. Substance is non combustible and as a result will not be detected by FID	Air sample using a particulate filter, Florisil sorbent tube with glass fiber filter. Hexane desorption and gas chromatography-electron capture detector. NIOSH 5503 (PCBs)	OSHA & ACGIH 0.5 mg/m^3 TWA (skin) NIOSH 0.001 mg/m^3 REL IDLH 5 mg/m^3	Inadequate - However due to the low volatility it is assumed unless agitated this substance does not present a volatile vapor or gas respiratory threat. For dusty conditions where this material may cling to particulates, use a HEPA filter APRs are approved for escape only when concentrations exceed the exposure limits. Concentrations greater than the exposure limits require PAPR or supplied air respirators. **Recommended glove:** Butyl rubber >24 hrs; Neoprene rubber >24.00 hrs; Silver shield or Viton (for pure product).	**Boiling Pt:** distillation range 689- 734°F; 365-390°C **Melting Pt:** -2 to 50°F; -19 to 10°C **Solubility:** Insoluble **Flash Pt:** Not applicable **LEL/LFL:** Not applicable **UEL/UFL:** Not applicable Nonflammable liquid, however, exposure to fire results in black soot containing PCBs, dibenzofurans, & chlorinated dibenzo-p-dioxins **Vapor Density:** N.A. **Vapor Pressure:** 0.00006 - 0.001 mmHg **Specific Gravity:** 1.566 @ 60°F; 15.5°C **Incompatibilities:** Strong oxidizers **Appearance and Odor:** Colorless to pale yellow, viscous liquid or solid (Aroclor 54 below 50°F) with a mild, hydrocarbon odor	This substance is irritating to the eyes and skin. Chronic effects of overexposure may include potential to cause liver damage, chloracne, and reproductive effects. Recognized as possessing carcinogenic properties by NIOSH, and NTP.
Arsenic	7440-38-2	Particulate form - This substance is unable to be detected by PID/FID	NIOSH Method #7900 or Method #7300	OSHA Organic compounds 0.5 mg/m^3 Inorganic compounds 0.01 mg/m^3 NIOSH ceiling 0.002 mg/m^3 ACGIH 0.2 mg/m^3	No identifiable warning properties to indicate presence and thereby detection **Recommended APR Cartridge:** Suitable for dust and fume. Organic vapor acid gases with HEPA filter. This substance may be presented as a pesticide, therefore a cartridge suitable for pesticides (MSA-GMP) **Recommended Gloves:** This is in the particulate form. Therefore any glove suitable to prevent skin contact (Nitrile has been the one most widely used for the other substances).	**Boiling Pt:** sublimation @ 612°C **Melting Pt:** 814°C @ 36 atm **Solubility:** Insoluble in water;soluble in nitric acid **Flash Pt:** Nonflammable, however, airborne in the form of a dust this substance will support combustion **LEL/LFL:** Nonflammable **UEL/UFL:** Nonflammable **Vapor Density:** N.A. **Vapor Pressure:** 1 mm @ 372°C (sublimes) **Specific Gravity:** 5.73 **Incompatibilities:** Oxidizers, halogens,zinc, lithium, azides, and acetylides **Appearance and odor:** Gray to black, brittle, crystalline, amorphous, odorless.	Overexposure to this substance through inhalation or ingestion may result in ulceration of the nasal septum, GI disturbances resulting in violent purging and vomiting,hoarse voice, sore throat, excessive salivation, peripheral neuropathy (numbness and burning sensations beginning at the extremities followed by motor weakness), respiratory irritation leading to possible pulmonary edema. Skin or eye contact may result in irritation, conjunctiva, dermatitis, and hyperpigmentation (darkening of thr areas exposed) of the skin. This substance has been judged to be a Human carcinogen by NTP, and IARC

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Benzene	71-43-2	I.P 9.24 eV, 100% response with PID and 10.2 eV lamp 150% response with FID	Air sample using charcoal tube and carbon disulfide desorption, OSHA 07 or NIOSH Method #1500	1 ppm OSHA 10 ppm ACGIH 0.1 ppm NIOSH 500 ppm IDLH	Inadequate - Odor threshold 34-199 ppm. OSHA accepts the use of air-purifying respirators with organic vapor cartridge up to 10 ppm despite the inadequate warning properties providing cartridges are changed at the beginning of each shift **Recommended gloves:** Butyl/neoprene blend - >8 00 hrs, Silver shield as a liner - >8 00 hrs. Viton - >8 00 hrs	**Boiling Pt:** 176°F; 80°C **Melting Pt:** 42°F; 5.5°C **Solubility:** 0.07% **Flash Pt:** 12°F; -11°C **LEL/LFL:** 1.3% **UEL/UFL:** 7 9% **Vapor Density:** 2 77 **Vapor Pressure:** 75 mmHg **Specific Gravity:** 0.88 **Incompatibilities:** Strong oxidizers, fluorides, perchlorates, and acids **Appearance and Odor:** Colorless to a light yellow liquid with an aromatic odor	Overexposure may result in irritation to the eyes, nose, throat, and respiratory system. CNS effects include giddiness,lightheadedness, headaches, staggered gait, fatigue, and lassitude and depression Additional effects may include nausea Long duration exposures may result in respiratory collapse. Regulated as an OSHA carcinogen. May cause damage to the blood forming organs and may cause a form of cancer called leukemia.
Benzo(a)pyrene	50-32-8	Volatility is minimal. No I.P. exist, therfore PID will not detect substance Substance is *noncombustible* and as a result will not be detected by FID	Air sample using a glass fiber or silver membrane filter analysis by ga chromotography / infrared or other *spectrophotometric* method or colorimeter; NIOSH 1(186)	0.2 mg/m^3 TWA, OSHA 0.1 mg/m^3 TWA, NIOSH	Adequate - use a full-face air-purifying respirator with dust/mist cartridge up to 10 mg/m^3 ≈ 1 ppm **Recommended glove:** Nitrile	**Boiling Pt:** 312°C **Melting Pt:** 179°C **Solubility:** Insoluble **Flash Pt:** N.A. **LEL/LFL:** N.A. **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** 10 mm @ 312°C **Specific Gravity:** N.A. **Incompatibilities:** N.A. **Appearance and Odor:** Yellow odorless crystals.	Regulated primarily as a result of potential carcinogenic properties. Listed by NTP, IARC and ACGIH as carcinogenic
Bis(2-ethylhexyl) phthalate	117-81-7	No information found This is a combustible liquid therefore the FID should detect it however the relative response ratio is unknown	Particulate filter, carbon disulfide desorption GC/FID NIOSH Method #5020	NIOSH ACGIH 5 mg/m^3 STEL 10 mg/m^3 OSHA 6 mg/m^3 IDLH 5000 mg/m^3	Irritating, tingling sensation **Recommended APR Cartridge:** Suitable for dust and fume. Organic vapor acid gases with HEPA filter. **Recommended gloves:** Nitrile >6.00 hrs has been the one most widely used for the other substances and is acceptable for this substance. Other options include butyl rubber >8.00 hrs or neoprene >6.00 hrs	**Boiling Pt:** 680°F; 386°C **Melting Pt:** freezes 6.8°F; -14°C **Solubility:** Insoluble **Flash Pt:** 419°F; 215°C **LEL/LFL:** 0.3% @ 473°F; 245°C **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** <0.01 mm **Specific Gravity:** 0.99 **Incompatibilities:** Nitrates, strong oxidizers, acids, and caustics. **Appearance and odor:** Colorless, oily liquid, odorless	This substance is a mild skin, eye, mucous membrane irritant, and mild gastric disturbance. In test animals liver damage and teratogenic effects have been noted.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Bromochloromethane	74-97-5	PID with 11.7 eV probe will respond; Not detected by FID	Air sample using charcoal/coconut sorbent tube with carbon disulfide desorption, and GC/FID analysis OSHA IMISO627 or NIOSH 1003	200 ppm TWA OSHA/NIOSHA/ ACGIH. APRs acceptable for lower concs.	Moderate warning properties. Has a characteristic odor of chloroform. However, no odor threshold accepted or published by the ACGIH.	**Boiling Point:** 155° F **Solubility:** Insoluble **Flash Point:** N/A **Specific Gravide:** 1.93 **Vapor Pressure:** 77° F @ 160 mmHg **LEL:** N/A **UEL:** N/A **Incompatibilities:** Chemically-active metals such as calcium, powdered aluminum, zinc & magnesium. **Appearance and odor:** Colorless to pale yellow liquid with a chloroform-like odor.	Symptoms of exposure include disorientation, dizziness, pulmonary edema, and irritation of the eyes, throat, and skin.
Cadmium	7440-43-9	Substance is not volatile. Unable to be easily detected by PID or FID. Not detected by FID.	Air sample using a mixed cellulose-ester filter / acid desorption and analysis by atomic absorption-flame; NIOSH 7300 or 7048.	OSHA 2 $\mu g/m^3$ (0.002 mg/m^3) PEL ACGIH 0.01 mg/m^3 TLV-TWA (total particulate) 0.002 mg/m^3 (respirable particulate)	The use of an air purifying, full face-piece respirator with a high efficiency particulate air filter for concentrations up to 0.25 mg/m^3.	**Boiling Pt:** 1412°F; 767°C **Melting Pt:** 610°F; 321°C **Solubility:** Insoluble **Flash Pt:** Not applicable (Airborne dust may burn or explode when exposed to heat, flame, or incompatible chemicals) **LEL/LFL:** Not applicable **UEL/UFL:** Not applicable **Vapor Density:** N.A. **Vapor Pressure:** 1 mm @ 741°F; 394°C **Specific Gravity:** 8.65 @ 90°F; 32°C **Incompatibilities:** Strong oxidizers, elemental sulfur, selenium, tellurium, zinc, nitric acid, and hydrazoic acid **Appearance and Odor:** Metal: Silver-white, blue-tinged lustrous, odorless solid. Fume: yellow-brown, finely divided particulate dispersed in air.	Overexposure to this substance may result in irritation to the respiratory tract, dyspnea, tightness in the chest, coughing, possibly pulmonary edema. Overexposure to fumes causes symptoms characteristic of the flu (headaches, chills, muscle aches, nausea, vomiting, diarrhea). Chronic exposure may result in damage to the lungs, kidneys and liver. This substance has been identified as a confirmed animal, potential human carcinogen by IARC and NTP.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Chlorine	7782-50-5	PID with an 11.7 eV lamp will respond; No response	Air sample using bubbler. Analyze via ion-specific electrodce OSHA ID 101	1 ppm ceiling OSHA 0.5 ppm ACGIH/NIOSH, with a STEL of 1.0 ppm	Adequate warning properties, odor threshold less than 1.0 ppm. APRs can be used for concentraitons up to 10 0 ppm	**Boiling Point:** -29°F **Solubility:** 0.7% **Flash Point:** Not applicable (N/A) **Vapor Pressure:** >1 atm **LEL:** N/A **UEL:** N/A **Incompatibilities:** Reacts explosively or forms explosive compounds with many common substances such as acetylene, ether, turpentine, ammonia, fuel gas, hydrogen & finely divided metals. **Appearance and odor:** Greenish-yellow gas with a pungent, irritating odor.	Symptoms of exposure include burning of the eyes, nose, and mouth, lacrimation, rhinitis, cough, choking, nausea, vomiting, headache, dizziness, pulmonary edema, pneumonia, hypoxemia, dermatitis, and eye and skin burns.
Chloroform	67-66-3	I.P. 11.42 eV 100% response with FID	Air sample using charcoal sorbent tube and carbon disulfide desorption with gas chromatography-flame ionization detector; NIOSH 1003	OSHA 50 ppm (ceiling); NIOSH STEL 2 ppm; ACGIH 10 ppm IDLH 500 ppm	Inadequate - Odor threshold 133 - 276. Chloroform has poor warning properties but will adhere to organic vapor cartridges. Supplied air respirators are recommended. **Recommended glove:** Polyvinyl Alcohol >8.00 hrs; Viton 9.50 hrs; Teflon >3.60 hrs	**Boiling Pt:** 143°F; 62°C **Melting Pt:** -81°F; -62°C **Solubility:** 0 5% **Flash Pt:** N/A **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** Not available **Vapor Pressure:** 160 mmHg @ 68°F; 20°C **Specific Gravity:** 1.48 **Incompatibilities:** Strong caustics, chemically active metals such as aluminum or magnesium powder, sodium and potassium, strong oxidizers **Appearance and Odor:** Colorless liquid with a sweet pleasant odor.	Overexposure to this substance may cause dizziness, mental dullness, nausea, headache, fatigue, anaesthesia, and irritation of the skin and eyes. Chronic overexposure may result in damage to the liver, kidneys, heart, eyes and skin.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Chromium Compounds	7440-47-3 (Element)	Properties vary depending upon the specific compounds. Not detectable by PID. Not detectable by FID.	Air sample using mixed cellulose - ester filter / acid desorption and analysis by atomic absorption; NIOSH 7024.	OSHA & NIOSH (Chromium II, III) 0.5 mg/m^3 TWA (Chromium VI) 0.1 mg/m^3 ceiling ACGIH 0.5 mg/m^3 TLV-TWA (Chromium II, III compounds) 0.05 mg/m^3 (Chromium VI compounds) IDLH 30 mg/m^3 (Chromium VI compounds)	The use of a air purifying, full face-piece respirator with a high efficiency particulate filter for concentrations up to 0.1 mg/m^3.	**Boiling Pt:** 4788°F; 2642°C **Melting Pt:** 3452°F; 1900°C **Solubility:** Insoluble **Flash Pt:** Not applicable (Airborne dust may burn or explode when exposed to heat, flame, or incompatible chemicals) **LEL/LFL:** Not applicable **UEL/UFL:** Not applicable **Vapor Density:** N.A. **Vapor Pressure:** 0 mmHg **Specific Gravity:** 7.14 **Incompatibilities:** Strong oxidizers, peroxides, and alkalis **Appearance and Odor:** Appearance and odor vary depending upon the specific compound.	Health hazards are characterized normally through chronic exposure manifesting as histologic fibrosis of the lungs and ulceration of the nasal septum and skin. IARC, NTP and ACGIH list various chromium compounds as possessing carcinogenic properties.
Copper	7440-50-8 (Cu) 1317-38-0 (CuO)	Substance is not volatile. Unable to be detected by PID or FID.	Air sample using a mixed cellulose ester filer / inductively coupled plasma/atomic emission spectroscopy; NIOSH 7300.	0.10 mg/m^3 TWA; OSHA and NIOSH. 0.2 mg/m^3 TWA; ACGIH.	The use of an air-purifying full-face respirator with a high efficiency particulate air filter. **Recommended gloves:** This is in the particulate form. Therefore any glove suitable to prevent skin contact (Nitrile has been the one most widely used for the other substances).	**Boiling Pt:** 2324°C **Melting Pt:** 1083°C **Solubility:** Insoluble **Flash Pt:** Not applicable (Airborne dust may burn or explode when exposed to heat, flame, or incompatible chemicals) **LEL/LFL:** Not applicable **UEL/UFL:** Not applicable **Vapor Density:** N.A. **Vapor Pressure:** 1 mm @ 1628°C **Specific Gravity:** 8.94 **Incompatibilities:** Oxidizers, alkalis, sodium azide, acetylene, bromates, chlorates, iodates, and acids. **Appearance and Odor:** Metal: Reddish, lustrous malleable, odorless solid. Fume: Finely divided black particulate dispersed in air.	Irritation to the nose, throat, and respiratory tract. Metallic taste Discoloration of skin (potential dermatitis) and hair. Chronic exposure may result in dermatitis and damage to the liver and kidneys. Overexposure to fumes causes symptoms characteristic of the flu (headaches, chills, muscle aches, nausea, vomiting, diarrhea). Ingestion may cause burning in the mouth, throat, and stomach. Metallic taste with colicky abdominal pain. Individuals with Wilson's disease are at greater risk of chronic exposure as a result of the bodies tendency to absorb and retain copper.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
DDT and the major metabolites; DDD and DDE.	50-29-3 72-54-8 72-55-9	Substance is not volatile no I.P. exists therefore, detection by PID poor. Substance non-combustible, therefore a FID will have no response to DDT.	Air sample using a binder free, glass fiber filter and isoctane desorption / gas chromatography-electron capture detector, NIOSH 3(S274)	1 mg/m^3 TWA, OSHA & ACGIH; 0.5 mg/m^3 TWA, NIOSH	Adequate - Can use air purifying respirator with high efficiency particulate air filter (HEPA) **Recommended glove:** Nitrile acceptable for incidental contact	**Boiling Pt:** 110°C **Melting Pt:** 108°C **Solubility:** Insoluble **Flash Pt:** 72°C-77°C **LEL/LFL:** N.A. **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** Low **Specific Gravity:** 0.99 **Incompatibilities:** Strong oxidizers and alkalis **Appearance and Odor:** Colorless crystals or off-white powder with a slight aromatic odor	Large doses are followed by vomiting due to gastric irritation, diarrhea may follow. Numbness and parethesias of the lips tongue and face associated with malaise, headache, sorethroat, fatique and weakness. Coarse tremors (usually first of the neck, head, and eyelids). This may be accompanied by confusion, apprehension, and depression. Convulsions may result and death may occur from respiratory failure. DDT is absorbed and retained in the fat of humans. Chronic exposure may result in damage to the liver, kidneys and Peripheral Nervous System. DDT is recognized as possessing carcinogenic properties by IARC and NTP
Ethylbenzene	100-41-4	I.P 8.76, High response with PID and 10.2 eV lamp 100% response with FID	Air sample using charcoal tube and carbon disulfide desorption, OSHA 07 NIOSH Method #1501 Aromatic Hydrocarbon	ACGIH & NIOSH 100 ppm TWA 125 ppm STEL OSHA 00 ppm	Adequate - Can use air-purifying respirator with organic vapor cartridge up to 1,000 ppm **Recommended gloves:** Neoprene or nitrile w/ silver shield when potential for saturation; Teflon >3.00 hrs	**Boiling Pt:** 277°F; 136°C **Melting Pt:** -139°F; -95°C **Solubility:** 0.01% **Flash Pt:** 55°F; 13°C **LEL/LFL:** 1.0% **UEL/UFL:** 6.7% **Vapor Density:** 3.66 **Vapor Pressure:** 10 mmHg @ 79°F; 26°C **Specific Gravity:** 0.87 **Incompatibilities:** Strong oxidizers **Appearance and odor:** Colorless liquid with an aromatic odor. Odor Threshold of 0.092-0.60.	Regulated primarily because of its potential to irritate the eyes and respiratory system. In addition, effects of overexposure may include headaches, narcotic effects, CNS changes (i.e., coordination impairment, impaired reflexes, tremoring) difficulty in breathing, possible chemical pneumonia, and potentially respiratory failure or coma.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Freon (1,1,2-[trichloro]-1,2,2-[trifluoroethane])	76-13-1	Poor response on PID (ionization potential 11.9 eV). Poor response.	Air sampling using charcoal sorbent tube, with carbon disulfide desorption, and GC/FID analysis OSHA IMIS2485	1,000 ppm TWA OSHA/NIOSH/ ACGIH 1,250 PPM STEL (ACGIH)	Moderate warning properties. APR acceptable for concentraitons up to 4,500 ppm	**Boiling Point:** 118°F **Solubility:** 0.02% @ 77°F **Vapor Pressure:** 285 mmHg **Flash Point:** Undetermined **LEL:** Undetermined **UEL:** Undetermined **Incompatibilities:** Chemically-active metals such as calcium, powdered aluminum, zinc, magnesium & beryllium **Appearance and odor:** Colorless to water-white liquid with an odor like carbon tetrachloride at high concentrations.	Expousre symptoms include irritation of the throat, drowsiness, and dermatitis.
Gasoline	8006-61-9	Relative response ratios for the components of gasoline range from 100 - 200%	See components for measurement considerations.	ACGIH & OSHA 300 ppm TWA 500 ppm STEL	**Respiratory Protection:** Odor threshold 0.7 ppm, adequate air purifying respirator with organic vapor cartridges up to 25 ppm. **Recommended Gloves:** Nitrile >6.00 hrs; PV alcohol >6.00 hrs; Viton/neoprene >8.00 hrs	**Boiling Pt:** 102°F; 39°C **Melting Pt:** Not available **Solubility:** Negligible **Flash Pt:** -50°F; -45°C **LEL/LFL:** 1.4% **UEL/UFL:** 7.6% **Vapor Density:** ~5 **Vapor Pressure:** 38-300 mmHg (varies seasonally) **Specific Gravity:** 0.74 @ 20/20°C **Incompatibilities:** Strong oxidizers, peroxides, strong acids, and perchlorates **Appearance and Odor:** Colorless liquid with gasoline odor.	Overexposure to this substance may result in irritation to the eyes, skin, and mucous membranes. Systemically, headache, fatique, blurred vision, dizziness, slurred speech, confusion, possible convusion, and chemical pneumonia (aspiration). Prolonged or chronic exposures may result in possible liver or kidney damage. Components of this substance have been determined to be confirmed human carcinogens.
Heptachlor	76-44-8	PID will not detect this substance. FID will not detect this substance.	Sample using a Chrom-102 sorbent tube with toluene desorption. Analyze using Gas chromatography - electron capture detector in accordance with OSHA method S287.	OSHA 0.5 mg/m^3 NIOSH 0.5 mg/m^3 ACGIH 0.05 mg/m^3 (skin)	An air purifying respirator equipped with a combination filter for organic vapors, pesticides, and High Efficiency Particulate Air (HEPA) filter is acceptble. **Recommeded glove:** Nitrile or neoprene gloves are adequate for protection against contact with the skin.	**Boiling Pt:** 293°F; 145°C **Melting Pt:** 203°F; 95°C **Solubility:** 0.0006% **Flash Pt:** Not available **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** Not available **Vapor Pressure:** 0.0003 mmHg **Specific Gravity:** 1.66 **Incompatibilities:** Iron and rust **Appearance and Odor:** White to light tan crystals with a camphor-like odor.	Exposure to this substance may cause tremors, convulsions, and liver damage. Target organs include the Central Nervous System (CNS) and liver Cases of liver cancer were noted in laboratory animals exposed to heptachlor.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Hexachlorobenzene	118-74-1	Response to PID is unknown; Response to FID is unknown	Sample using glass fiber binder free filter. Analyze via gas chromatography - electron capture detector in accordance with OSHA method IMIS 1376	ACGIH TLV of 0.025 mg/m^3	An air purifying respirator equpped with a High Efficiency Particulate Air (HEPA) filter is acceptable. **Recommended glove:** Nitrite or neoprene gloves are adequate for protection against contact with the skin	**Boiling Pt:** 614° F, 323° C **Melting Pt:** 231°F, 111° C **Solubility:** Insoluble **Flash Pt:** 468° F, 242° C **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** 98 **Vapor Pressure:** 10 mmHg **Specific Gravity:** Not available **Incompatibilities:** Unknown **Appearance and Odor:** Fungicide - appearance and odor unknown	Historical data regarding exposure to hexachlorobenzene (HCB) is limited. Information indicates that exposure to HCB occurred as a result of ingestion of wheat treated with HCB. Exposure resulted in bulbous skin lesions which were aggravated with exposure to sunlight and alcohol. Other symptoms include weight loss, atrophy of skeletal muscles, corneal opacity, and damage to the kidneys. HCB is a confirmed carcinogen with experimental carcinogenic, neoplatigenic, and teratogenic data.
Lead	7439-92-1	Substance is not volatile. Unable to be detected by either PID or FID.	Air sample using a mixed cellulose ester filter / HNO_3 or H_2O_2 desorption / Atomic absorption; NIOSH 7082 or 7300.	OSHA 0.05mg/m^3 PEL ACGIH 0.15mg/m^3 TLV-TWA NIOSH 0.10mg/m^3 REL IDLH 100 mg/m^3 as lead	The use of a air purifying, full-face respirator with high efficiency particulate air filter for up to 2.5 mg/m^3. **Recommended gloves:** This is in the particulate form. Therefore any glove suitable to prevent skin contact (Nitrile has been the one most widely used for the other substances).	**Boiling Pt:** 3164°F; 1740°C **Melting Pt:** 621°F; 327°C **Solubility:** Insoluble **Flash Pt:** Not applicable (Airborne dust may burn or explode when exposed to heat, flame, or incompatible chemicals) **LEL/LFL:** Not applicable **UEL/UFL:** Not applicable **Vapor Density:** Not available **Vapor Pressure:** 0 mmHg **Specific Gravity:** 11.34 **Incompatibilities:** Strong oxidizers, peroxides, sodium acetylide, zirconium, and acids **Appearance and Odor:** Metal: A heavy ductile, soft gray solid	Overexposure to this substance via ingestion or inhalation may result in metallic taste in the mouth, dry throat, thirst, Gastrointestinal disorders (burning stomach pain, nausea, vomiting, possible diarrhea sometimes bloody or black, accompanied by severe bouts of colic), CNS effects (muscular weakness, pain, cramps, headaches, insomnia, depression, partial paralysis possibly coma and death. Extended exposure may result in damage to the kidneys, gingival lead line, brain, and anemia.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Lindane	58-89-9	PID will not detect this substance.	Sample using a glass fiber, binder free filter with a midget impinger. Analyze with Gas Chromatography - electr0lytic conductivity detector in accordance with NIOSH method 5502.	OSHA 0.5 mg/m^3 NIOSH 0.5 mg/m^3 ACGIH 0.5 mg/m^3 (skin)	An air purifying respirator equipped with a combination filter for organic vapors, pesticides, and High Efficiency Particulate Air (HEPA) filter is acceptble. **Recommeded glove:** Nitrile or neoprene gloves are adequate for protection against contact with the skin.	**Boiling Pt:** 614°F; 323°C **Melting Pt:** 235°F; 113°C **Solubility:** 0.001% **Flash Pt:** Not available **LEL/LFL:** Not available **UEL/UFL:** Not available **Vapor Density:** Not available **Vapor Pressure:** 0 00001 mmHg **Specific Gravity:** 1.85 **Incompatibilities:** Corrosive to metals **Appearance and Odor:** White to yellow, crystalline powder with a slight musty odor.	Exposure to lindane may cause irritation to the eyes, nose, and throat, headache, nausea, convulsions, respiratory difficulty, cyanosis (dark bluish or purplish coloration of the skin), aplastic anemia, and muscle spasms. Lindane is listed as a carcinogen by IARC (Class 2B), NTP (Class 2), and EPA (Class B2). Target organs include the eyes, skin, blood, liver, and kidneys.
Mercury	7439-97-6	Jerome Mercury Vapor Analyzer Particulate form - This substance is unable to be detected by PID/FID	NIOSH Method # 6009	OSHA NIOSH ACGIH as alkyl compounds 0.01 mg/m^3; STEL 0.03 mg/m^3	No identifiable warning properties to indicate presence and thereby detection **Recommended APR Cartridge:** Suitable for Metallic mercury with HEPA filter. Preferably, with an end-of-service life indicator. **Recommended gloves:** This is in the liquid form. Therefore any glove suitable to prevent skin contact (Nitrile has been the one most widely used for the other substances).	**Boiling Pt:** 356.9°C **Melting Pt:** -38.89°C **Solubility:** Insoluble **Flash Pt:** N.A. **LEL/LFL:** N.A. **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** 0.0012 mm @ 25°C **Specific Gravity:** 13.6 **Incompatibilities:** Acetylene, ammonia, chlorine dioxide, azides, calcium, sodium carbide, lithium, rubidium, and copper **Appearance and odor:** Silvery-white heavy mobile liquid, odorless	This substance is corrosive to all points of contact. Systemic symptoms include irritability, wakefulness, muscle weakness and tremors, increased reflexes, gingivitis, anorexia, headache, tinnitus, hypermotility, GI disturbances (nausea, vomiting), diarrhea (sometimes bloody), liver changes, dermatitis, and fever. Symptoms experienced via inhalation include to those above coughing, chest pain, dyspnea, bronchial pneumonitis, and excessive salivation.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Mercury Vapor	7439-97-6	Jerome Gold Film Mercury Vapor Analyzer used to locate and quantify mercury vapor emissions. Range of detection specified by manufacturer: 0.000 to 1.999 mg/m^3 mercury. I.P. Not determined. No response with PID. No response with FID.	Air sample using mixed cellulose-ester filter, or passive diffusion badge. OSHA ID 140	0.05 mg/m3 TWA ACGIH and NIOSH, and 1.0 mg/10 m3 ceiling OSHA	Inadequate warning properties. However, air purifying respirators with a protection factor of at least 10 and End of Service Life indicators are acceptable for concentrations up to 0.5 mg/m3.	**Boiling Pt:** 674°F **Solubility:** Insoluble **Flash Pt:** Not Applicable **LEL/LFL:** Not Applicable **Vapor pressure:** 0.0012 mmHg **Incompatibilities:** Acetylene, ammonia, chlorine dioxide, azides, calcium, sodium carbide, lithium, rubidium, and copper **Appearance and Odor:** Silver-white, heavy, odorless liquid	Overexposure may result in cough, chest pain, dyspnea, bronchial pneuitis, tremor, insomnia, irritabilty, indecision, headache, fatigue, weakness, salivation, gastrointestinal (GI) disturbances, anorexia, loss in weight, proteinuria, eye and/or skin irritation
Methyl ethyl ketone (2-Butanone)	78-93-3	I.P. 9.54 eV High response with PID and 10.2 eV lamp 80% Relative Response with FID	Air sample using Ambersorb tube and carbon disulfide desorption, OSHA 16, 84 / NIOSH 2500	OSHA, NIOSH and ACGIH; 200 ppm NIOSH and ACGIH have established STEL of 300 ppm	Adequate - Can use air purifying respirator with organic vapro cartridges up to 2000 ppm **Recommended glove:** Ply vinyl alcohol or natural rubber	**Boiling Pt:** 175°F **Melting Pt:** NA **Solubility:** 28% **Flash Pt:** 16°F **LEL/LFL:** 1.4% **UEL/UFL:** 11.4% **Vapor Density:** NA **Vapor Pressure:** 71 mm **Specific Gravity:** 0.81 **Incompatibilities:** Strong oxidizers, amines, ammonia, inorganic acids, caustics, copper, isocyanates, pyridines **Appearance and odor:** Colorless liquid with a moderately sharp, fragrant mint- or acetone like odor	Expsoure may result in irritation to the eyes and nose. Overexpsoure may cause headache, dizziness, and vomiting. Target organs are the Central Nervous System and lungs

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Methylene chloride	75-09-2	I.P. 11.32 eV, High response with PID and 11.7 eV lamp 100% response with FID	Air sample using charcoal or Anasorb CMS sorbent tube and carbon disulfide desorption with gas chromatography-flame ionization detector; OSHA 59 or 80, NIOSH 1005	OSHA 50 ppm TWA, 100 ppm ceiling, ACGIH 50 ppm TWA, NIOSH Lowest feasible concentration, IDLH 2300 ppm	Inadequate - Odor threshold 160 ppm. Use a gas mask with a Type N canister for concentrations up to 25 ppm. In excess of 25 ppm, use a supplied air respirator (airline respirator with emergency escape cylinder or a Self-Contained Breathing Apparatus - SCBA) **Recommended gloves:** Nitrile rubber latex glove 3.00 hrs (vendor specific), supported Polyvinyl alcohol glove, unsupported 1-8 hrs; Silver shield 1.90 hrs	**Boiling Pt:** 104°F; 39.8°C **Melting Pt:** -141°F; -96°C **Solubility:** 2% **Flash Pt:** Not available **LEL/LFL:** 13% **UEL/UFL:** 12% **Vapor Density:** 2.93 **Vapor Pressure:** 380 mmHg @ 72°F, 22°C **Specific Gravity:** 1.33 **Incompatibilities:** Strong oxidizers, caustics, metals (i.e. aluminum, magnesium, potassium, sodium, lithium), and concentrated acids **Appearance and Odor:** Colorless liquid with a chloroform-like odor. (Note: A gas above 104°F).	Effects of overexposure may include CNS effects - cause sleepiness, fatigue, weakness, lightheadedness, numbness of the limbs, altered cardiac rate and incoordination. These signs and symptoms may be accompanied by nausea, gastric and pulmonary irritation leading possibly to pulmonary edema. In addition to the narcosis long term effects may include liver injury. Listed as possessing carcinogenic properties by NTP, IARC, and ACGIH.
Sulfuric Acid	7664-93-9	pH paper This substance is unable to be detected by PID/FID	NIOSH Method # 7903	OSHA & NIOSH 1 mg/m^3 ACGIH 1 mg/m^3 3 mg/m^3 Ceiling NIOSH 1 mg/m^3 IDLH 15 mg/m^3	Adequate - Irritating, tingling sensation. Odor threshold 0.15 ppm. **Recommended APR Cartridge:** Suitable for acid gases and dusts and mists for concentrations less than 80 mg/m^3. **Recommended gloves:** Nitrile 6.00 hrs has been the one most widely used for the other substances and is acceptable for this substance. Other options include butyl rubber >8.00 hrs; silver shield 6.00 hrs; neoprene 1-3 hrs; and Viton >8.00 hrs	**Boiling Pt:** 554°F; 290°C **Melting Pt:** 51°F; 10°C **Solubility:** Miscible **Flash Pt:** N.A. **LEL/LFL:** N.A. **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** 1 mmHg @ 295°F; 146°C **Specific Gravity:** 1.84 **Incompatibilities:** Organic materials, chlorates, carbides, fulminates, water, and powdered metals. Liberates excessive heat when mixed with water. **Appearance and odor:** Colorless, oily liquid, odorless	This substance is corrosive at all points of contact. Severe exposure may result in burns, chemical pneumonitis, conjunctivitis, stomatitis, and erosion of the teeth. Depending on the severity shock and collapse may result.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Toluene	108-88-3	I.P 8.82 eV, High response with PID and 10.2 eV lamp 110% response with FID	Air sample using charcoal tube and carbon disulfide desorption, OSHA 07, or NIOSH Method 1500	OSHA 200 ppm 300 ppm Ceiling ACGIH 50 ppm (skin) NIOSH 100 ppm REL 150 ppm STEL IDLH 500	Adequate - Odor threshold 1 6 ppm is considered good. Can use air-purifying respirator with organic vapor cartridge up to 1,000 ppm **Recommended gloves:** Teflon >15.00 hrs; Viton >16.00 hrs, silver shield >6,00 hrs; supported nitrile (Useable time limit 0 5 hr, complete submersion for the nitrile selection); PV alcohol >25.00 hrs	**Boiling Pt:** 232°F; 111°C **Melting Pt:** -139°F; -95°C **Solubility:** 0.05% (61°F;16°C) **Flash Pt:** 40°F; 4°C **LEL/LFL:** 1.2% **UEL/UFL:** 7 1% **Vapor Density:** 3.14 **Vapor Pressure:** 20 mmHg @ 65°F; 18°C **Specific Gravity:** 0.87 **Incompatibilities:** Strong oxidizers **Appearance and odor:** Colorless liquid with a sweet pungent aromatic odor.	Overexposure to this substance may result in mild to moderate irritation at all points of contact, and CNS changes including euphoria, confusion, nervousness, and possibly paresthesia characterized by an abnormal burning sensation, pricking, or numbness. At 200-500 ppm exposure has resulted in headaches, nausea, eye irritation, loss of appetite, bad taste, impair coordination, fatigue, and weariness. Chronically, toluene overexposure may result in dermatitis, liver, and kidney damage.
Trichloroethylene	79-01-6	I.P. 9.45 eV, High response with PID and 10.2 eV lamp 70% Response with FID	Air sample using charcoal tube and carbon disulfide desorption, OSHA 07, or NIOSH Method 1022 or 1003	OSHA 50 ppm PEL 200 ppm ceiling ACGIH 50 ppm TLV-TWA 100 ppm STEL NIOSH 25 ppm REL IDLH 1000 ppm	Inadequate - Odor threshold 82 ppm. APRs with organic vapor/acid gas cartridges may be used for escape purposes. Exceedances over the exposure limits require the use of positive pressure-demand supplied air respirator. **Recommended gloves:** PV Alcohol unsupported >16.00 hrs; Silver shield >6.00 hrs; Teflon >24.00 hrs; or Viton >24.00 hrs; Nitrile (Useable time limit 0.5 hr, complete submersion for the nitrile selection)	**Boiling Pt:** 188°F; 86.7°C **Melting Pt:** -99°F; -73°C **Solubility:** 0.1% @ 77°F; 25°C **Flash Pt:** 90°F; 32°C **LEL/LFL:** 8% @ 77°F; 25°C **UEL/UFL:** 10.5 @ 77°F; 25°C **Vapor Density:** 4.53 **Vapor Pressure:** 100 mm @ 32°C **Specific Gravity:** 1.46 **Incompatibilities:** Strong caustics and alkalis, chemically active metals (barium, lithium, sodium, magnesium, titanium, and beryllium) **Appearance and Odor:** Colorless liquid with a chloroform type odor. Combustible liquid, however, burns with difficulty.	Central nervous system effects including euphoria, analgesia, anesthesia, paresthesia, headaches, tremors, vertigo, and somnolence. Damage to the liver, kidneys, heart, lungs, and skin have also been reported. Contact may result in irritation to the eyes, skin, and mucous membranes. Ingestion may result in GI disturbances including nausea, and vomiting NIOSH lists this substance a potential human carcinogen.

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TABLE 3-1
CHEMICAL, PHYSICAL, AND TOXICOLOGICAL DATA
PORTSMOUTH NAVAL SHIPYARD

Substance	CAS No.	Air Monitoring/Sampling Information		Exposure Limits	Warning Property Rating	Physical Properties	Health Hazard Information
Waste Oils All information is based on mineral oil	N.E. 8012-95-1 for mineral oil	Varies between fractions however waste oils tend to be less volatile. This instrument tends to handle the longer chained aliphatic hydrocarbons more efficiently than its PID counterpart	#5026 is the recommended method for mineral oil mist	ACGIH & NIOSH 5 mg/m^3 (Oil mists) 10 mg/m^3 STEL OSHA 5 mg/m^3 (Oil mists)	Non-volatile substance, therefore no respiratory protection is required. In an aerosol form dust and mist respirator would be considered acceptable for up to 500 mg/m^3. **Recommended gloves:** Any glove suitable to prevent skin contact (Nitrile has been the one most widely used for the other substances, and will be acceptable).	**Boiling Pt:** 360°C **Melting Pt:** N.A. **Solubility:** Insoluble **Flash Pt:** 275-500°F depends on the distillation fraction **LEL/LFL:** N.A. **UEL/UFL:** N.A. **Vapor Density:** N.A. **Vapor Pressure:** <0.5 mmHg **Specific Gravity:** 0.90 **Incompatibilities:** None reported **Appearance and odor:** Colorless, oily, with an odor of burned lubricating oil.	Minor irritation to the eyes, skin, and respiratory system.
Xylene All isomers o-,m-, p-	1330-20-7	I.P. 8.56 eV, High response with PID and 10.2 eV lamp 110% response with FID	Air sample using charcoal tube and carbon disulfide desorption, OSHA 07, or NIOSH Method 1500	ACGIH, & NIOSH 100 ppm TWA 150 ppm STEL OSHA 100 ppm PEL IDLH 900 ppm	Adequate - Odor thresholds for the following isomers: 0.6 m-; 5.4 p-; 20 o-ppm. Can use air-purifying respirator with organic vapor cartridge up to 1,000 ppm concentrations. **Recommended gloves:** PV Alcohol >12.67 hrs; Viton >8.00 hrs; CPE >1.00 hr; Butyl 0.87 hrs; Nitrile is acceptable for limited operations and contact (>0.20 hrs)	**Boiling Pt:** 269-281°F; 132-138°C **Melting Pt:** -13o/-54m/56p°F; -25o/-48m/13p °C **Solubility:** 0.02 % **Flash Pt:** 81-90°F;27-32°C **LEL/LFL:** 0.9% **UEL/UFL:** 7.0% **Vapor Density:** 3.66 **Vapor Pressure:** 7-9 mmHg @ 70°F; 21°C **Specific Gravity:** 0.86-0.88 **Incompatibilities:** Strong oxidizers and strong acids **Appearance and odor:** Colorless liquid with an aromatic odor.	Effects may of overexposure include irritation at all points of contact, CNS changes (i.e. dizziness, excitement, drowsiness, incoherent, staggering gait), difficulty in breathing, pulmonary edema, and possibly respiratory failure. Chronic effects may include dermatitis and cornea vacuolization.

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4.0 CONFINED SPACE ENTRY OPERATIONS

None of the planned operations have any potential to require activities that would involve personnel entry into structures or containers that could be considered to be permit-required confined spaces, as defined by OSHA standard §1910.146. Therefore, no activities of this kind are addressed further in, or authorized by, this HASP.

To ensure all personnel understand what type of spaces qualify as a confined space are as follows:

- The space may not contain (or have the potential to contain) a hazardous atmosphere (as defined in that OSHA regulation).
- The space must not contain a material that has the potential to engulf or entrap an entrant.
- Must be so that the configuration is not such that an entrant could be trapped or asphyxiated by inwardly converging sides or by a floor which slopes downward in the work area and tapers to a smaller cross-section.
- Space does not contain any other recognized serious safety or health threat.

If any one of these conditions is suspected to exist, absolutely no entry will be permitted. In such an instance, the Project HSO or the CLEAN HSM must be contacted for guidance.

5.0 AIR MONITORING

This section presents requirements for the use of real-time air monitoring instruments during site activities involving potential for exposure to site contaminants. It establishes the types of instruments to be used, the frequency of which they are to be used, techniques for their use, action levels for upgrading/downgrading levels of protection, and methods for instrument maintenance and calibration.

5.1 INSTRUMENTS AND USE

The information provided in this section addresses the use of real-time monitoring instrumentation during onsite activities. These instruments will be used primarily to monitor source points and worker breathing zone areas, while observing conservative instrument action levels. This approach (coupled with the use of personal protective equipment, observance of the other control requirements presented in this Health and Safety Plan) has been selected to minimize any potentials for personnel exposures to hazardous concentrations of airborne contaminants. These instrument will be utilized as a screening tool to detect the presence of some of the site contaminants identified within Table 3-1 as being more mobile presenting a greater threat of exposure during this activity. It is not anticipated that personnel air sampling/analyses efforts will be necessary during the planned activities to further support information provided through the use of real-time monitoring instrumentation data.

5.1.1 HNu-PI101 Photoionization Detector

A HNu PI-101 photoionization detector (PID) with a 11.7 eV lamp will be used to monitor potential source areas and to screen the breathing zones of employees during the initial opening and venting of the well head spaces. The PID has been selected because it is capable of detecting organic gases and vapors and some inorganic gases and vapors, including most of the identified contaminants of concern associated with this activity. Detection is based on the contaminants' ionization potentials in comparison to the lamp energy (which has to be equal to or greater than the ionization potential of the contaminant).

Prior to the commencement of any field activities, the background levels of the site must be determined and noted. Daily background readings will be taken away from any areas of potential contamination. These readings, any influencing conditions (i.e., weather, temperature, humidity), location, and the other information specified on the form included as Figure 5-1 of this HASP must be documented throughout the performance of site activities (documenting the information on Figure 5-1 in a field Health and Safety Logbook is a suitable recordkeeping alternative).

FIGURE 5-1

DIRECT-READING INSTRUMENT RESPONSE DATA

Site Name: Portsmouth Naval Shipyard **Project No.:** _____
Page 1 **of** _____

Date and Time(s)	Instrument Operator Name	Instrument Used	Instrument Reading and Duration	Location (e.g., Borehole vs. Breathing Zone)	Operation(s) Being Performed	Personnel in Vicinity at Time of Readings and Level of PPE Worn
Example: 2-12-94/14:30	Joe Field	HNu 101	15 ppm/15 min	Breathing Zone	Installation of Well No. 12	Jim Technician/Level B, George Jones/Level B

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FIGURE 5-1
DIRECT-READING INSTRUMENT RESPONSE DATA
Page _____ of _____

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Date and Time(s)	Instrument Operator Name	Instrument Used	Instrument Reading and Duration	Location (e.g., Borehole vs. Breathing Zone)	Operation(s) Being Performed	Personnel in Vicinity at Time of Readings and Level of PPE Worn

5.1.2 OVA-Model 128 Flame Ionization Detector

The use of a Flame Ionization Detector may also be utilized to screen potential source emissions and the breathing zones of employees during the execution of the scope of work, in the same application as noted above. The FID has been selected because it may detect the presence of long chain hydrocarbons more efficiently than a photoionization detector (PID). The relative response of this instrument to most of the contaminants of concern is high (relatively accurate). Both the PID and the FID instruments are suitable for use, and are offered here as alternatives. Instrument selection will consider the field technicians knowledge and level of comfort in using these instruments.

If positive readings are indicated by either the HNu PI-101, or FID, well heads will be permitted to vent prior to sample acquisition to allow readings to settle. If readings continue to be elevated colorimetric tubes (Draeger tubes) will be used to determine if either methylene chloride or benzene is the contaminant that is detected. Exposure to either of these substances at concentrations that could present a health hazard is unlikely, given the low percentage detected in previous samples, and the low probability of free product being present at these sites. These instruments are primarily used to detect airborne (volatile) contaminants which may be released into the environment, which may pose an exposure concern to site workers.

NOTE: It should be realized that some of the contaminants of concern are nondetectable using these types of screening instruments. Therefore, in addition to the use of these screening instruments, emphasis will also be given to work hygiene practices, and effective use of PPE to protect against dermal introduction as a route of exposure.

5.1.3 Draeger (Colorimetric Tubes)

Draeger tubes shall be employed in conjunction with the HNu or FID as part of the air monitoring program supporting site activities. This approach has been specified in order to meet the requirements of 29 CFR 1910.120 (h). That regulation specifies that efforts must be taken to determine the identity and quantity of potential site contaminants. The use of the HNu or the FID in the survey mode of operation will not identify airborne substances, only detect them at very low levels. However, the use of the Draeger tubes in conjunction with these instruments permits a semi-quantitative result.with positive identification within the restrictions of the limitations of this detection method.

Draeger tube 100/a for methylene chloride (tube no. 6724601) has been selected for use due to the previous detection of this substance in groundwater. An action level of any color change from white to brownish green indicating layer will indicate this substances' presence. The measuring range for these tubes begins at 50 ppm. The effective use of these tubes, and appropriate timely response to retreat if the color change is observed, will effectively minimize the potentials for workers to be over exposed to this substance.

Draeger tube 0.5/c for benzene (tube no. 8101841) will be used to detect the presence of this substance. These tube will detect concentrations of benzene in concentrations ranging form 0.5 to 10 ppm. Effective use of these tubes, and prompt response (as above) will minimize potentials for personnel over exposures to benzene.

Any positive instrument responses on the HNu, or FID observed above background levels will be considered to indicate contaminant release. As such, the following actions will be taken:

- Monitor work areas continuously, concentrating on worker breathing zones (BZ) areas (head and face regions) when positive source results are reported. If readings are observed at these areas to be at background levels, continue monitoring and work efforts.

- If sustained or repeated intermittent readings in the workers' BZ are detected above determined background levels, workers are to retreat to an unaffected area, upgrade the level of protection to Level C (Air Purifying respirator equipped with organic vapor cartridges with High Efficiency Particulate Air Filters). Additional analysis (colorimetric tubes) will be used to confirm that the contaminant is not methylene chloride or benzene. Further actions will be dependant upon results of colorimetric tube analysis and levels of contaminant concentration as indicated by the HNu or FID (refer to Table 5-2, Instrument Action Levels).

5.2 AIR MONITORING REQUIREMENTS - HNu and FID

Air monitoring with the HNu PI-101 and the FID will be initiated at potential sources of vapor emissions. Examples of potential sources and corresponding activities are as follows:

- Initial opening of the well casing and then periodically as the purge and sample cycle proceed.

5.2.1 Air Monitoring Frequency

As previously specified, all site readings must be recorded using Figure 5-1. Recording this information in a site Health and Safety Logbook is an acceptable alternative to using Figure 5-1, provided that all of the specified information is recorded. Other relevant influencing factors (e.g. weather conditions, wind direction and speed, humidity, etc.) should also be recorded.

In general, during all nonintrusive efforts, initial and periodic monitoring frequencies will be considered to be adequate. However, based on instrument responses and site observations, the Site Safety Officer may decide to increases these frequencies. Reduction in monitoring frequencies will not be permitted without obtaining the prior consent of the Project Health and Safety Officer and the CLEAN HSM.

Table 5-1 presents the frequencies that air monitoring instruments are to be utilized, along with the corresponding potential hazards, on a task-specific basis for this project.

TABLE 5-1

AIR MONITORING TYPE AND FREQUENCY

TASK(S)	ATMOSPHERIC HAZARD(S)	MONITORING TYPE & FREQUENCY
Groundwater investigations	Toxic gas/vapor	**PID/FID:** Initial monitoring of the potential sources (i.e. opening of the well casing) and the workers' BZs. Periodically thereafter based on results and the cycle of the purge and sample interval. **Draeger tubes:** As conditions or instrument results indicate.
Seep sampling	Possible toxic gas/vapor and to an even lesser extent particulates	**PID:** Initially monitor at the source. If possible, readings above background are observed, monitor the workers breathing zone.

5.3 ACTION LEVELS

The following monitoring instrument action levels will apply to this project:

TABLE 5-2
INSTRUMENT ACTION LEVELS

INSTRUMENT	ACTION LEVEL	RESULTANT ACTION
HNu PID	Above background levels at a potential point source release (i.e. well casing).	Continue work while closely monitoring the workers' Breathing Zone (BZ) areas based on positive results.
	Background levels are exceeded in worker BZ areas	Retreat to an unaffected area and let the work area ventilate. Reapproach work area cautiously with monitoring instruments. If background levels are not regained, don APRs with organic vapor-HEPA filtered cartridges and perform Draeger tube analysis. Test first for methylene chloride and then for benzene. If any positive indication is seen in either analysis, immediately retreat and contact the Project HSO or the CLEAN HSM for guidance. If the presence of methylene chloride and benzene is positively ruled out, work may resume using the APR protection with periodic retesting with the Draeger tubes.
	Greater than 50 ppm	Retreat to an unaffected area. Work can continue with APR protection when readings decrease to levels below 50 ppm. Otherwise, work can continue only in Level B (supplied air respiratory protection).
FID	Same action levels as those specified for the HNu PID	Same response actions as those specified for the HNu PID.
Draeger tubes	Observe the directions provided with the tubes.	Any positive indication on either the methylene chloride or the benzene tube will be cause for immediate retreat to an unaffected area.

5.4 INSTRUMENT MAINTENANCE AND CALIBRATION

Air monitoring instruments will be maintained and pre-field calibrated by the B & R Environmental Equipment Manager. Operational checks and field calibration will be performed on all instruments each day prior to their use. Field calibration will be performed on instruments which require it (for example, the HNu and FID -if used- must be field calibrated daily. An additional field calibration must be done on this instrument at the end of each day to determine any significant instrument drift). These operational checks and calibration efforts will be performed in a manner that complies with the employees health and safety

training, the manufacturer's recommendations, and with applicable B & R Environmental instrument Standard Operating Procedures (a copy of which will be maintained on site for reference). All calibration efforts must be documented. Figure 5-2 is provided for documenting these calibration efforts. This information may instead be recorded in a field Health and Safety Logbook, provided that all of the information specified in Figure 5-2 is recorded. This required information includes the following:

- Date calibration was performed
- Individual calibrating the instrument
- Instrument name, model, and serial number
- Any relevant instrument settings and resultant readings (before and after) calibration
- Identification of the calibration standard (lot no., source concentration, supplier)
- Any relevant comments or remarks

Field maintenance will consist of daily cleaning of the instruments using a damp towel or rag to wipe off the instrument's outer casing and overnight battery recharging.

5.5 RECORDKEEPING

All instrument readings above and including background levels must be recorded using Figure 5-1, or in a field book or field Health and Safety Logbook. This recordkeeping should also indicate any corrective actions taken. In addition, results of any colorimetric analysis must be recorded in the log book. Instrument calibration efforts and results must also be recorded, as specified in section 5.5. Lastly, information concerning potential influencing factors on instrument responses (i.e. weather, activities, interferences) shall also be recorded.

FIGURE 5-2

DOCUMENTATION OF FIELD CALIBRATION

Site Name: Portsmouth Naval Shipyard Project No.: _____

Date of Calibration	Instrument Name and Model	Instrument I.D. Number	Person Performing Calibration	Instrument Settings		Instrument Readings		Calibration Standard (Lot No.)	Remarks/ Comments
				Pre-Calibration	Post-Calibration	Pre-Calibration	Post-Calibration		

ROUGH DRAFT

6.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

This section presents requirements for the use of personal protective equipment for each of the activities being conducted as defined in this HASP. This section includes anticipated levels of protection for each of the activities, the criteria used for selecting various levels of protection, and criteria for modifying levels of protection based on monitoring instrument readings and personal observations.

6.1 ANTICIPATED LEVELS OF PROTECTION

The levels of protection which is anticipated to be used for the tasks identified within the scope of work is levels D, and possibly C (as defined in Appendix B of OSHA Standard 29 CFR 1910.120 - "Hazardous Waste Operations and Emergency Response"). It is anticipated that Level D will be appropriate for the majority of work in this effort. This level of protection is only anticipated to be modified to level C should monitoring instrument readings or colorimetric tube analyses results indicate this is the most appropriate action. Dermal protection for the identified tasks may include inner nitrile gloves for sampling purposes, and outer nitrile gloves for the purpose of decontamination (i.e. pump maintenance, etc.).

6.1.1 Minimum Requirements (All Tasks)

Minimum requirements for all tasks include steel-toe and steel shank work boots, chemical resistant boot covers (as necessary for climatic conditions), with standard field dress consisting of long pants and long-sleeved shirts. Hard hats and safety glasses will be worn when overhead or eye hazards exist based on the task, or if working in and around operating machinery that could present or contribute to these threats. The use of protective equipment specified as optional will be at the discretion of the FTL or the SSO based on tasks, site conditions, and other influencing factors. This is of course providing that action levels or the requirements of this plan are not compromised, indicating a need for additional elements of personal protection.

6.1.2 Mobilization/Demobilization

As mobilization and demobilization present limited potential for contacting any hazardous materials that could adversely effect site personnel, the minimum requirements specified in 6.1.1, above, will be adhered to for these efforts.

6.1.3 Groundwater Investigations

Minimum requirements as stipulated in Section 6.1.1 will apply for this task. If the potential for saturation of work clothes exists the use of PVC or PE-coated Tyvek® will be incorporated into this protective measure.

6.1.4 Seep Sampling

Minimum requirements shall include steel-toe steel shank work boots, nitrile outer gloves, and latex or nitrile inner gloves. The following items may be required based on the selection criteria discussed in Section 6.3 PPE Modification Criteria: hard hat, safety glasses, Tyvek® coveralls, and boot covers. Activities that will be performed near or over bodies of water will require the use of U.S. Coast Guard approved personal flotation devices. In addition, personnel shall be properly tied-off with lifelines and lifeline attendants, and (if wading into water bodies is necessary to perform the task), personnel shall be provided appropriate hip or chest waders.

6.1.5 Decontamination Activities

The requirements for decontamination activities will include the minimum requirements for all tasks (See Section 7.1.1) and the use of PE-coated Tyvek® or PVC with nitrile outer and inner gloves when the potential for saturation of work clothing exists, and splash shield as necessary or as directed by the FTL or SSO. This will be the required level of protection when performing large scale decontamination activities. The general rule of thumb for respiratory protection will be to use the same level as, or one level below, that of the field personnel who were using the equipment. This will be determined by the SSO for specific decontamination activities.

6.2 PPE SELECTION CRITERIA

Based on the relatively low volatility and anticipated low concentrations of the identified contaminants of concern, as well as the probabilities for dispersion of any potential vapor releases via natural ventilation (i.e. wind currents), vapor concentrations in worker breathing zones are not anticipated to be at levels which would warrant a respiratory hazard protection.

Nitrile gloves were selected to provide protection against the potential site contaminants that could be encountered, and to help reduce the potential for the ingestion of transferred contaminants as a result of incidental hand-to-mouth contact. Nitrile was selected as the glove construction material based on

available research data on permeation characteristics of the contaminants of concern. Hard hats, safety glasses, and work boots were selected to provide protection against some of the physical hazards associated with the proposed operations. Disposable boot covers were selected to help as climatic conditions dictate. PVC/PE coated coveralls were selected for use in the event that activities could have the potential to result in the saturation of work clothes.

6.3 PPE MODIFICATION CRITERIA

This section presents criteria for upgrading and downgrading chemical protective clothing and/or respiratory protection. Where uncertainties arise, the more protective requirement will apply.

6.3.1 Chemical Protective Clothing Modification Criteria

Polyvinyl chloride (PVC) or PE-coated Tyvek® coveralls must be worn anytime there is a reasonable potential for saturation of work clothes. Nitrile gloves (inner and outer) must be worn anytime there is a reasonable potential for hand contact with site contaminants.

6.3.2 Respiratory Protection Modification Criteria

The use of level C protection incorporating organic vapor/acid gas cartridges and a full-face respirator will be incorporated should elevated levels of contaminants at a well head present an inhalation hazard as determined through the use of screening instruments. This level of protection is not anticipated and listed only as a contingency. The use of respiratory protective equipment will require the documentation of use as specified in Figure 6-1.

FIGURE 6-1
AIR PURIFYING
RESPIRATOR USE LOG

Site:_____

Location:_____

Dates of Investigation:_____

User	Date of Use	Cleaned and Inspected Prior to Use (Initials)	Cartridges Changed Prior to Use (Yes/No)	Total Hours on Cartridge

SUBMIT TO HEALTH SCIENCES DEPT. AT COMPLETION OF PROJECT

_____ Site Manager (FTL)

_____ Date

7.0 DECONTAMINATION

Decontamination is the procedure to be employed to remove and/or neutralize site contaminants encountered through the execution of the scope of work. This procedure will be employed for the purpose of preventing cross contamination, protecting onsite personnel, and protecting the individuals outside this operation from the spread of contamination.

7.1 STANDARD PROCEDURES

1. Establish a personnel decontamination station (PDS) suitable to handle the activities, type and the amount of contamination, and level of protection. This area will be located adjacent to the exclusion zone or work area, and will consist of the stations described in Section 7.2.

2. Upon leaving the contamination area (exclusion zone), all personnel shall proceed through the appropriate contamination reduction sequence.

3. All protective gear should be left onsite during any lunch break following decontamination procedures.

4. All equipment will be inspected by the FTL or SSO and approved prior to leaving the decontamination area within the contamination reduction corridor.

5. All discarded materials (i.e. used PPE) will be bagged and disposed of in a dumpster identified by the Base Contact. Decontamination fluids will be drummed, labeled, and staged to await sample analyses and ultimate disposal fate.

7.2 PERSONNEL DECONTAMINATION REQUIREMENTS

The decontamination of personnel and their protective clothing shall be performed in sequential stages. These stages shall include:

- Removing contamination from protective clothing and equipment with a detergent/water solution and soft bristle scrub brushes.

- Removal of protective clothing (disposable items shall be discarded into a container as identified above).

- Workers washing hands and face with potable water and soap whenever they remove PPE and leave the exclusion zone.

7.3 SAMPLE CONTAINER/EQUIPMENT DECONTAMINATION

Sample containers will be wiped free of any residual material prior to packaging. The sampling equipment will be removed from the specified wells and decontaminated only as maintenance purposes dictate. When this does take place these items will be high pressure soap/water wash or steam cleaned as necessary. It is not anticipated that any other downhole equipment will be employed other than those dedicated pieces of equipment. Should a piece of equipment be replaced decontamination will be done prior to introduction to the well. All equipment will be cleaned to a level which it is visibly cleaned and supports no positive through a scanning of the equipment with the monitoring instruments previously specified.

7.4 CLOSURE OF THE PERSONNEL DECONTAMINATION STATION

Decontamination-generated liquid wastes generated during onsite activities will be containerized, labeled, and staged onsite to await disposal. The disposal method used will be based upon available information regarding the characteristics of the site, sample analyses, and contaminant levels. Reusable protective equipment will be cleaned, dried, and prepared for future use. (If gross contamination has occurred, the item will be properly disposed.)

All wash tubs, pail containers, etc., will be thoroughly washed, rinsed, and dried prior to removal from the site. The Site Safety Officer will be responsible for inspecting and clearing equipment to leave the site.

7.5 DECONTAMINATION EVALUATION

The decontamination process effectiveness will be judged in the following manner.

- Visual observation - Discoloration, stains, dirt, and alterations of the fabric due to chemical contact will be the primary method used to determine effectiveness.

The following methods may be used if gross contamination is encountered:

- Monitoring Instrumentation - Instruments used to detect site contaminants may be employed to scan garments and equipment for the presence of site contaminants after decontamination procedures have been employed.

- Decontamination Solution Analyses - An analyses of the solution (final rinse) and the presence of contaminants may suggest additional cleaning is required. This information may be useful in the ultimate disposal of the fluids generated.

- Sample Analyses - sample analyses may indicate the level of contamination and therefore the potential for contamination. Once again this information may be useful in the ultimate disposal.

It is suggested that a combination of methods be used to determine the effectiveness of the decontamination of the process used.

8.0 TRAINING REQUIREMENTS

This section describes the minimum requirements for initial, refresher, supervisory, and site-specific training.

8.1 INTRODUCTORY AND REFRESHER TRAINING

8.1.1 Requirements for Brown & Root Environmental Personnel

All Brown & Root Environmental personnel must complete 40 hours of introductory hazardous waste site training prior to performing work at the Portsmouth Naval Shipyard. Additionally, Brown & Root Environmental personnel who have had introductory training more than 12 months prior to site work must have completed 8 hours of refresher training within the past 12 months before being cleared for site work.

All Brown & Root Environmental personnel functioning in the supervisory capacity will have had Management and Supervisory training as required by 29 CFR 1910.120 (e)(4).

Documentation of Brown & Root Environmental introductory, supervisory, and refresher training and a site-specific training will be maintained at the project. Copies of certificates or other official documentation will be used to fulfill this requirement.

8.1.2 Requirements for Subcontractors

All Brown & Root Environmental subcontractor personnel must have completed introductory hazardous waste site training or equivalent work experience as defined in OSHA Standard 29 CFR 1910.120(e) and 8 hours of refresher training (as appropriate) meeting the requirements of 29 CFR 1910.120(e)(8) prior to performing field work at the Portsmouth Naval Shipyard. All subcontractor personnel serving in the supervisory capacity will have had Management and Supervisory training as required by 29 CFR 1910.120(e)(4). Brown & Root Environmental subcontractors must certify that each employee has had such training by sending Brown & Root Environmental a letter, on company letterhead, containing the information in the example letter provided as Figure 8-1. Figures 8-1 and 9-2 can be combined into one letter. The letter is required to accompany official documentation (i.e. certificates, etc.).

8.1.3 Subcontractor Exceptions

Subcontractors who will not perform any activities in the exclusion zone or areas where there is no potential for exposure, will be excluded from the requirements stipulated in Section 8.1.2. The use of these exceptions is permitted only by obtaining the prior approval of the CLEAN HSM.

8.2 SITE-SPECIFIC TRAINING

Brown & Root Environmental will provide site-specific training to all Brown & Root Environmental employees and subcontractor personnel who will perform work on this project. Site-specific training will include:

- Names of personnel and alternates responsible for site safety and health
- Safety, health and other hazards present on site
- Use of personal protective equipment
- Work practices to minimize risks from hazards
- Safe use of engineering controls and equipment
- Medical surveillance requirements
- Signs and symptoms of overexposure
- The contents of the health and safety plan
- Emergency response procedures (evacuation and assembly points)
- Review the contents of relevant Material Safety Data Sheets

8.2.1 Site-Specific Training Documentation

Brown & Root Environmental and subcontractor personnel will be required to sign a statement indicating receipt of site-specific training and understanding of site hazards and control measures. Figure 8-2 will be used to document site-specific training.

FIGURE 8-1

OSHA TRAINING CERTIFICATION

The following statements must be typed on company letterhead, accompany certificates or some other acceptable official documentation, and signed by an officer of the company:

LOGO
XYZ CORPORATION
555 E. 5th Street
Nowheresville, Kansas 55555

Month, day, year

Mr. Mark Perry
Project Manager
Brown & Root Environmental
Foster Plaza VII 661 Andersen Drive
Pittsburgh, Pennsylvania 15220

Subject: Hazardous Waste Site Training - Portsmouth Naval Shipyard

Dear Mr. Perry:

The employees listed below have had introductory hazardous waste site training or equivalent work experience as required by 29 CFR 1910.120(e). In addition, those employees listed below who have received their introductory training more than 12 months ago have also received 8 hours of refresher training in accordance with 29 CFR 1910.120 (e)(8) within the past 12 months.

LIST FULL NAMES OF EMPLOYEES AND THEIR SOCIAL SECURITY NUMBERS HERE

Should you have any questions, please contact me at (555) 555-5555.

Sincerely,

(Name of Company Officer)

FIGURE 8-2

SITE-SPECIFIC TRAINING DOCUMENTATION

My signature below indicates that I am aware of the potential hazardous nature of performing investigation activities at Portsmouth Naval Shipyard, and that I have received site-specific training which included the elements presented below:

- Names of personnel and alternates responsible for site safety and health
- Safety, health and other hazards present on site
- Use of personal protective equipment
- Work practices to minimize risks from hazards
- Safe use of engineering controls and equipment
- Medical surveillance requirements
- Signs and symptoms of overexposure
- The contents of the health and safety plan
- Emergency response procedures (evacuation and assembly points)
- Review contents of relevant Material Safety Data Sheets

I further state that I have been given the opportunity to ask questions and that all of my questions have been answered to my satisfaction.

NAME	SIGNATURE	DATE

9.0 MEDICAL SURVEILLANCE

9.1 REQUIREMENTS FOR BROWN & ROOT ENVIRONMENTAL PERSONNEL

All Brown & Root Environmental personnel participating in project field activities will have had a physical examination meeting the requirements of Brown & Root Environmental' medical surveillance program and will be medically qualified to perform hazardous waste site work using respiratory protection. At the Pittsburgh office, the Medical Surveillance Program is administered by the Health Sciences Department, with consultation provided by the Partners in Corporate Health Care department of Ohio Valley General Hospital. Our Medical Consultant at that hospital is Teresa Silvaggio, M.D., MPH, Director. Dr. Silvaggio is experienced, very knowledgeable (and Board eligible) in Occupational Medicine, as required by OSHA standard 1910.120 (f) (5), and residency-trained. She has over five years experience in serving as the Pittsburgh Office's Medical Consultant. All Ohio Valley General Hospital physicians participating in this program have been thoroughly informed of the nature of operations that Brown & Root Environmental employees perform, and on the potential chemical and physical hazards that may be encountered in fulfilling their assigned duties. This has also included educating these physicians in the various types of respiratory and other personal protective equipment commonly used by our personnel.

Documentation for medical clearances will be maintained in the Brown & Root Environmental Pittsburgh office and made available as necessary.

9.2 REQUIREMENTS FOR SUBCONTRACTORS

Subcontractors are required to obtain a certificate of their ability to perform hazardous waste site work and to wear respiratory protection. The "Subcontractor Medical Approval Form" (Figure 9-1) can be used to satisfy this requirement providing it is properly completed and signed by a licensed physician.

Subcontractors who have a company medical surveillance program meeting the requirements of paragraph (f) of OSHA 29 CFR 1910.120 can substitute Figure 9-1 with a letter, on company letterhead, containing all of the information in the example letter presented as Figure 9-2. Figures 8-1 and 9-2 can be combined into one letter.

9.3 EXCEPTIONS FOR SUBCONTRACTORS

Subcontractor personnel who will not perform any activities in the exclusion zones during intrusive operations, or where there is no potential for exposure will be exempted from the requirements stipulated in Section 9.2. This exception can be utilized only with the prior approval of the CLEAN HSM.

9.4 REQUIREMENTS FOR ALL FIELD PERSONNEL

Each field team member (including subcontractors) shall be required to complete and submit a copy of Medical Data Sheet. These will be handed out and collected as part of the site-specific training. This shall be provided to the SSO, prior to participating in site activities.

FIGURE 9-1

SUBCONTRACTOR MEDICAL APPROVAL FORM

For employees of _____
Company Name

Participant Name: _____ Date of Exam: _____

Part A

The above-named individual has:

1. Undergone a physical examination in accordance with OSHA Standard 29 CFR 1910.120, paragraph (f) and found to be medically -

   ( ) qualified to perform work at the Portsmouth Naval Shipyard work site
   ( ) not qualified to perform work at the Portsmouth Naval Shipyard work site

and,

2. Undergone a physical examination as per OSHA 29 CFR 1910.134(b)(10) and found to be medically -

   ( ) qualified to wear respiratory protection
   ( ) not qualified to wear respiratory protection

My evaluation has been based on the following information, as provided to me by the employer.

( ) A copy of OSHA Standard 29 CFR 1910.120 and appendices.
( ) A description of the employee's duties as they relate to the employee's exposures.
( ) A list of known/suspected contaminants and their concentrations (if known).
( ) A description of any personal protective equipment used or to be used.
( ) Information from previous medical examinations of the employee which is not readily available to the examining physician.

Part B

I, _____, have examined _____
Physician's Name (print) Participant's Name (print)
and have determined the following information:

FIGURE 9-1
SUBCONTRACTOR MEDICAL APPROVAL FORM
PAGE TWO

1. Results of the medical examination and tests (excluding finding or diagnoses unrelated to occupational exposure):

   _____

   _____

   _____

2. Any detected medical conditions which would place the employee at increased risk of material impairment of the employee's health:

   _____

   _____

   _____

3. Recommended limitations upon the employee's assigned work:

   _____

   _____

   _____

   _____

I have informed this participant of the results of this medical examination and any medical conditions which require further examination of treatment.

Based on the information provided to me, and in view of the activities and hazard potentials involved at the Portsmouth Naval Shipyard work site, this participant

( ) may
( ) may not

perform his/her assigned task.

Physician's Signature _____

Address _____

Phone Number _____

NOTE: Copies of test results are maintained and available at:

_____
Address

FIGURE 9-2

MEDICAL SURVEILLANCE LETTER

The following statements must be typed on company letterhead and signed by an officer of the company:

LOGO
XYZ CORPORATION
555 E. 5th Street
Nowheresville, Kansas 55555

Month, day, year

Mr. Mark Perry
Project Manager
Brown & Root Environmental
Foster Plaza VII 661 Andersen Drive
Pittsburgh, Pennsylvania 15220

Subject: Medical Surveillance - Portsmouth Naval Shipyard

Dear Mr. Perry:

As an officer of XYZ Corporation, I hereby state that the persons listed below participate in a medical surveillance program meeting the requirements contained in paragraph (f) of Title 29 of the Code of Federal Regulations (CFR), Part 1910.120 entitled "Hazardous Waste Operations and Emergency Response: Final Rule." I further state that the persons listed below have had physical examinations under this program within the past 12 months and that they have been cleared, by a licensed physician, to perform hazardous waste site work and to wear positive and negative pressure respiratory protection. I also state that, to my knowledge, no person listed below has any medical restriction that would preclude him/her from working at the Portsmouth Naval Shipyard worksite.

LIST FULL NAMES OF EMPLOYEES AND THEIR SOCIAL SECURITY NUMBERS HERE

Should you have any questions, please contact me at (555) 555-5555.

Sincerely,

(Name of Company Officer)

10.0 SITE CONTROL

This section outlines the means by which Brown & Root Environmental will delineate work zones and use these work zones in conjunction with decontamination procedures to prevent the spread of contaminants into previously unaffected areas of the site. It is anticipated that a three zone approach will be used during work at this site; exclusion zone, contamination reduction zone, and support zone.

10.1 EXCLUSION ZONE

The exclusion zone will be considered those areas of the site of known or suspected contamination. For purposes of this activity the exclusion zone will include the well head plus ten feet, when the wellhead is open. Therefore, the exclusion zones for this project will be limited to those areas of the site where active work is being performed and/or anywhere there is believed to be the potential for encountering any of the potential hazards defined in this HASP

10.2 CONTAMINATION REDUCTION ZONE

The contamination reduction zone (CRZ) will be a buffer area between the exclusion zone and any area of the site where contamination is not suspected. This area will serve as a focal point in supporting exclusion zone activities. In addition, this area will serve as the access and control points to the exclusion zone. For the purposes of supporting this activity decontamination will take place at a central location and not in the CRZ. All potentially contaminated equipment will be bagged to be moved from the exclusion zone to this central location.

10.3 SUPPORT ZONE

The support zone for this project will include a staging area where site vehicles will be parked, equipment will be unloaded, and where food and drink containers will be maintained. In all cases, the support zones will be established at areas of the site where exposure to site contaminants would not be expected during normal working conditions or foreseeable emergencies.

10.4 SITE MAP

Site maps are presented in previous sections of this Work Plan, and are therefore not repeated here.

10.5 BUDDY SYSTEM

Personnel engaged in onsite activities will practice the "buddy system" to insure the safety of all personnel involved in this operation.

10.6 MATERIAL SAFETY DATA SHEET (MSDS) REQUIREMENTS

Brown & Root Environmental personnel will provide MSDS's for all chemicals brought on site. The contents of these documents will be reviewed by the Site Safety Officer with the user(s) of the chemical substances prior to any actual use or application of the substances on site. The MSDS's will then be maintained in a central location (i.e.temporary office) and will be available for anyone to review upon request. Subcontractors will be required to similarly satisfy these requirements.

10.7 COMMUNICATION

As personnel may not always be working in close proximity to one another during field activities, a secondary means of communication may be necessary. If this need arises, 2-way radio communication may be used. All means of communication will have the approval of the Shipyard, prior to its use.

External communication will be done so utilizing the telephones at predetermined and approved locations. External communication will primarily be used for the purpose of resource and emergency resource communications. Prior to the commencement of site activities, the FTL and Shipyard contact will determine and arrange for telephone communications as necessary.

11.0 STANDARD WORK PRACTICES

The following Standard Work Practices are to be applied in addition to the Health and Safety Standard Operating procedures:

* Eating, drinking, chewing gum or tobacco, taking medication, and smoking are prohibited in the exclusion or decontamination zones, or any location where there is a possibility for contact with site contaminants exists.

* Upon leaving the exclusion zone, hands and face must be thoroughly washed with soap and potable water. Any protective outer clothing is to be decontaminated and removed as specified in this HASP, and left at a designated area prior to entering the clean area.

* Contact with potentially-contaminated substances must be avoided. Contact with the ground or with contaminated equipment must also be avoided.

* No facial hair, which interferes with a satisfactory fit of the mask-to-face seal, is permitted on personnel required to wear respiratory protective equipment.

* All personnel must satisfy all training requirements (40-hr Introductory, 8-hr Refresher, Site-specific training, Emergency response training, and Supervisory as applicable) prior to commencing site activities.

* All personnel must have a working knowledge of this HASP. Including being aware of the action levels for upgrading/downgrading levels of protective equipment, and emergency procedures.

* All personnel must satisfy medical monitoring procedures.

* All personnel must complete a medical data sheet, to be maintained on site.

* All personnel working in sight restriction areas of heavy vegetation or where the topography does not permit line of sight contact must utilize the buddy system.

* When lifting or moving equipment or material, use proper lifting techniques, the proper number of personnel, or equipment to move heavy loads.

* All work areas must be kept free of ground clutter.

* No flames or open fires will be permitted on site.

* Site personnel must immediately notify Brown & Root Environmental Health Sciences of all incidents for OSHA recordkeeping purposes.

* If personnel note any warning properties of chemicals (irritation, odors, symptoms, etc.) or even remotely suspect the occurrence of exposure, they must immediately notify the SSO for further direction.

* Site personnel are not to undertake any activity which would be considered a confined-space entry.

* A full-sized copy of the OSHA poster included as part of this HASP shall be conspicuously posted on site.

* Any new information must be promptly conveyed to the Project SSO and the Field Team Leader.

* All compressed gas cylinders used (empty or full) must be stored, secured, and used properly to protect from damage.

12.0 EMERGENCY RESPONSE

In the event of an emergency, all site personnel will be evacuated to a predetermined location away from the work place. As a result of this approach, this Emergency Action Plan has been developed in accordance with OSHA standard 29 CFR 1910.38(a), as provided for in 29 CFR 1910.120 (l) (1) (ii). Brown & Root Environmental shall utilize Base Fire Protection and Emergency Services and offsite emergency response agencies, as necessary and appropriate, in order to respond to emergency situations.

12.1 PRE-PLANNING

Upon initial arrival at the base, the Brown & Root Environmental FTL/SSO will meet with the Shipyard Fire Department and available emergency services to notify coordinators of the nature, location, and schedule of planned activities. Representatives from these organizations, as well as representatives of the offsite emergency response organizations specified in Table 12-1 will be contacted as part of initial site mobilization efforts and invited to the initial Site-Specific Health and Safety training session referenced in section 8.2 of this Health and Safety Plan. This will enable all parties to understand the nature of the work to be performed, the types of possible emergency response activities which could conceivably arise in the performance of those activities, and their potential role in participating in those response activities.

Based on the nature of the planned activities, the occurrence of any significant emergency situation is not anticipated (i.e., major spills or releases, fires or explosions, etc.) However, as a precautionary measure, all site personnel will be trained in the contents of these Health and Safety and Emergency Response Plans, and will be directed to follow base emergency procedures. Brown & Root Environmental will rely on base services and (if/as necessary) offsite emergency support services to handle emergency situations, if encountered.

12.2 EMERGENCY ESCAPE PROCEDURES AND ASSIGNMENTS

Upon notification of a site emergency requiring evacuation, all site personnel will proceed to predetermined locations based on emergency location and wind directions. If personnel cannot reach those locations without endangering life or health, they shall instead report to a previously-selected alternate meeting place. Personnel shall be instructed to remain at this refuge location until directed to either resume work or leave the site.

12.3 PROCEDURE TO ACCOUNT FOR SITE PERSONNEL

The site work force will be small enough so that accounting for personnel will easily accomplished. Accounting for personnel will be the FTL's responsibility. This will be accomplished by taking a roll call using the site log book.

12.4 RESCUE AND MEDICAL DUTIES

Site personnel shall be prohibited from participating in any emergency rescue or response operations. The only authorized response for site personnel in the event of an emergency situation will be to evacuate the work site and await further instructions.

12.5 ACTIVATION OF EMERGENCY RESPONSE PROCEDURES

Should any emergency occur which requires the support of outside services, the appropriate contacts shall be made by the FTL/SSO. A list of the appropriate contacts can be found in Table 12-1.

Examples requiring outside services are as follows:

- Any field crew member involved in an accident or experiencing signs and symptoms of exposure.
- A condition discovered which suggests the activity is more hazardous than anticipated.
- Emergency conditions in the nearby areas which directly impact operations.

Persons who observe an emergency situation must notify Shipyard contacts and Brown & Root Environmental office contacts (as presented in this HASP), as appropriate, based on the emergency situation.

TABLE 12-1

EMERGENCY INFORMATION

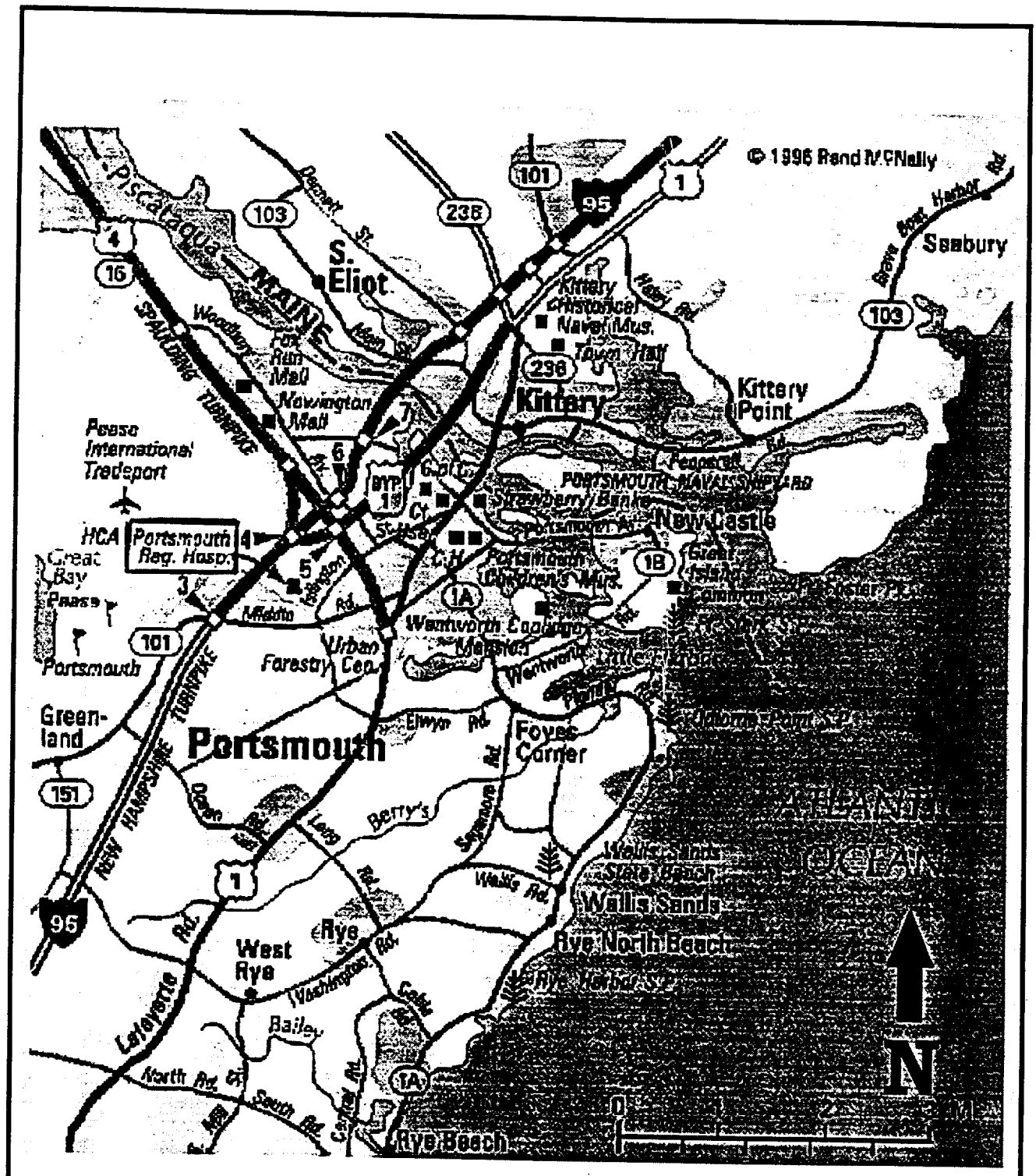
Police (Shipyard)	(207) 438-2555 or Ext. 2555
Fire Department (Shipyard)	(207) 438-2333 or Ext. 2333
Ambulance (Shipyard)	(207) 438-2555 or Ext. 2555
Hospital: Shipyard Portsmouth	 (207) 438-2555 or Ext. 2555 (603) 433-4042
Poison Control Center: Maine New Hampshire	 1-800-442-6305 1-800-562-8236
Base Contact: Fran Endyke, Environmental Affairs	(207) 438-2071
Brown & Root Environmental Project Manager Ms. Linda Klink	(412) 921-8650
Brown & Root Environmental Site Safety Officer	To Be Announced
CLEAN Health and Safety Manager Matthew M. Soltis, CIH, CSP	(412) 921-8912
Agency for Toxic Substances and Disease Registry (ATSDR)	(404) 639-6300

A map depicting directions from the site to the local hospital follows. Additionally, an On Base hospital is present.

Written directions to the hospital:

Off Base: Portsmouth Regional Hospital

Exit the Shipyard through Gate No. 1. At signal light, continue straight down Walker Street. Proceed to second set of signal lights, and continue straight until road ends at Route 1 Bypass. Enter underpass rotary on left side. Go under Route 1 Bypass and loop onto Route 1 Bypass South. Cross bridge and continue straight to traffic circle. At traffic circle, go around to the right 270 degrees, 3/4 circle from entrance to traffic circle. Exit right. Go straight through first set of lights. At second set of traffic lights, turn right onto Borthwick Ave. Ext. Follow Borthwick Ave. Ext. 1/2 to 1 mile. Portsmouth Regional Hospital will be on the right side.



Brown & Root Environmental

Figure 12-1
Hospital Location Map
Portsmouth Naval Shipyard
Kittery, Maine

12.6 INCIDENT FOLLOW-UP

On receiving a report of an incident (or near incident) occurrence the FTL/SSO shall immediately investigate and make the appropriate recommendations to prevent reoccurrence. The CLEAN HSM shall be immediately be notified by telephone on occurrence of an incident. At his discretion he may wish to participate in the investigation. Details of the incident shall be documented on an Incident Report within 24 hours of the occurrence and distributed to the Project Manager and CLEAN HSM.

13.0 SPILL CONTAINMENT PROGRAM

13.1 SCOPE AND APPLICATION

It is not anticipated that bulk hazardous materials (over 55-gallons) will be handled at any given time as part of this scope of work. It is also not anticipated that such spillage would constitute a danger to human health or the environment. However, as the job progresses, the potential for accumulating decontamination fluids in a central staging area exists. Once characterized, these fluids can be removed from this area for proper disposal. While these fluids are stored in the staging area await characterization, this spill containment program will be instituted.

13.2 POTENTIAL SPILL AREAS

In an ongoing attempt to prevent and control further potential contamination of the environment, efforts will be taken to minimize the potential for spill releases. Based on planned activities and available information, there are limited areas and/or operations where this potential threat can be reasonably expected. One of these is the area intended to be used for the central staging area for potentially contaminated decontamination fluids and purge waters. Additionally, the handling, loading and unloading areas present limited potential for leaks or spills. At the time of the preparation of this Health and Safety Plan, it is anticipated all investigation derived wastes (such as decontamination fluids and purge waters) generated, as a result of this scope of work, will be containerized, labeled, and staged to await determination of proper disposal procedures. Until the ultimate fate of these substances can be determined, there exists a possibility to accumulate multiple drums of waste materials.

13.2.1 <u>55-Gallon Drums</u>

All drums containing liquids will be staged within a constructed (temporary) lined bermed area capable of holding a maximum of 10 drums. The capacity of the bermed area should be capable of containing the contents of the largest container placed within it (plus volumes reduced caused by the displacement of the containers, or approximately 110% of the total capacity of the largest container). Rainwater captured inside the lined area will be allowed to evaporate providing it does not exceed 1% of the bermed areas' capacity. If this capacity is exceeded, the collected rainwater will be removed (provided that close inspection of the bermed area and all containers located within it do not indicate any possibility that captured rainwater may be contaminated).

13.3 LEAK AND SPILL DETECTION

To establish an early detection of potential spills or leaks, a daily walk around by the personnel staging or disposing of drums will be conducted during working hours to visually determine that containers are not leaking, and that the bermed staging area is not compromised. If a leak is detected, the drum contents will be transferred using a hand pump into a new 55-gallon drum. The leak will be collected and contained using absorbents such as Oil-dry, vermiculite, or sand, stored at the staging area in a drum conspicuously marked. This material will then also be handled as discussed for other investigation derived wastes. All inspections will be documented in the Project logbook.

13.4 PERSONNEL TRAINING AND SPILL PREVENTION

All personnel will be instructed on appropriate spill prevention procedures as part of the site-specific health and safety training. This will include training on the following:

- using only appropriate (and approved, as applicable) drums or other vessels to contain substances used, stored, or generated as a result of site activities.
- inspecting such containers frequently for signs of damage or leaks.
- inspecting the integrity of the berms of drum storage areas for damage, and immediately notifying the FTL or the SSO of any evidence that the berms have been (or appear to be imminently) compromised.
- placing any such containers in appropriate, designated locations, where they will be protected from hazards such as those presented by vehicular traffic.

The FTL and the SSO will serve as the Spill Response Coordinators, should the need arise.

13.5 SPILL PREVENTION AND CONTAINMENT EQUIPMENT

The following represents the minimum equipment which will be maintained at the staging area at all times for the purpose of supporting this Spill Prevention/Containment Program.

- Sand, clean fill, vermiculite, or other noncombustible absorbent (oil-dry);
- Drums (55-gallon U.S. DOT 17-E or 17-H)

- Shovels, rakes, and brooms
- Hand operated drum pump with hose
- Container Labels

This equipment is only to be used by Brown & Root Environmental personnel for non-emergency, incidental spill response efforts, and will be made available to base or off site emergency responders, as necessary.

13.6 SPILL CONTROL PLAN

This section describes the procedures the Brown & Root Environmental field crew members will employ upon the detection of a spill or leak.

1) Notify the SSO or FTL immediately upon the detection of a leak or spill.

2) Follow the direction of the SSO and the FTL. Rotate the leak above the liquid level, transfer the contents into a new vessel.

3) Apply inert absorbent to the spill, collect, containerize, and label.

It is not anticipated that a spill will occur in which the field crews cannot handle. Should this occur notification of the Base Hazardous material teams will be carried out by the FTL or SSO.

14.0 DOCUMENTATION AND EQUIPMENT

This section summarizes documentation and equipment required for the support of this Health and Safety Plan (HASP). Its purpose is a final checklist to help ensure all of the necessary resources are available to carry out the requirements of this HASP.

14.1 Documentation

The use of any level of respiratory protection must be documented by the SSO or FTL. For the tasks performed in Level C protection, this is to include the completion of all entries in Figure 6-1 ("Air Purifying Respirator Use Log"). In this instance, appropriate entries on this document are to be made for each instance of use, on at least a daily basis. All entries must be completed, and the FTL must sign and date this form and submit it to the Health Sciences Department upon the completion of this project.

Other health and safety documentation requirements relative to this project are defined as follows:

- Health and Safety Log Book
- HASP (Signed Copy)
- OSHA Poster 11 x 14 (posted on site)
- MSDS's (as applicable)
- Medical Data Sheets
- Employee Training Certificates
- Medical Surveillance Documentation
- Incident Reports
- Fit Test Records
- Instrument Calibration Logs
- Instrument Response Data Logs

14.2 Health and Safety Equipment

- ANSI approved eye wash
- Full face air purifying respirators (APRs): MSA Ultra Twin
- APR cartridges: MSA GMC type H
- Respirator Cleaner/Sanitizer solution
- Nitrile gloves (inner and outer)
- PVC/PE coated coveralls

- Boot covers
- Duct tape
- Decontamination kit (Alconox, wash/rinse tubs, brushes, sorbents, step stool)
- Hard hats, safety glasses
- Splash shield
- Steel toe/shank boots
- Hearing protection

JOB SAFETY & HEALTH PROTECTION

The Occupational Safety and Health Act of 1970 provides job safety and health protection for workers by promoting safe and healthful working conditions throughout the Nation. Requirements of the Act include the following:

Employers

All employers must furnish to employees employment and a place of employment free from recognized hazards that are causing or are likely to cause death or serious harm to employees. Employers must comply with occupational safety and health standards issued under the Act.

Employees

Employees must comply with all occupational safety and health standards, rules, regulations and orders issued under the Act that apply to their own actions and conduct on the job.

The Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor has the primary responsibility for administering the Act. OSHA issues occupational safety and health standards, and its Compliance Safety and Health Officers conduct jobsite inspections to help ensure compliance with the Act.

Inspection

The Act requires that a representative of the employer and a representative authorized by the employees be given an opportunity to accompany the OSHA inspector for the purpose of aiding the inspection.

Where there is no authorized employee representative, the OSHA Compliance Officer must consult with a reasonable number of employees concerning safety and health conditions in the workplace.

Complaint

Employees or their representatives have the right to file a complaint with the nearest OSHA office requesting an inspection if they believe unsafe or unhealthful conditions exist in their workplace. OSHA will withhold, on request, names of employees complaining.

The Act provides that employees may not be discharged or discriminated against in any way for filing safety and health complaints or for otherwise exercising their rights under the Act.

Employees who believe they have been discriminated against may file a complaint with their nearest OSHA office within 30 days of the alleged discrimination.

Citation

If upon inspection OSHA believes an employer has violated the Act, a citation alleging such violations will be issued to the employer. Each citation will specify a time period within which the alleged violation must be corrected.

The OSHA citation must be prominently displayed at or near the place of alleged violation for three days, or until it is corrected, whichever is later, to warn employees of dangers that may exist there.

Proposed Penalty

The Act provides for mandatory penalties against employers of up to $1,000 for each serious violation and for optional penalties of up to $1,000 for each nonserious violation. Penalties of up to $1,000 per day may be proposed for failure to correct violations within the proposed time period. Also, any employer who willfully or repeatedly violates the Act may be assessed penalties of up to $10,000 for each such violation.

Criminal penalties are also provided for in the Act. Any willful violation resulting in death of an employee, upon conviction, is punishable by a fine of not more than $10,000, or by imprisonment for not more than six months, or by both. Conviction of an employer after a first conviction doubles these maximum penalties.

Voluntary Activity

While providing penalties for violations, the Act also encourages efforts by labor and management, before an OSHA inspection, to reduce workplace hazards voluntarily and to develop and improve safety and health programs in all workplaces and industries. OSHA's Voluntary Protection Programs recognize outstanding efforts of this nature.

Such voluntary action should initially focus on the identification and elimination of hazards that could cause death, injury, or illness to employees and supervisors. There are many public and private organizations that can provide information and assistance in this effort, if requested. Also, your local OSHA office can provide considerable help and advice on solving safety and health problems or can refer you to other sources for help such as training.

Consultation

Free consultative assistance, without citation or penalty, is available to employers, on request, through OSHA supported programs in most State departments of labor or health.

More Information

Additional information and copies of the Act, specific OSHA safety and health standards, and other applicable regulations may be obtained from your employer or from the nearest OSHA Regional Office in the following locations:

Atlanta, Georgia
Boston, Massachusetts
Chicago, Illinois
Dallas, Texas
Denver, Colorado
Kansas City, Missouri
New York, New York
Philadelphia, Pennsylvania
San Francisco, California
Seattle, Washington

Telephone numbers for these offices, and additional area office locations, are listed in the telephone directory under the United States Department of Labor in the United States Government listing.

Washington, D.C.
1985
OSHA 2203

William E. Brock, Secretary of Labor

U.S. Department of Labor
Occupational Safety and Health Administration

Under provisions of Title 29, Code of Federal Regulations, Part 1903.2(a)(1) employers must post this notice (or a facsimile) in a conspicuous place where notices to employees are customarily posted.

APPENDIX F

RESPONSES TO REGULATORY AGENCY COMMENTS ON PREVIOUS VERSION OF THE PLAN

- 10/8/96 Comment Response Letter Addressing Additional MEDEP Follow-up Comments
- Revision to EPA Comments 18 and 19 Comment Response
- 9/12/96 Comment Response Letter Addressing EPA and MEDEP Follow-up Comments
- 7/3/96 Comment Response Letter Addressing EPA and MEDEP Comments

10/8/96 Comment Response Letter Addressing

Additional MEDEP Follow-up Comments

To: Linda Klink
Fx: 412-921-4040
From: Fred Evans
Ph: 610-595-0567, x159

October 8, 1996

Commanding Officer
Attn: Code 1823/Lt. Conroy
NORTHNAVFACENGCOM
10 Industrial Hwy, MSC 82
Lester, PA 19113-2090

RE: Comments on Navy's September 12, 1996 responses to MEDEP Seep comments dated June 10, 1996 and follow-up comments on the Draft Groundwater Investigation and Monitoring Plan dated July 16, 1996, PNS Kittery, Maine

Dear Jim:

The Maine Department of Environmental Protection (MEDEP) has reviewed the Navy's September 12, 1996 responses to our June 10, 1996 comments on the Draft Technical Memorandum on Seep Sampling and to our July 16, 1996 follow-up on the Draft Groundwater Investigation and Monitoring Plan. The MEDEP provides the following comments.

General Comments on Seep Sampling

It is the MEDEP's clear understanding that seep, sediment, and groundwater sampling will be conducted concurrently to the extent possible. It is the MEDEP's understanding that the Navy wishes to expedite the sampling effort and get the first event completed in November 1996. The MEDEP supports this schedule and will work to expedite any review that is required prior to the sampling event. Provided that the MEDEP receives a detailed workplan soon, the MEDEP will make every effort to meet the November sampling timeframe.

The MEDEP was told that the Navy delayed sending their responses on the Seep Sampling Report until after the Navy could determine whether the seep sampling devices proposed for use would actually work in the field. I could not, however, find any mention of the results of the pilot study in the Navy's responses and therefore cannot see any justification for delaying the issuance of the responses.

Specific Comments on Seep Sampling Responses

Response #3. The MEDEP believes that the seeps should be analyzed for TPH (gasoline and diesel range), phenols, and TCL (Volatiles) plus Freon. It is our strong recommendation that these parameters be included in at least this first round of sampling. The objective of sampling the seeps it not exclusively to examine off-shore concerns, as the response suggests. The objective of sampling seeps is to determine if contamination is moving from onshore areas to offshore areas via seeps.

Response #5. The in-text table is not clear in its correlation of McClaren/Hart Station Numbers and URI Seep Station Numbers. Please clarify if possible. The Navy's response to EPA's General Comment #1 states that all eight of the stations sampled by UNH will be included. Only seven stations are included in the table. In the Navy's response to EPA General Comment #1 the text states that five seeps were sampled by URI in the fall of 1993. The table is unclear, but according to the table it looks like only two seep locations were sampled. A figure should accompany the revised table.

Specific Comments on Groundwater Investigation and Monitoring Plan

Response #4. Remedial action decisions will not be made based solely on the results of the contaminant fate and transport modeling. The modeling results will be considered together with the existing and proposed groundwater, seep, and sediment data.

If you have any comments or questions, please call me at 207-287-7713. Thank you.

Sincerely,

Nancy Beardsley
Project Manager, Division of Remediation
Bureau of Remediation and Waste Management

pc:Meghan Cassidy, USEPA
Patty Marajh-Whittemore, USEPA
Fran Endyke, PNS
Mark Hyland, MEDEP
Richard Heath, MEDEP
Harrison Bispham, MEDEP
John Nelson, NH Fish & Game
Ken Munney, US Fish & Wildlife Service
Jeff Clifford, RAB
Juanita Bell, RAB
Doug Bogen, RAB
Michele Dionne, RAB
Eilene Foley, RAB
Phil McCarthy, RAB
Jack McKenna, RAB
Guy Petty, RAB
Onil Roy, RAB
Cathy Wolff, TAG Representative

Revision to EPA Comments

18 and 19 Comment Response

Revision to Comment Responses 18 and 19 from EPA:

Upon futher review of technical issues related to comments 18 and 19, the previous comment response is no longer valid. According to the USEPA's Addendum to the Statistical Guidance Document for Groundwater Monitoring (1992), the tolerance interval approach for comparison to downgradient data is appropriate and will be employed. Page 51 of the Draft document dated 01/28/93 states "The background data should first be tested to check distributional assumptions. Once the interval is constructed, each compliance point sample is compared to the Upper Tolerance Limit. If any compliance point sample exceeds the limit, the well from which it was drawn is judged to have significant evidence of contamination." The proposed tolerance limit method will be employed as stated in the 1992 guidance document.

9/12/96 Comment Response Letter Addressing

EPA and MEDEP Follow-up Comments

DEPARTMENT OF THE NAVY
NORTHERN DIVISION
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY
MAIL STOP #82
LESTER PA 19113-2090

IN REPLY REFER TO

5090
Code 1823/JMC

SEP 12 1996

Ms. Meghan Cassidy
U.S. Environmental Protection Agency New England Region
JFK Federal Building, Mailcode HBT
Boston, MA 02203-2211

Ms. Nancy Beardsley
Maine Department of Environmental Protection
State House Station 17
Augusta, ME 04333-0017

Subj: GROUNDWATER AND SEEP SAMPLING WORK PLANS, PORTSMOUTH NAVAL SHIPYARD, KITTERY, ME

Dear Ms. Cassidy and Ms. Beardsley:

The responses to comments on the Draft Seep Sampling Work Plan are at enclosure (1). Responses to follow-up comments on the Groundwater Investigation and Monitoring Plan are at enclosure (2).

Please provide any comments you have on these responses within 30 days of receipt. If you have any questions on this matter please call me at (610) 595-0567 extension 117.

For the Community Restoration Advisory Board (RAB) members; if you have any comments or questions on these issues, they can be provided to the Navy at a RAB meeting, by calling the Public Affairs Office at (207) 438-1140 or by writing to:

Portsmouth Naval Shipyard
Code 121.10 Bldg 44
Attn Marty Raymond
Portsmouth, NH 03804-5000

Sincerely,

Jim Conroy

JAMES M. CONROY, PE
LT, CEC, USN
Remedial Project Manager
By direction of the
Commanding Officer

Encl: 1) Response to comments, Draft Seep Sampling Work Plan
2) Responses to follow-up comments, Groundwater Investigation and Monitoring Plan

Distribution:
NOAA (K. Finkelstein)
US Fish & Wildlife Service (K. Munney)
ME Dept. of Marine Resources (D. Card)
NH Fish & Game (J. Nelson)
PNS (Code 121.10, M. Raymond)
COMSUBGRU TWO (R. Jones)
Ms. Juanita Bell
Mr. Jeff Clifford
Ms. Eileen Foley
Mr. Phil McCarthy
Mr. Guy Petty
Ms. Cathy Wolff
Mr. Doug Bogen
Ms. Michele Dionne
Ms. Mary Marshall
Mr. Jack McKenna
Mr. Onil Roy
Shipyard (100PAO) w/o encl
Brown and Root Environmental (L. Klink, B. Horne)

RESPONSE TO EPA COMMENTS DATED JUNE 24, 1996
DRAFT TECHNICAL MEMORANDUM ON SEEP SAMPLING
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

EPA GENERAL COMMENTS

1. **Comment:** The report is not clear on whether the stations that were sampled in the Spring and Fall of 1993 will be re-sampled in this program since the station numbers are different. Clarify whether all previously sampled locations will be resampled.

   Response: All 8 seep stations, sampled in the Spring of 1993 by UNH, will be resampled. The 5 seeps, sampled by URI in the Fall of 1993 correlate with UNH stations. To clarify this, the stations will be correlated by the addition of the following in-text table:

Seep/Mussel Station	*McLaren/Hart Station Number*	*URI Seep Station Number*	*UNH Seep Station Number*
A	—	—	*1001* *1002*
B	—	—	*1003*
C	—	—	*1004*
D	*S1, S2, S3*	*7152* *7252*	*1006* *1007*
E	—	*7151, 7251, 7351*	*1008*

2. **Comment:** Analysis for both dissolved and total suspended solids would provide a more complete picture of contaminant loading.

   Response: Agree. Analysis for both dissolved and total suspended solids will be conducted for the seeps.

3. **Comment:** It would be helpful to coordinate seep sampling and groundwater sampling activities. Additionally, analytical COC parameters should be the same for both seep and groundwater sampling, unless rationale can be shown to support different analytical programs. This would be useful in trying to establish a complete picture of contaminant transport.

   Response: Seep sampling will be coordinated with groundwater sampling, resolution of regulatory agency comments permitting. There is no reason to sample for TCL volatiles (plus Freon), TPH (gasoline range), TPH (diesel range), phenols, or TOX since these are not off-shore concerns. However, the analysis will be expanded to include the following water quality parameters from Table 4-2 of the groundwater monitoring plan: TOC,

chloride, sulfate, pH, and alkalinity. Additionally, as provided in the groundwater monitoring plan, salinity, specific conductance, and oxidation reduction potential (and temperature and dissolved oxygen in response to MEDEP Specific Comment 10; TSS and TDS in response to EPA General Comment 2) will be included as field measurements. Also, as requested by the MEDEP Specific Comment 9, nitrate and bromide analysis will be conducted.

4. **Comment:** Sediment sampling down gradient of the seeps is not imperative, but concurrent sediment sampling would show whether seep discharges are contaminating sediments or are simply being diluted by receiving waters. Additionally, it is always preferable to obtain simultaneous analytical data for mixed media rather than relying on past COC concentrations for certain media, especially if solid/liquid partitioning factors are going to be calculated from the data.

   Response: Agree to expand the scope of work to include sediment sampling at each seep sample location and collected concurrently.

5. **Comment:** Though it is not clear from the text, EPA assumes that all standard water quality parameters should be measured. These measurements include pH, temperature, conductivity, salinity, redox, and dissolved oxygen. The addition of anion analysis would also provide information that could be used to differentiate sources of seep water. However, it is not clear if these anions are included in the groundwater monitoring plan.

   Response: The plan will be revised to include water quality parameters, as discussed in the response to EPA General Comment 3.

6. **Comment:** Quarterly sampling should be considered for at least one year. This would be beneficial to determine seasonal and tidal trends. Significant storm events may also influence seep discharges.

   Response: Regarding tidal trends, seep sampling will always be conducted at low tide for the following reasons: (1) most if not all seeps are only visible during low tide, and (2) at low tide, contaminant concentrations are expected to be at a maximum, therefore, providing conservative data (at high tide, inflow of "clean" water would potentially dilute the contaminants).

   Regarding significant storm events, seep sampling will occur at least 48 hours after a significant storm event. This statement will be added to the text.

   Long-term sampling requirements would be as determined by a Record of Decision (ROD).

EPA SPECIFIC COMMENTS

1. **Comment:** Section 4.1, Sampling Locations : It is unclear whether the proposed sampling includes Jamaica Island as an area to be sampled. This area must be included since "Jamaica Island seep/mussel stations had the highest metals levels for all metals except for Hg."

   Response: All existing seep stations will be sampled. Additionally, new seep sampling locations will be selected in consultation with the regulators following a site visit to identify any new seeps. The number of seeps selected for sampling will be dependent on feasibility of sampling (access), proximity to other seeps, past sampling, flow volume, proximity to contamination sources, etc.

2. **Comment:** Section 4.1, Sampling Locations: All the observed seeps should be sampled to better evaluate the impact to pelagic, epibenthic and infaunal communities. Limiting the sampling to 20 locations is premature at this stage in the process.

   Response: Twenty seep locations were estimated for budgetary purposes only; references to 20 locations will be removed from the plan. However, it is expected that 20 locations is a conservative number, based on previous seep sampling events.

3. **Comment:** EPA suggests that seep sampling during the winter be considered since AVS conditions make this the worst-case scenario for exposure.

   Response: AVS analysis is not being considered for seep sampling, but will be included for sediment sampling occurring concurrent with the seep sampling. Although the first event may not happen to occur in the winter, at least one of the seep/sediment sampling rounds will be conducted during the winter to determine the lowest expected AVS/metal levels in sediment which would correspond with the highest expected metal concentrations in surface water.

RESPONSE TO MEDEP COMMENTS DATED JUNE 10, 1996
DRAFT TECHNICAL MEMORANDUM ON SEEP SAMPLING
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

MEDEP GENERAL COMMENTS

1. Comment: Meaningful assessment of contaminant migration at the seeps will require concurrent collection of seep water and sediment for each sampling event. See Specific Comment 3.

   Response: Agree to add sediment samples to the scope of work to be used in developing empirical partitioning K_d coefficients for on-shore/off-shore modeling purposes. Note that for the off-shore work to date, literature values of K_d were utilized. It had been planned to once again use literature values for the modeling efforts, as well as previous sediment sampling data to develop empirical partitioning coefficients.

   Sediment samples will be collected at each location of seep sampling and analyzed for TCL semivolatiles, TCL pesticides/PCBs, TAL metals, pH, TOC, and AVS. Changes will be required throughout the text. Additionally, the B&R Environmental SOP for sediment sampling will be included as an appendix (see attached).

2. Comment: Assessment of seep volume calculations will require determining the surface area of seeps as well as flow rates. See Specific Comment 8.

   Response: Agree that the net discharge of groundwater to the surface water is important to the on-shore/off-shore modeling effort. It was planned to measure seep flow rates by making a rough approximation of the amount of groundwater discharging to the surface water. The measured seep flow rate, however, only represents the groundwater flow discharging to the surface water body above the elevation of the surface water. Based on the potentiometric surface elevation of the groundwater table, groundwater may also discharge to the surface water body below the elevation of the surface water. It is agreed that the measurement of the seep flow rate cannot alone quantitatively estimate the total flow of groundwater to the surface water. In addition, determination of the seep surface area (needed to estimate the seep flow) will be difficult in some areas (e.g., where the seep surfaces from beneath a rock covered slope). This difficulty will increase the uncertainty in the measurement of the seep flow. Since flow of groundwater to the surface water cannot be accurately measured and the inherent uncertainty in relating the seep flow to the total groundwater flow, quanititative measurement of seeps will be deleted from the plan; however, during the planned site visit, a qualitative estimate of the seep flow rates will be attempted.

   As outlined in the on-shore/off-shore modeling Work Plan, the following text describes how net discharge of groundwater to surface water will be estimated. This information is not integral to the seep sampling plan and so will not be included.

   The total flow of groundwater to the surface water will be quantified using two methods. The first method consists of estimating the total flow of groundwater toward the surface

water body using a simple groundwater flow equation (i.e., Darcy's Law). The total flow of groundwater will be estimated outside of the range of tidal influence. The groundwater flow within the tidal influence zone is complicated due to the cyclic flow of surface water into and out of the ground. The groundwater flow toward the surface water body outside the area of tidal influence must eventually enter the surface water body due to conservation of mass (based on the groundwater flow directions it cannot go elsewhere). The groundwater flow outside the tidal influence zone is the net flow of groundwater to the surface water. Based on data currently available (e.g., hydraulic conductivity, groundwater surface elevations, and geologic cross sections) the total flow of groundwater to surface water can be quantitatively estimated. The second method will consist of performing a water budget. It is anticipated that there is less uncertainty in using Darcy's Law than the water budget. Regardless, there is uncertainty in each method and, hopefully, using both will decrease the uncertainty through confirmation.

3. **Comment**: Seep sample analyses should include all parameters proposed as part of the groundwater monitoring plan for the Jamaica Island Landfill (Table 4-2[1]). See Specific Comment 9.

   Response: There is no reason to sample for TCL volatiles (plus Freon), TPH (gasoline range), TPH (diesel range), phenols, or TOX since these are not off-shore concerns. However, the analysis will be expanded to include the following water quality parameters from Table 4-2 of the groundwater monitoring plan: TOC, chloride, sulfate, pH, and alkalinity. Additionally, as provided in the groundwater monitoring plan, salinity, specific conductance, and oxidation reduction potential (and temperature and dissolved oxygen in response to MEDEP Specific Comment 10; TSS and TDS in response to EPA General Comment 2) will be included as field measurements. Also, as requested, nitrate and bromide analysis will be conducted.

4. **Comment**: Seep sampling data collected by McClaren/Hart must be included in this report.

   Response: Seep sampling data collected by McClaren/Hart will be included as an appendix to the seep sampling plan. In referring to the appendix, the text will note that ..."As identified in the McLaren/Hart Phase I Report, deficiencies in the collection methods contribute to difficulties in evaluating the data. The McLaren/Hart data indicated elevated concentrations of lead, mercury, zinc, chromium, and copper collected from the back side of the Jamaica Island Landfill (Sample number S2). The elevated aluminum, iron, and manganese concentrations could reflect that sediment was present in the seep sample. Subsequent seep sampling by UNH in the same area using improved methodologies did not confirm the McLaren/Hart results." Refer to the attached data.

[1]Brown and Root Environmental, op. cit.

5. **Comment**: Seep identification numbers for the three seep sampling events; McClaren/Hart, UNH, and URI, should be correlated. The numbering scheme differs for each event even though the locations appear similar.

Response: Seep identification numbers for the previous seep sampling events will be correlated by the addition of the following in-text table:

Seep/Mussel Station	*McLaren/Hart Station Number*	*URI Seep Station Number*	*UNH Seep Station Number*
A	—	—	*1001* *1002*
B	—	—	*1003*
C	—	—	*1004*
D	*S1, S2, S3*	*7152* *7252*	*1006* *1007*
E	—	*7151, 7251, 7351*	*1008*

6. **Comment**: To conserve resources, please print on both sides of the page.

Response: The memorandum is copied double-sided (cover and title page are single sided and each major section begins on a new page) in accordance with the Navy Style Guide dated October 1995. Single sided pages are present because three of the four major sections are one page or less in length. No changes will be made in order to maintain a consistent format among documents prepared by the Navy.

7. **Comment**: The final document must be signed and/or stamped by a Maine Certified Geologist.

Response: The final document will be signed by a Maine Certified Geologist.

MEDEP SPECIFIC COMMENTS

1. **Comment**: 2.0 Background, Page 2-1, Paragraph 3

"A work plan for the follow-on sampling..."

Proposed "follow-on" sampling should be described. I don't believe the MEDEP has received a copy of the Offshore Interim Monitoring/Verification and Data Gap Studies. The relationship between the Offshore Interim Monitoring/Verification and Data Gap Studies report and the Offshore Rough Draft Work Plan is unclear. Please clarify and

consider rewriting the paragraph. The first two sentence of this paragraph don't appear to be relevant.

Response: References to the Offshore Interim Monitoring/Verification and Data Gap Studies or the Offshore Rough Draft Work Plan will be removed.

2. **Comment**: 2.0 Background, Page 2-1, Paragraph 4

"With two exceptions, this technical memorandum..."

The MEDEP has not received the Rough Draft Offshore Interim Monitoring/Verification etc. report and therefore cannot comment on the accuracy of these statements. Is the report a "Rough Draft ..." as stated in this paragraph, or an "Offshore Interim..." as stated in the previous paragraph? Consider rewriting the paragraph.

Response: References to the Offshore Interim Monitoring/Verification and Data Gap Studies or the Offshore Rough Draft Work Plan will be removed.

3. **Comment**: 3.0 Objectives, Page 3-1, Paragraph 4

"Contaminant-specific solid/liquid partitioning coefficients and retardation factors can be estimated using the seep concentrations and available sediment concentrations that have been measured around the same area as the seeps."

The development of solid/liquid partitioning coefficients and retardation factors is useful for the estimation of adsorptive properties of ions relative to a solid matrix. While this is an important consideration when assessing contaminant migration, of equal importance are the changes in aqueous chemistry within the landfill groundwater and Clark Cove as a result of the mixing of fresh and saltwater. Changes in ionic strength, pH, and redox conditions which occur through this mixing and groundwater emergence from the landfill can result in precipitation or dissolution of metal ions. The associated chemistry is dependent on the thermodynamic equilibrium of the system and rate of reactions between constituents which may not be easy to predict. However, reliable data must be available for a reasonable estimation of adsorption or solution/solid phase equilibrium.

Meaningful assessment of contaminant migration at the seeps will require concurrent collection of seep water and sediment at the seep locations for each sampling event. At a minimum, sediment samples should be analyzed for TAL metals, SVOCs, and pesticides. If possible, seeps, sediment at seep locations, and groundwater should be sampled concurrently.

Response: Refer to the response to MEDEP General Comment 1 agreeing to add concurrent sediment samples to the scope of work and identifying TCL semivolatiles, TCL pesticides/PCBs, TAL metals, pH, TOC, and AVS analysis for sediments. If possible, seep/sediment and groundwater will be sampled concurrently, depending on the timing of regulatory comment resolution.

4. **Comment**: Table 4-1 Seep Sampling Locations and Analytical Parameters, PNS, Kittery, Maine, Page 4-3

a. "Station Number[2]: Clark Cove - 8, 1004, 1004.8; Sullivan Point - 9; Back Channel - 19, 167"

Would it be possible to assign sample location designations that are less cryptic. (e.g., a simple sequential alphanumeric numbering scheme).

Response: Sample location designations for previously sampled seeps cannot be changed in order to maintain consistency (also requested by NOAA, see NOAA Comment CL-2). Additionally, Figure 4-2 will be revised to show all previous seep sampling locations.

Future sampling designations will be revised. A new section on sample ID numbers (similar to the text in the Groundwater Investigation and Monitoring Plan) will be added. Basically, the UNH station location (1001, 1002, etc.) will be retained with other identifiers to indicate that the sample is a seep sample and to indicate the round of sampling. New seep locations would expand on the UNH station numbering system.

The following text will be added: *"Each sample collected will be assigned a unique sample tracking number. The sample tracking number will consist of a two-segment, alpha-numeric code that identifies the sample medium and location, and sample round identifier. Any other pertinent information regarding sample identification will be recorded in the field log books.*

The alpha-numeric coding to be used in the sample system is explained in the diagram and the subsequent definitions:

(AA[N])	***(NNNN)***	***(AANNNN)***
(Station ID)	*(Sample Location)*	*(Medium & Sampling Date)*

Character Type:
A = Alpha
N = Numeric

Station ID:
BC = Back Channel
CC = Clark Cove
SP = Sullivan Point

Sample Location:
Seep Sample = UNH Station No. (1001, 1002, etc.)
Sediment Sample = UNH Station No. (1001, 1002, etc.)

Media:

SP = Seep
SD = Sediment

Sampling Date:

Month and Year

For example, a seep sample collected from Station 1005 during September 1996 would be designated as BC-1005-SP-0996.

Field quality control (QC) samples will be designated using a different coding system. The QC code will consist of a two-segment, alpha-numeric code that identifies the sample medium (for duplicates only), QC type, and date. The sample medium codes will be used as for the standard environmental sample (i.e., SP). The QC types are identified as:

RB = Rinsate Blanks
FB = Field Blanks
FD = Field Duplicates

For example, a duplicate of a seep sample obtained on September 4, 1996 would be designated as: SPFD-090696. This allows duplicates to be submitted as "blind" samples to the analytical laboratory. Sample log sheets, not received by the analytical laboratory, will document duplicate sample location.

Matrix Spike and Matrix Spike Duplicate (MS/MSD) samples will be designated on the field documentation forms and sample labels. MS/MSDS are collected at a frequency of 1 per 20 samples per matrix and double or triple volumes of sample are required for analytical purposes.

The sampling time recorded on the chain-of-custody form for duplicate and matrix spike/matrix spike duplicate samples will be 00:00 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded in the field log book and on sample log sheets. A separate sample log sheet will be completed for duplicate samples sent blind to the laboratory."

b. "(4) Flow rates may be measured at additional seeps, if identified, as discussed in Section 4.0."

This is not referenced to any statement in Table 4-1.

Response: Flow rates will no longer be measured as stated in the response to MEDEP Specific Comment 8. The footnote will be removed from Table 4-1.

5. **Comment**: 4.1 Sampling Locations, Page 4-2, Paragraph 1

"As part of the seep sampling task, current and previous storm sewer outfalls will be compared with all seep locations to ensure that sampling is not being conducted at a storm sewer outfall, unless appropriate (i.e., infiltration occurring)."

What method will be used to determine if groundwater infiltration is occurring into a storm sewer outfall?

Response: The following text will be added: "Storm sewer outfalls will be observed following an extended period (at least 48 hours) of dry weather when no stormwater flow would be expected. Therefore any flow would be attributed to groundwater infiltration. In support of investigating storm sewers, a records review is planned, followed by a camera survey inspection and mapping effort."

6. **Comment**: 4.2 Sample Collection Procedures, Page 4-4, Paragraph 2

"The sampling device will be installed by excavating soils/fill from the side of the band at the seep location and inserting the capped well screen into the hole. The space around the well screen would then be filled in."

The area around the well screens must be filled using appropriate sized filter sand to prevent clogging of the screen.

Response: The sampling device is pre-packed with sand to prevent clogging. This sentence will be added to the text.

7. **Comment**: 4.2 Sample Collection Procedures, Page 4-4, Paragraph 3

"The seep sampling device with the pre-packed well screen..."

Does this mean the interior portion of the well screen will be packed with filter sand?

Response: Yes, the area between the outer and inner well screen is packed with sand. This explanation will be added to the text.

8. **Comment**: 4.2 Sample Collection Procedures, Page 4-4, Paragraph 5

"Flow rates will be measured for all seep locations where sampling devices have been installed. Flow rates will be measured by placing a vessel of known volume (e.g., graduated cylinder of 5 gallon bucket) and measuring the time it takes to fill the vessel. The flow rate will be used to approximate the seep flow velocity."

Measurement of flow rates in this manner assumes that the total volume of the seep water will flow through the sampling device, which is very unlikely. Perhaps a two dimensional measurement rather that a volume measurement would provide more reliable results. For

example, the physical timing of a liquid or solid tracer may be effective in estimating seep flow rates. Regardless of the measurement method, the seep surface area must be determined to estimate the total seep volume.

Response: Refer to the response to MEDEP General Comment 2. Quantitative measurement of seeps will be deleted from the plan (although during the site visit, a qualitative estimate of the seep flow rates will be attempted). Instead, Darcy's Law and a water budget will be used during the on-shore/off-shore modeling effort.

9. **Comment**: 4.3 Analytical Testing Parameters, Page 4-7, Paragraph 2

"The selected parameters are the COCs identified in the EERA and the Human Health Risk Assessment (McLaren/Hart, 1994) or are crustal metals (Fe, Al, and Mn) useful for comparison."

The MEDEP believes there is a discrepancy between the parameters proposed for the Draft Groundwater Investigation and Monitoring Plan[2] and those proposed for the analysis of seep samples. The seeps will provide information regarding groundwater which is being released directly to the Piscataqua River. The MEDEP proposes seep sample analyses include all parameters proposed as part of the groundwater monitoring plan for the Jamaica Island Landfill (Table 4-2[3]). The rationale behind this is based on the assumptions used for the proposed groundwater analyses at the JILF.

The MEDEP proposes that, in addition to the proposed TAL inorganic analyses included groundwater monitoring plan[4], the major anions (Cl^-, So_4^{2-}, NO_{3-}, Br^-, and alkalinity) be analyzed for each seep sample. Inclusion of these additional anions in the monitoring plan would provide complete major ion chemistry for each monitoring location. The MEDEP sees the following benefits for performing these additional analyses:

- Results from comprehensive major ion analyses would provide a general chemical characterization of seep quality relative to groundwater conditions within the JILF;
- Comparison of total ion chemistry using stiff and/or piper diagrams may reveal common or distinct sources of groundwater between groundwater and seep monitoring locations and dilution effects by intrusion of river water within tidal portions of the aquifer;
- Charge balances can be performed on total ion chemistry to assess the quality of laboratory results; and

[2]Brown and Root Environmental, Draft Groundwater Investigation and Monitoring Plan for Portsmouth Naval Shipyard, Kittery, Maine, April 1996.

[3]Brown and Root Environmental, op. cit.

[4]Brown and Root Environmental, op. cit.

- Finally, geochemical modeling can be performed on total ion chemistry and field parameters (e.g. Eh, DO, pH) using equilibrium computer models such as MINTEQ or PHREEQE. The models have the ability to assess aqueous speciation and possible precipitation of inorganic components for groundwater under equilibrium conditions. Higher ion strength solutions (greater than 0.5 M) may require expansion of the activity coefficient equations[5]. This may be helpful in determining the groundwater transport of metals within the aquifer.

Response: Refer to response to MEDEP General Comment 3 concerning parameters included for seep samples.

Although it is agreed that the collection of water quality parameters can be used qualitatively to aid in fate and transport analysis, geochemical modeling will add insignificant value to the project when direct measurements of contaminant concentrations are available. Geochemical modeling will not be included. Geochemical modeling of the fate of contaminants in the natural environment is best used to interpret field and/or laboratory measurements. However, the uncertainty of typical geochemical modeling is still too high to be used alone as a predictive tool for remedial decision making in complex environments.

Most geochemical models require data from a typical chemical analysis (i.e., the concentrations of various elements or species). Other inputs such as alkalinity, pH, Eh, temperature, and solution density are also required, as well as specification of the aqueous species needed to balance the charge and ensure electrical neutrality. In general, two types of codes are used to model aqueous and solution geochemistry: distribution-of-species codes, which represent the thermodynamics of a static system, and reaction-progress codes, which examine the consequences of an evolving system in which various phases in a system react with one another. The comment suggests the use of distribution-of-species codes assuming the site is under equilibrium conditions. However, under steady-state equilibrium conditions, the direct measurements of contaminant concentrations in groundwater and seep samples will reflect the effects of all the on-going geochemical processes between the source and discharge point. Therefore, the measured contaminant concentrations will provide all the necessary information for risk assessment purposes. Geochemical modeling can only confirm the direct measurements.

10. **Comment**: 4.3 Analytical Testing Parameters, Page 4-7, Paragraph 2

"Salinity will be measured in the field."

Field parameters including pH, specific conductance, temperature, dissolved oxygen, and Eh should also be measured in the field.

[5] Allison, J.D., et. al., Minteqa2/Prodefa2, A Geochemical Assessment Model For Environmental Systems: Version 3.0 User's Manual, Environmental Research Laboratory, Office of Research and Development, USEPA, Athens, Georgia, March 1991.

Response: Specific conductance, pH, temperature, dissolved oxygen, and Eh will be added to the list of field parameters.

11. **Comment**: Appendix A, Previous Seep Sampling Information, Table 5-6, Page 5-91

Mean results values reported for sample locations 1006 and 1007 are exactly the same with the exception of Mn. Review of the raw data indicates this is probably a transcription error in the table.

Response: Agree. NCCOSC has provided a corrected version of the table which will replace the existing table of Appendix A.

RESPONSE TO NOAA COMMENTS DATED MAY 17, 1996
DRAFT TECHNICAL MEMORANDUM ON SEEP SAMPLING
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

CL-1 Cover Letter Comment: Previously, 8 seep samples were collected in the Spring of 1993 and another 5 in the fall of 1993. In this workplan, the Navy is committing to only 6 seep locations although they mention that "up to 14 additional seep locations may be identified during field activities." I am puzzled why all the seep locations previously sampled in 1993 are not included as definite sampling locations.

Response: Seep sampling locations will be selected in consultation with the regulators following a site visit to identify seeps. The number of seeps selected for sampling will be dependent on feasibility of sampling (access), proximity to other seeps, past sampling, flow volume, proximity to contamination sources, etc.. The 20 seep sampling locations were used for budgetary purposes only and the actual number of seep samples is expected to be lower based on previous seep sampling events; references to 20 seep sampling locations will be removed from the plan.

Although 6 seep sampling locations were planned under future off-shore monitoring activities, it is agreed that to begin with, all 8 stations (UNH) should be sampled regardless of previous results. The plan will be revised to incorporate the 2 additional locations. The 5 samples collected in the fall of 1993 (by URI) were not collected at new stations.

CL-2 Cover Letter Comment: Some of the seep location numbering is confusing. Spring 1993 seep samples at Sullivan Point were numbered 1001, 1002, and 1003. Now the sample number is 9. In addition, Back Channel seep location numbers are shown as #s 16 and 167. Do they correspond with Spring/1993 seep sample locations 1005, 1006, or 1007? It would be wise to reoccupy previous seep locations (e.g., as was done for seep location #1004 in Clark Cove) keeping the numbering consistent and all new locations (and new location numbers) as appropriate.

Response: Agree. Numerous sample location designations have been previously used, as well as identification of seeps by biota sampling location. The plan will be revised to identify sample location designations for previously sampled seeps as 1001, 1002 .. 1008 based on the UNH identification system. New seep stations will continue with 1009, etc.

RESPONSE TO EPA FOLLOW-UP COMMENTS DATED AUGUST 9, 1996
DRAFT GROUNDWATER INVESTIGATION AND MONITORING PLAN
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

EPA found the Navy's responses satisfactory, but continues to recommend the following:

1. **Follow-up to Specific Comment No. 4 (09Aug96)**: (Page 1-4, Section 1.3, part 4); The Plan should acknowledge that additional rounds of water levels may be required to properly characterize groundwater flow patterns and dynamics.

   Follow-up Response: The following sentence will be added: *"In the future, additional rounds of water levels may be required to properly characterize groundwater flow patterns and dynamics."*

2. **Follow-up to Specific Comment No. 5 (09Aug96)**: (Page 1-4, Section 1.3, part 4); The Plan should include provisions to install additional monitoring wells, if necessary, to characterize the extent of potential LNAPL contamination, before designing a removal system. This would allow the development of a better design, potentially reducing the costs of remediation significantly.

   Follow-up Response: The following sentence will be added: *"The first event analytical results may identify "hot spot" or other interest zones where more frequent monitoring is required in the future."*

3. **Follow-up to Specific Comment No. 6 (09Aug96)**: (Page 3-1, Section 3.1); The Navy is strongly encouraged to install piezometers to characterize groundwater levels and flow patterns more completely than can be done with water levels measured only at perimeter monitoring wells.

   Follow-up Response: The following sentence will be added: *The first event water level measurements may identify areas where piezometers should be installed to more completely characterize groundwater levels and flow patterns."*

4. **Follow-up to Specific Comment No. 10 (09Aug96)**: (Page 4-1, Sampling and Analysis); Although we understand that the Navy wants to limit the number of parameters tested for at this stage of the project, we continue to suggest that the design could be expedited if data for design of the treatment system were collected now. One possible way of doing this would be to review the data collected from the first round of sampling, and determine whether or not the design could be expedited by sampling specific wells for design-related parameters as part of the second round of sampling.

   Follow-up Response: The following text will be added: *"Subsequent to the first sampling event, design-related parameters may be included in the future to expedite any groundwater remediation design, if any. It is currently unknown whether any groundwater*

remediation is required; this decision depends on the results of the contaminant fate and transport modeling."

5. **Follow-up General Comment (09Aug96)**: EPA also requests that the Navy forward a schedule for the groundwater monitoring program to our office. This will ensure that EPA can provide oversight during the first sampling event.

Follow-up Response: The EPA (and MEDEP) will be informed of all groundwater sampling events, including the pilot test for low flow sampling. The field work will be scheduled after resolution of regulatory agency comments on the subject planning document.

RESPONSE TO MEDEP FOLLOW-UP COMMENTS DATED JULY 16, 1996
DRAFT GROUNDWATER INVESTIGATION AND MONITORING PLAN
PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

MEDEP GENERAL FOLLOW-UP COMMENTS

- **MEDEP Follow-up Comment:** The Navy's response refers to the following comment from the MEDEP review of the initial Draft Interim Groundwater Monitoring Plan dated May 1995:

  [Comment no. 17 from MEDEP 7/3/95 letter repeated below]

  17.) 4.3.4 Well Purging, Page 4-24, Paragraph 5

  "Prior to obtaining samples, water levels will be measured and the wells will be purged using a dedicated bailer or a 2-inch submersible pump or a peristaltic pump." "Low flow sampling will be employed if possible."

  To ensure comparability of groundwater data, sample collection methods should be consistent between all monitoring wells. The protocol for collecting low-flow samples presented in the GMP must be consistent with EPA procedures. The following EPA documents are attached for guidance in developing low-flow sampling procedures for the GMP.

  - EPA, RCRA Groundwater Monitoring: Draft Technical Guidance, Office of Solid Waste, USEPA, Washington, DC., November 1992.
  - EPA, Groundwater Sampling Procedures Low Flow Purge and Sampling; SOP# GW 0001, Draft Final, August 10, 1994.
  - EPA, Low Flow Purge and Sample Data Sheet, Revised June 30, 1995.

  The primary concern of the MEDEP in the initial draft work plan was the proposed use of bailers for the collection of groundwater samples. Our comment could have been more specific in this regard, but given the preliminary stage of the monitoring plan, the MEDEP believed that at that point we must emphasize the importance of consistency in sample collection methodology and compliance with EPA procedures. In order to avoid future misinterpretations, the MEDEP requests that the Navy communicate with the MEDEP if questions arise stemming from any of the MEDEP's comments.

  The Navy initiated a conference call with the MEDEP on June 6,1996 to discuss our May 15, 1996 comment concerning the use of peristaltic pumps at low yielding wells. During the conference call the MEDEP expressed concerns that low-flow sampling using a bladder pump may not be effective in low yielding wells. The Navy noted that the use of a peristaltic pump may cause a potential loss of volatile organic compounds from groundwater samples. The MEDEP indicated it was our understanding that the loss of volatiles would be minimal and that a peristaltic pump could be used to meet drawdown and turbidity requirements if bladder pumps were unable to do so. The Navy indicated

that they intend to have peristaltic pumps on hand for the pilot study, and will use these pumps at the low K wells, if the requirements of low-flow sampling cannot be met using the bladder pumps.

The MEDEP is committed to assessing advances in Low-Flow sampling technology. The most current Low-Flow sampling information is outlined in EPA's Groundwater Issue Document on Low-Flow Sampling[1] and the DEP Information Sheet on Low-Flow Groundwater Sampling[2]. It is the MEDEP understanding that the use of peristaltic pumps, though not considered optimal, is not discouraged if conditions are not conducive to the use of bladder of submersible pumps (e.g. low hydraulic conductivity's and shallow groundwater).

- **Navy Follow-up Response**: As stated previously, the Navy's original intent on this Plan (May 1995 initial Draft Interim Groundwater Monitoring Plan) was to use peristaltic pumps on shallow monitoring wells (less than 20-feet) and wells which exhibited slow recovery; while installing low-flow submersible pumps in the remaining wells. However, the MEDEP commented (Comment no. 18) that "use of a peristaltic pump is limited to wells with water levels of approximately 20-feet or shallower. Therefore, submersible pumps designed for use in 2-inch diameter wells are preferable to maintain sampling consistency between wells." The Navy has since committed to installing low-flow submersible pumps into as many wells as possible for the sake of consistency. Peristaltic pumps will only be used in monitoring wells which exhibit slow recovery or a lack of sufficient groundwater to submerge the pump in during the low-tide cycle.

MEDEP SPECIFIC FOLLOW-UP COMMENTS

9. **MEDEP Follow-up Comment: 3.3 Surveying, Page 3-7, Paragraph 2**: The MEDEP was not aware of the Navy's intention to use GIS at PNS. The MEDEP believes the use of GIS is important for the assessment of contaminant distribution on both the off-shore and on-shore environment at PNS. The MEDEP has already located the monitoring wells at PNS by digitizing figures provided with the RFI Data Gap Report. The MEDEP requested the survey information for comparison to digitized locations. Sediment sample locations have also been located using latitude/longitude data provided with the off-shore databases. The MEDEP has been using, and will continue to use, GIS to assess historical and future sample data. Any information the Navy can contribute will be appreciated.

   Navy Follow-up Response: As additional data becomes available, it will be provided to MEDEP.

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[1]Puls, Robert, W., Michael J. Barcelona, EPA Groundwater Issue, Low-Flow (Minimal Drawdown) Groundwater Sampling Procedure.

[2]MEDEP, DEP Information Sheet, Low-Flow Groundwater Sampling; issued: June 1996.

12. **MEDEP Follow-up Comment: 3.4.1 Available Groundwater Monitoring Data, DRMO Salvage Yard, Page 3-8, Paragraph 3:** This response does not address the issue. If DW-4 and DW-10B are contaminated due to tidal effects as indicated in Section 3.4.1, then they re not appropriate upgradient wells for the DRMO.

Navy Follow-up Response: The intent of the initial groundwater monitoring is to collect groundwater data to establish conditions for subsequent sampling; not to establish which monitoring wells are positioned upgradient at the DRMO. If and when additional fieldwork is performed at the DRMO, gradient may be established based on existing and future data. All existing monitoring wells are included in the monitoring program.

19. **MEDEP Follow-up Comment: Tables 4-1 thru 4-5, Rational for Selection of Analytes, Groundwater Monitoring, PNS, Kittery, Maine, Pages 4-5 thru 4-14:** As stated in the initial comments, the MEDEP believes the use of geochemical equilibrium computer models may be helpful in assessing the aqueous characteristics of metal contaminants. These models require the input of inorganic analysis results for filtered groundwater samples. The current proposal limits the number of filtered inorganic analysis to approximately 15% of the total number of samples collected. In order to use geochemical models effectively, monitoring wells where metal contamination is a concern (e.g. JILF) should be sampled and analyzed for both filtered and unfiltered inorganic constituents.

Navy Follow-up Response: The Navy disagrees with the reliance on geochemical modeling. Geochemical modeling of the fate of contaminants in the natural environment is best used to interpret field and/or laboratory measurements. However, the uncertainty of typical geochemical modeling is still too high to be used alone as a predictive tool for remedial decision making in complex environments.

Currently not enough data exists to complete geochemical modeling. After completion of the interim groundwater monitoring and seep/sediment sampling programs, more data for geochemical modeling will be available, however, not all. Most geochemical models require data from a typical chemical analysis (i.e., the concentrations of various elements or species). Other inputs such as alkalinity and solution density are also required, as well as specification of the aqueous species needed to balance the change and ensure electrical neutrality. In general, two types of codes are used to model aqueous and solution geochemistry: distribution-of-species codes, which represent the thermodynamics of a static system, and reaction-progress codes, which examine the consequences of an evolving system in which various phases in a system react with one another. Assuming steady-state equilibrium conditions (static system), the direct measurements of contaminant concentrations in groundwater and seep samples will reflect the effects of all the on-going geochemical processes between the source and discharge point. Therefore, the measured contaminant concentrations will provide all the necessary information for risk assessment purposes. Geochemical modeling can only confirm the direct measurements.

Geochemical modeling can only add insignificant value to the project since limited data presently exists to complete geochemical modeling and once the analytical results of the interim groundwater monitoring and seep/sediment sampling programs are available,

the measured contaminant concentrations will provide all of the information necessary for risk assessment purposes.

34. **MEDEP Follow-up Comment: Data Management and Reporting, Page 6-2, Paragraph 1**: The MEDEP maintains that inclusion of field parameters in the database is important for it's overall usefulness. Comparison of field parameters such as pH, Eh, dissolved oxygen, and turbidity are important factors in controlling the characteristics of groundwater chemistry. Comparison of these parameters to other chemical constituents is only complicated if they are not included with the original database.

Navy Follow-up Response: The Navy will make modifications to the data base to allow for the incorporation of the field parameters (i.e.; pH, specific conductance, temperature, dissolved oxygen, Eh, and turbidity).

7/3/96 Comment Response Letter Addressing

EPA and MEDEP Comments

DEPARTMENT OF THE NAVY
NORTHERN DIVISION
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY
MAIL STOP, #82
LESTER, PA 19113-2090

IN REPLY REFER TO

5090
Code 1823/JMC

JUL 0 3 1996

MEMORANDUM -

FOR THE MEMBERS OF THE RESTORATION ADVISORY BOARD (RAB), INSTALLATION RESTORATION PROGRAM, PORTSMOUTH NAVAL SHIPYARD, KITTERY, MAINE

Enclosed are the responses to regulatory comments on the Draft Groundwater Investigation and Monitoring Plan for Portsmouth Naval Shipyard. If you have any comments or questions on this document, they can be provided to the Navy at a RAB meeting, by calling the Public Affairs Office at (207) 438-1140 or by writing to:

Portsmouth Naval Shipyard
Code 121.10 Bldg 44
Attn Fran Endyke
Portsmouth, NH 03804-5000

As always, we appreciate your time and efforts spent in support of the Portsmouth Naval Shipyard Installation Restoration Program.

Sincerely,

Jim Conroy

JAMES M. CONROY, PE
LT, CEC, USN
Remedial Project Manager
By direction of the
Commanding Officer

Encl: Response to Comments

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Shipyard (Code 121, 121.10, 100PAO) w/o encl
Brown and Root Environmental (L. Klink) w/o encl
Brown and Root Environmental (B. Horne) w/o encl

RESPONSE TO EPA COMMENTS DATED JUNE 5, 1996
DRAFT GROUNDWATER INVESTIGATION AND MONITORING PLAN
PNS, KITTERY, MAINE

GENERAL COMMENTS

1. Comment: It is recommended that a detailed review of data coverage be performed after the first round of sampling and analysis is completed. At this time, we must make the assumption that the set of wells selected for the first round of sampling is adequate for meeting the objectives of the program. However, all parties should acknowledge that additional locations for sampling may need to be defined, based on analysis of the data collected and on the analysis and modeling that will be performed using the data. This aspect of the Monitoring Plan is highly important, because the overall approach should be to collect some data, improve and update the conceptual model(s) of the site, identify significant data gaps, fill them, and then collect more data – in a more focused way. This focus can only be gained by analyzing the data. Such modifications will include deletions, additions, and changes in which wells are sampled and what analytical testing is done.

   Response: Agree.

SPECIFIC COMMENTS

1. Comment: Page 1-1, Section 1.2, 1st paragraph

   The St. sentence says the objective of the Plan is to "provide information [on low-flow sampling]" and to "facilitate implementation ... of the long-term groundwater monitoring plan." However, the second sentence says that the data collected will be used to determine impacts. The overall objectives should be clarified. The second sentence should tell how the data will be used to determine impacts.

   Response: The second sentence will be revised to read: "The data will be used *as input concentrations for the offshore migration modeling effort* to determine the sites impact on the quality of groundwater in the aquifer and impact on State waters.

2. Comment: page 1-2, Section 1.3, part (1)

   It is good to see the use of "indicator" parameters that are not part of the TCL/TAL list. However, the specific parameters should be listed in the Plan, if possible, and the text should not say "may be tested" if specific parameters can be identified now. If it is not possible to list specific parameters now, then a list of candidate parameters should be presented, and guidance and/or criteria given that will be used for deciding whether or not to include them in the Plan.

Response: In response to MEDEP comments, indicator parameters (TOC, TOX, pH, nitrate, bromide, chloride, sulfate, and alkalinity) will now be analyzed throughout for each of the monitoring wells sampled during the first and second event sampling at PNS. In addition, pH and specific conductivity will be measured both in the field and in the laboratory and specific conductivity will be measured in the field. The text will be modified accordingly.

3. **Comment**: Page 1-3, Section 1.3, part (2)

The use of "tailored" analytes, and of lower-cost but adequate analytic procedures in concept is acceptable. However, these analyte series and testing methods must still meet the requirements for demonstrating potential impacts, and as stated in the text they must be approved by the agencies prior to implementation. In addition, the Navy must ensure comparability of data from round to round, especially as applies to the statistical analysis of trends and significance.

Response: Agreed. As already stated in the plan, future modifications to the Groundwater Investigation and Monitoring Plan regarding the addition or deletion of analytical parameters will be made with concurrence from the EPA and MEDEP.

4. **Comment**: Page 1-4, Section 1.3, part (4)

Two rounds of water levels annually may not be sufficient for characterizing groundwater flow patterns and dynamics. Additional rounds may be useful at selected wells. Such a determination can be made without delaying approval of the Plan. However, the Plan should acknowledge that water level data collection is driven not only by contaminant impact identification, but more so by the requirements of groundwater flow pattern analyses, including modeling.

Response: At the current time, it is not anticipated that additional rounds of water-levels will be collected other than those identified in the Groundwater Investigation and Monitoring Plan.

5. **Comment**: Page 1-4, Section 1.3, part (4)

The Plan should acknowledge that there may be locations (wells) where additional sample collection may be warranted, based on the results of the first round(s). For example, if LNAPL is still found in one or more of the FW series wells, it may be worthwhile tracking the LNAPL thickness more frequently than twice annually. The Plan should therefore acknowledge that the first round may identify "hot spot" or other "interest" zones where more frequent monitoring is warranted.

Response: It is not the intent of the Groundwater Investigation and Monitoring Plan to evaluate whether additional groundwater sampling is merited between the first and second event sampling rounds. Additional sampling will be recommended, if necessary, in the Groundwater Investigation and Monitoring Report following the second sampling event. For the given example, if free phase product is encountered it will be removed rather than monitored.

6. **Comment**: Page 3-1, Section 3.1

The mapping of wells (Map A) shows a lack of monitoring points in the interior section of the islands. From the perspective of groundwater flow analysis and modeling, this may prove to be a serious shortcoming for model development and calibration efforts. Similar to another comment above, this should not be a reason to delay the Plan's implementation. The Plan's emphasis is properly on the collection of contamination data along the perimeter of the islands, as the highest priority, and in the source areas as well. For the water level collection efforts, it may be more appropriate for the Navy to develop an addendum to the Plan, or a separate plan, specifically for the collection of water level data. This would offer the opportunity for the Navy's consultants to tailor the water level sampling to the needs of groundwater flow analysis and modeling, which are in some ways significantly different from the needs of perimeter and source are monitoring.

Response: As indicated previously, additional sampling may be recommended at the completion of the second sampling event. In response to the development of an addendum to the Groundwater Investigation and Monitoring Plan which addresses water level collection; there are currently no plans to undertake this activity, however during future field work, piezometers could be installed to provide additional groundwater level information.

7. **Comment**: Page 3-7, Section 3.4.1

This section contains the specification of how MPSs will be sued to help select analytes. This section only acknowledges MPSs without mentioning the use of "indicator" or "tracer" parameters. This section should acknowledge other criteria that may be used for selection of parameters, not just the MPS-related ones.

In addition, it should be noted that groundwater data that is lower than the on-shore MPS will not be valid justification for omitting wells/parameters from the sampling program, since the on-shore MPS are reflective of protection of human health only do not take potential impacts to the off-shore environment into account.

Response: Agreed. The text will be modified accordingly.

8. **Comment**: Page 3-11, Fuel Storage Area

EPA notes that this "site" must be redefined by the parties. As such, determining the appropriate sampling program for the area cannot be done. Specifically, identifying "cross-gradient" wells is difficult until the site is fully defined.

Response: Agree. Currently all of the existing RFI and RFI Data Gap wells are being sampled. If new wells are installed in the future, they will be included in the groundwater monitoring plan.

9. **Comment**: Page 3-11, Section 3.4.3

This section does not appear complete or pertinent.

Response: Section 3-11 will be deleted from the text.

10. **Comment**: Page 4-1, Sampling and Analysis

In general, the Plan should include analysis-testing for parameters that are needed for design of remediation systems. For example, if groundwater pumping and treatment may be used, even in limited zones, then parameters affecting treatment system performance should be analyzed for, if possible.

Response: At the current time, additional parameters are not being considered for analysis. Alkalinity and TOC are two key parameters already included in the sampling program that were not part of the RFI. Additional parameters may be recommended, if necessary, after the first and second event sampling rounds and as the need becomes apparent (as a site approaches the design phase). For feasibility study purposes, existing data is adequate.

11. **Comment**: Section 4 Tables

Those tables listing analytes should include any field parameters that are to be tested for, and any "conventionals" to be tested in the lab. Such parameters include but are not limited to: pH, eH, DO, turbidity, specific conductivity, and temperature. Some of these parameters may be very useful in evaluating and identifying impacted groundwater. Others, like temperature, are needed so that empirical equations for determining hydraulic conductivity are properly corrected for ambient conditions.

Response: These tables present parameters to be analyzed by a fixed-base laboratory. Field parameters are identified in the footnotes at the bottom of Table 4-8. Any modifications occurring during the review process will be noted.

12. Comment: Page 4-22, Section 4.3

The standard operating procedures should ensure that the water level readings to be conducted on or near the same dates as the water quality sampling, are not disturbed by the sampling. Water levels should be collected in advance of the sampling. This is especially important in any low-yield wells.

Response: Agree. This is standard Brown & Root Environmental practice. A sentence will be added to the text to read "water level measurements will be obtained before purging and sampling activities are conducted."

13. Comment: Page 4-32

It must be noted in the Plan that EPA and DEP should be consulted prior to implementing any deviations to an approved work plan.

Response: The following sentence will be added at the end of Paragraph 5: The EPA and MEDEP will be consulted of any scope changes that may occur while fieldwork is ongoing.

14. Comment: Page 5-1, Section 5.1

Similar to EPA's previous comment on the 1995 Plan, data validation using current Region I guidelines is strongly recommended for the planned re-sampling events. If data collected during the re-sampling events are not validated, potential data problems could be missed; the consequences of addressing such problems at a later date could result in significant expense and schedule delays.

Response: The Navy has decided to change the data validation scope provide complete data validation of 10% of the data. The plan to perform limited data validation separately from what the analytical lab conducts will be dropped from the workplan. Depending on the findings from validating 10% of the samples, further validation can be conducted if warranted. The plan will be revised accordingly.

15. **Comment**: Page 5-2, 4th paragraph, 2nd sentence

The three reasons for concluding that "statistics (sic) are not expected to be utilized in determining variance" are not valid. (1) Statistical techniques may be used to evaluate situations where contaminant migration has occurred. These techniques are detailed under corrective action monitoring in RCRA guidance referenced later in this section of the Navy's report. (2) Multivariate statistical techniques can often help discern contaminant behavior in complex geologic settings. (3) The distribution of contaminants in impacted groundwater would not be expected to follow a normal distribution but transformations that would allow for parametric statistics to be applied should be considered. Even if transformations are not successful the use of distribution free statistical techniques should not be dismissed outright.

Response: Agreed. Statistical assessments were not dismissed outright. However, the Navy believes statistics will only have limited use based on site conditions (tidal influences, non-homogeneous fill, difficulty in establishing upgradient and downgradient monitoring locations).

16. **Comment**: Page 5-2, 4th paragraph, 3rd sentence

Data that follows a log normal distribution is skewed to the left or towards the detection limit.

Response: The sentence will be changed to read "to the right".

17. **Comment**: Page 5-3, 4th paragraph, last sentence

Statistical methods are only useful if properly applied and interpreted. How will the navy determine if a statistical analyses is useful?

Response: Joint efforts between the Navy, EPA and MEDEP will determine the usefulness of statistical analyses.

18. Comment: Page 5-3, St. paragraph

The tolerance interval approach for comparison of downgradient data for each constituent to the background data is inappropriate. The USEPA's Addendum to the Statistical Guidance Document for Groundwater Monitoring (1992) indicates that the tolerance interval approach should be used when downgradient data is being compared to an established ACL or MCL for those cases where a release has been determined (even in these cases use of tolerance intervals has been shown to result in unacceptably high false positive rates). comparison of downgradient data to upgradient data should be performed using confidence intervals. If contamination has not been established prediction intervals or control chart procedures should be used.

Response: Agreed.. The text will be modified accordingly. However, most sites are adjacent to the river and there is no downgradient.

19. Comment: Page 5-3, 3rd paragraph

EPA does not believe that the proposed approach is a valid statistical procedure. Corrective action monitoring procedures employing confidence intervals should be used.

Response: Agreed. The text will be modified accordingly.

21. Comment: Page 7-1, Section 7.0

The second to last sentence in this section should be rewritten as follows: "Frequency of monitoring will be determined based on consultation...; it is expected that monitoring will occur semi-annually until such time that remedial decisions are made pursuant to CERCLA."

Response: The frequency of future sampling events beyond the initial first and second events cannot be committed to at the current time by the Navy. Decisions regarding future monitoring will be made in consultation with the EPA and MEDEP. The sentence will be modified as suggested except "may occur" will be used rather than "will occur".

RESPONSE TO MEDEP COMMENTS DATED MAY 15, 1996
DRAFT GROUNDWATER INVESTIGATION AND MONITORING PLAN
PNS, KITTERY, MAINE

MEDEP GENERAL COMMENTS

- **Comment**: Low-flow sampling protocols at PNSY should be modified to meet the requirements of EPA final low-flow sampling guidance once it is available in the next several months. (See Comment No. 16.)

  Response: The Region I EPA final low-flow sampling procedures will be incorporated into the future Groundwater Monitoring Plans' purging and sampling requirements being used at PNS when they become final and as appropriate given specific site conditions. The interim low flow sampling procedures appended in the Groundwater Monitoring Plan will be used until the final guidance document is approved.

- **Comment**: The MEDEP strongly recommends the groundwater monitoring pilot study assess the use of peristaltic pumps as well as the proposed bladder pumps, particularly on monitoring wells with low hydraulic conductivity. The MEDEP has found that for certain low hydraulic conductivity wells, use of a peristaltic pump is the only effective means of meeting low-flow sampling drawdown and turbidity requirements. (See Comment No. 13.)

  Response: The MEDEP makes a good point with the recommendation of using peristaltic pumps at certain locations. It was the intent of the Navy to use both submersible bladder pumps (deeper high yield monitoring wells) and peristaltic pumps (shallow low yield water table wells) initially; however, in the last version of the plan the MEDEP made exception, citing the need for consistency and specifying the use of like pumps for all wells. In addition, the EPA Region I Low-Flow Guidance Document does not recommend the use of peristaltic pumps during groundwater sampling for VOCs. The pilot study will include a low yield well. A peristaltic pump will be made available during the pilot study in case the bladder pump cannot maintain a low enough flow rate.

- **Comment**: The MEDEP proposes that, in addition to the proposed TAL inorganic analyses, the major anions (Cl^-, SO_4^{2-}, NO_3^-, Br^-, and alkalinity) be analyzed for each water sample collected for the initial two sampling rounds. (See Comment No. 15.)

  Response: Chloride and sulfate were already included throughout as part of the initial analytical suite as was alkalinity for approximately 80 percent of the monitoring wells. Alkalinity will be added to the remaining 20 percent of the monitoring wells and the additional requested anions (nitrate and bromide) will be added to the analytical suite.

- **Comment**: The Final Report must be stamped and signed by a Maine Certified Geologist.

Response: The standard practice for PNS reports and work plans has been to have the final version reviewed and signed by a Maine Certified Geologist. The final report will be signed by a Maine Certified Geologist.

MEDEP SPECIFIC COMMENTS

1. **Comment**: 1.3 Approach, Page 1-2, Paragraph 2

"Monitoring wells previously installed throughout PNS (to evaluate groundwater parameters and geology) will be re-sampled. This sampling effort will be conducted to determine if the spatial distribution of chemicals in groundwater have changed over the last several years."

The low-flow sampling methods proposed for the current sampling effort are significantly different from sampling techniques associated with previous water quality data. Sample collection methods should be considered when comparing historical water quality results with data generated from the current investigation.

Response: The sentence will be revised to read: "This sampling effort will be conducted *and a qualitative assessment will be performed* to determine if the spatial distribution of chemicals in groundwater have changed over the last several years. *A quantitative comparison may not be possible when comparing historical water quality results with data generated from the current investigation due to differences in sampling techniques.*"

2. **Comment**: 1.3 Approach, Page 1-2, Paragraph 3

"Also, indicator parameters may include pH, specific conductance, total organic carbon (TOC), total organic halogen (TOX), chloride, and sulfate."

The parameters pH and specific conductance are routinely monitored and recorded as part of the low-flow sampling methodology. does the above statement imply laboratory pH and specific conductance will also be performed?

Response: pH and specific conductivity will be measured and recorded in the field as part of the low-flow sampling. Additionally, pH will be analyzed in the laboratory.

3 **Comment**: 1.3 Approach, Page 1-3, Paragraph 1

"It is anticipated that those wells installed solely to investigate site hydrogeology and those wells in excess of that required for adequate upgradient and down gradient monitoring of a site will be excluded for subsequent long-term monitoring rounds."

The Navy, MEDEP, EPA, and the RAB must reach a consensus regarding future monitoring locations and sampling frequency based on a careful review of the initial two rounds of monitoring and all other pertinent information.

Response: We agree that it is best to have all parties concurrence on all aspects of the IR Program. We agree that the Navy, EPA and MEDEP should hopefully agree on future efforts, however the RAB is not a consensus body. We do take seriously the concerns of the RAB members and will address them to the extent practical. No changes to the text are necessary.

4. **Comment**: 3.1 Monitoring Well Locations, Page 3-1, Paragraph 1

"The location of all existing wells proposed for monitoring can be found on the enclosed Map A."

In addition to wells proposed for monitoring, Map A should identify all the islands by name.

Response: Map A will be revised to include the location of Pumpkin Island and Fernald Island.

5. **Comment**: 3.1 Monitoring Well Locations, Page 3-1, Paragraph 2

"To elaborate, two of the existing former waste oil site monitoring wells (installed during Phase VI) will be replaced. New monitoring well HW-2 will replace damaged monitoring well WOT-6. New monitoring well HW-3 replaces monitoring well WOT-1; the screened interval of the new well extends into shallow bedrock. These new monitoring wells will be located during implementation of the Groundwater Investigation and Monitoring Plan."

Remove "To elaborate", clarify by spelling out which "new well extends into shallow bedrock", and change "wells will be located..." to "have been installed...".

Response: The 2nd paragraph will revised to read: "Two existing monitoring wells at the former waste oil site have been damaged and are being replaced with overburden monitoring well HW-2 (replacement for WOT-6) and shallow bedrock monitoring well HW-3 (replacement for WOT-1), respectively. These two additional monitoring wells will be identified and located during the implementation of the Groundwater Investigation and Monitoring Plan."

6. **Comment**: 3.2.1 RFI Data Gap Monitoring Wells, Page 3-1, Paragraph 2

HW-2 and HW-3 were both drilled to a depth of 12 feet. HW-2..."

Consolidate information by either moving this paragraph up to 3.1, para 2, or moving 3.1, para 2, down to this section.

Response: Agreed. Information will be consolidated.

7. **Comment**: 3.2.3 Stems & Wheler Monitoring Wells, Page 3-3, Paragraph 2

"Five of the sixteen new monitoring wells could not be sampled, for the most part because of a lack of groundwater for sampling."

Please clarify why five of the sixteen wells could not be sampled.

Response: The sentence will be revised to read: "Five of the sixteen new monitoring wells could not be sampled because the wells were dry."

8. **Comment**: 3.2.3 Stems & Wheler Monitoring Wells, Page 3-3, Paragraph 4

"Groundwater contamination is associated with No. 6 fuel oil, with lesser..."

Identify which well is contaminated.

Response: Agreed.

9. **Comment**: 3.3 Surveying, Page 3-7, Paragraph 2

"All monitoring wells have been surveyed. Monitoring well horizontal locations are surveyed to the nearest 0.10 foot. Vertical elevations are referenced to the 1929 North American Datum. Monitoring well elevations are surveyed to the nearest 0.01 foot at the measuring point where the uncapped riser pipe is notched."

The MEDEP would like a copy of the horizontal monitoring well location coordinates for all monitoring wells at PNSY. The MEDEP is attempting to track data associated with the monitoring well network using ArcView, a PC based GIS software package. The survey information would provide the most accurate location information for the monitoring wells.

Table 3-2 indicate fourteen (14) monitoring wells were re-surveyed during the RFI Data Gap Investigation. When were the remaining monitoring wells last surveyed? Freeze and thaw cycles over several years may cause monitoring well elevation reference points to shift.

Response: The Navy is currently pursuing a GIS system at PNS. Duplication of efforts is not cost effective. Therefore, when the Navy has completed the GIS data base will be provided to the State.

As indicated in the footnotes at the bottom of Table 3-2, these wells were repaired necessitating resurveying or were resurveyed because existing survey information could not be found. The remaining wells were surveyed when installed and will not be resurveyed as a matter of course except when necessary (i.e., modified due to repair).

10. **Comment**: 3.4.1 Available Groundwater Monitoring Data, Pages 3-8, 3-11

The site summaries should be identified by SWMU # in addition to the site name. Sites are shown on Map A by SWMU #.

SWMU #10 should be discussed in some manner, despite the fact that there are no wells currently present at the site. There is the potential that wells may be installed at SWMU #10 and these wells will be evaluated for inclusion in the groundwater monitoring plan.

Data presented within the individual site data summaries should be organized and written in the same way for each site, i.e., detections or non-detections of metals, SVOCs, VOCs, pesticides, etc., should be described in an identical manner for each site.

Response: Due to the sites being transferred from RCRA to CERCLA, the references to SWMU are being deleted from the text. Map A will be revised to reflect this.

Site 10 will be addressed in the future and not as part of the Groundwater Monitoring Plan in its current stage (sampling of the existing wells). When Site 10 is investigated further and better defined it may be incorporated as part of the Groundwater Monitoring Plan. This applies to other new sites as well.

The data summaries for each of the current sites will be revised to read in a similar order. The current text presents contaminants in order of concern.

11. Comment: 3.4.1 Available Groundwater Monitoring Data, DRMO Salvage Yard, Page 3-8, Paragraph 2

"In addition, during the RFI Data Gap Investigation, total diesel (EPA Method 8100, modified) was present in monitoring well DW-06 groundwater at a concentration of 160 µg/l."

Table 4-8 of the RFI Data Gap Report indicated 160 J µg/l diesel range total petroleum in monitoring well DW-07DB.

Response: The sentence will be revised to read: "In addition, during the RFI Data Gap Investigation, total diesel (EPA Method 8100, modified) was present in monitoring well DW-07DB groundwater at a concentration of 160 J µg/l.

12. Comment: 3.4.1 Available Groundwater Monitoring Data, DRMO Salvage Yard, Page 3-8, Paragraph 3

"Monitoring wells slightly upgradient of the DRMO (DW-1, DW-1B, DW-5, DW-4, and DW-10B) are contaminated as well, likely because of tidal effects."

Section 4.2.2 Subsequent Groundwater Monitoring, Page 4-21, Para 4 of this report indicates "Map B of the RFI Data Gap Report (Halliburton NUS, 1995a) supports the selection of monitoring wells DW-4 and DW-10B as being upgradient [of contamination?]." This would contradict the above statement.

Response: The sentence on Page 4-21, Para 4, will be revised to read "Map B of the RFI Data Gap Report (Halliburton NUS, 1995a) supports the selection of monitoring wells DW-4 and DW-10B as being *slightly* upgradient."

13. Comment: 3.4.1 Available Groundwater Monitoring Data, Former Waste Oil Tanks, Page 3-10, Paragraph 4

"However, no measurable free product layer was encountered at either the overburden well JW-16 or the bedrock well JW-16B."

Free product would not be observed in monitoring well JW-16B because the top of the well screen is approximately 10 feet below the water table. The top of the well screen for JW-16 is the approximate depth of the water table and may not be effective in intercepting free product.

Response: The following sentences will be added at the end of Paragraph 4. "It is unlikely that free product would be observed in monitoring well JW-16B because the top of the well screen is approximately 10 feet below the water table. The top of the well screen for JW-16 is at an elevation of 101.7', the approximate elevation of the water table is 101.4'. If free product is present in the area this well should intercept it. "

14. Comment: 3.4.1 Fuel Oil Spillage Area, Page 3-11

The site has not been delineated or defined. The MEDEP, EPA and Navy must define SWMU #27.

Response: The Navy is aware that the site has not been fully defined and has made reference to that in Paragraph 2 on Page 3-11. The plan will be updated in the future as necessary.

15. Comment: 3.4.3 Source Contamination, Page 3-11

This section doesn't seem to fit here. Consider either removing or expanding it.

Response: Section 3.4.3 Source Contamination, will be deleted from the text.

16. Comment: 4.1.1 Sampling Rationale, Page 4-1, Paragraph 2

"The primary objective of the pilot study will be to determine whether or not field measurements collected during low-flow purging of the monitoring wells will stabilize within the guidelines established for each of the individual groundwater quality parameters, as follows, in accordance with EPA guidance provided in Appendix B: pH, ± 0.2 standard units; specific conductance, ± 10%; temperature, ± 10%; turbidity, ±10%; Eh, ±10%; dissolved oxygen (DO), ±10%; and salinity."

Minimal drawdown of water levels in monitoring wells during purging is also critical to the low-flow sampling protocol, as noted in Section 4.1.2.

The MEDEP understands the EPA will be issuing a final low-flow sampling guidance document in the next several months. Low-flow sampling protocols at PNSY should be modified to meet the requirements of the final guidance once it is available. Substantial changes to the low-flow sampling protocol are not anticipated in the final guidance document.

Response: When the final guidance document becomes available, it will be incorporated into the Groundwater Monitoring Plan as appropriate for site specific conditions. The Navy will implement the Groundwater Monitoring Workplan following regulatory concurrence.

17. Comment: 4.1.1 Sampling Rationale, Page 4-1, Paragraph 4

"The pilot study will consist of low-flow purging using stainless steel, bladder-style submersible pumps on five monitoring wells selected based on several criteria, as described below."

The MEDEP strongly recommends the pilot study assess the use of peristaltic pumps as well as the proposed bladder pumps, particularly on monitoring wells with low hydraulic conductivity. Peristaltic pumps are only effective on monitoring wells with water levels no deeper than approximately 20 feet below ground surface, which is the case for the majority of the monitoring wells at PNSY. The MEDEP has found that for certain low hydraulic conductivity wells, use of a peristaltic pump is the only effective means of meeting low-flow sampling drawdown and turbidity requirements. The MEDEP suggests assessment of three of the lowest hydraulic conductivity wells at PNSY (JW-14B, DW-07DB, FA-01) using peristaltic pumps. Comparison between bladder and peristaltic pumps should also be performed on at least two of the proposed pilot study wells.

Peristaltic pumps are not dedicated equipment as are the bladder pumps. It is anticipated that the number of monitoring wells will be reduced after the initial two rounds of sampling. Use of peristaltic pumps at certain wells would avoid the cost of the installation of dedicated pumps which may be used only twice.

Response: The MEDEP makes a good point with the recommendation of using peristaltic pumps at certain locations. It was the intent of the Navy to use both submersible bladder pumps (deeper high yield monitoring wells) and peristaltic pumps (shallow low yield water table wells) initially, however, the MEDEP made exception, citing the need for consistency and specifying the use of like pumps in all wells. In addition, the EPA Region I Low-Flow Guidance Document does not recommend the use of peristaltic pumps during groundwater sampling for VOCs. We will include a low yield well in the pilot study and have a peristaltic pump ready in case the bladder pump cannot maintain a low enough flow rate.

18. Comment: 4.1.2 Technical Approach, Page 4-3, Paragraph 1

"Water level parameters will be monitored and recorded approximately every 5 minutes throughout the purging cycle until all of the parameters have stabilized and a minimum purge volume of two saturated screen lengths is removed."

Parameters must stabilize within the required measurement ranges for a minimum of three consecutive readings taken at three to five minute intervals.

Response: The sentence will be revised to read: "Water quality parameters will be measured and recorded ~~approximately~~ every 5 minutes during the purging cycle until such time that 3 consecutive readings are recorded within the required measurement ranges."

19. Comment: Tables 4-1 thru 4-5, Rational for Selection of Analytes, Groundwater Monitoring, PNS, Kittery, Maine, Pages 4-5 thru 4-14

Tables 4-1 thru 4-5 indicated that both filtered and unfiltered TAL inorganic analyses will be performed on all groundwater samples collected for the initial two sampling rounds. Analytes included in previous TAL inorganic analyses performed at PNSY included major cations (Ca, Mg, K,

Na), minor cations (Al, Ba, Fe, Mn), and trace cations (Sb, As, Be, Cd, Cr, Co, Cu, Pb, Hg, Ni, Se, Ag, Tl, V, Zn).

Analysis of the major anions chloride (Cl^-), sulfate (So_4^{2-}), and alkalinity (~HCO_3^-) have been proposed for groundwater collected form the DRMO, JILF, and the Former Waste Oil Tanks site. Analysis of Cl^- and SO_4^{2-} has been proposed for the Fuel Oil Spill area at Berth and the Non-site Monitoring Wells.

The MEDEP proposes that, in addition to the proposed TAL inorganic analyses, the major anions (Cl^-, SO_4^{2-}, NO_3^-, Br^-, and alkalinity) be analyzed for each water sample collected for the initial two sampling rounds. Inclusion of these additional anions in the monitoring plan would provide complete major ion chemistry for each monitoring location. The MEDEP sees the following benefits for performing these additional analyses:

- Results from comprehensive major ion analyses would provide a general characterization of groundwater conditions throughout PNSY;
- Comparison of total ion chemistry using stiff and/or piper diagrams may reveal common or distinct sources of groundwater between monitoring locations and dilution effects by intrusion of river water within tidal portions of the aquifer;
- Charge balances can be performed on total ion chemistry to assess the quality of laboratory results; and
- Finally, geochemical modeling can be performed on total ion chemistry and field parameters (e.g. Eh, DO, pH) using equilibrium computer models such as MINTEQ or PHREEQE. These models have the ability to assess aqueous speciation and possible precipitation of inorganic components for groundwater under equilibrium conditions. This may be helpful in determining the groundwater transport of metals within the aquifer.

In addition, the MEDEP proposes water samples be collected from the Piscataqua River at high and low tide and analyzed for the major cations and anions proposed above to aid in assessing dilution effects within the tidal portions of the aquifer. Given the fact the Piscataqua River is part of a tidal estuary, ionic concentrations in the surface water should change based on the tidal stage due to the relative mixing of fresh and salt water. Comparison of groundwater chemistry to river chemistry requires quantification of the ionic concentrations in both systems.

This proposed modification to the groundwater monitoring program would mean the inclusion of two (NO_3^- and Br^-) or three anions (NO_3^-, Br^-, and alkalinity) per well and the addition of four surface water samples (two per sampling round). The MEDEP believes the added benefit to the investigation as outlined above far out-weighs the additional cost, especially given the relative low-cost of inorganic analyses.

<u>Response</u>: The Navy will add the additional major anions (Cl^-, SO_4^{2-}, NO_3^-, Br^-, and alkalinity) to the analytical suite for the initial two rounds of sampling. In addition, two surface water samples will be collected during each of the sampling rounds (one sample will be collected during high tide and one during low tide) for the cations and anions mentioned above. Please note that both filtered and unfiltered samples will not be taken from all groundwater wells. Table 4-7 indicates the number of

filtered and unfiltered samples. A footnote will be added to Tables 4-1 to 4-5 to refer readers to Tables 4-7.

20. **Comment**: 4.3 Sampling and Analysis Procedures, Page 4-22, Paragraph 1

"Ceimic has been selected to perform the analytical services for the groundwater monitoring."

Wasn't Ceimic dropped from performing analytical analyses for Phase II offshore samples because of performance problems encountered with Phase I analyses? Does this have any bearing on their ability to perform analyses on groundwater samples?

Response: Ceimic was not included in the offshore phase II study because the very low detection limits used were not achievable by a standard lab. Ceimic's ability to achieve the desired detection limits for this study is currently under evaluation.

21. **Comment**: 4.3.1 Inspection of Existing Monitoring Wells, Page 4-23, Paragraph 2

"Prior to sampling each monitoring well, a brief inspection will be conducted, evaluating the following conditions: ..."

Assessment for the presence of immiscible layers should be performed as part of the initial well inspection. Section 4.3.3 describes procedures for performing this task but it should also be mentioned in the summary list.

Response: Agreed. The presence of immiscible layers will be evaluated during the monitoring well inspection and will be added to the summary list noted in Section 4.3.1 Inspection of Existing Monitoring Wells.

22. **Comment**: 4.3.3 Measurement of Immiscible Layers, Page 4-24, Paragraph 1

"To address this problem wells containing LNAPL will be purged with a peristaltic pump before the submersible pump is installed."

Define LNAPL.

Response: Agreed on purging of LNAPL before pump installation. The definition of LNAPL (Light Non-aqueous Phase Liquid) will be provided on Page 4-24, paragraph 1.

23. **Comment**: 4.3.5 Sampling Wells, Page 4-26, Paragraph 1

"Monitoring wells sampled as part of the baseline conditions assessment will be sampled using a low-flow 1.66-inch diameter low flow bladder..."

Use consistent terminology. is "baseline conditions assessment" equivalent to First and Second Event Groundwater Sampling?

Response: The sentence will be revised to read "Monitoring wells will be sampled *during each event* using a low-flow 1.66-inch diameter low flow bladder-type pump and dedicated teflon or teflon-lined polyethylene tubing."

24. **Comment**: 4.3.5 Sampling Wells, Page 4-26, Paragraph 1

"Samples will be collected directly from the discharge pump."

The MEDEP assumes the flow-through cell will be disconnected prior to sample collection which would be the correct procedure.

Response: Agreed. The sentence will be revised to read: "*After purging is completed the flow-through cell will be disconnected and* samples will be collected directly from the discharge of the pump."

25. **Comment**: 4.3.8 Sample Identification System page 4-29, Paragraph 1

"Therefore the proposed baseline conditions sampling, first event, will be considered Round 7."

See Comment No. 23.

Response: The sentence will be revised to read "Therefore the proposed *first event* sampling will be considered Round 7."

26. **Comment**: 4.3.8 Sample Identification System, Page 4-29, Paragraph 5

"Matrix Spike and Matrix Spike Duplicates (MS/MSD) samples will be designated on the field documentation forms and sample labels. MS/MSDS are collected at a frequency of 1 per 20 samples per matrix and double or triple volumes of sample are required for analytical purposes."

In the interest of performing sample collection within a reasonable time, only "high hydraulic conductivity" monitoring sells should be selected for the collection of MS/MSD samples. MS/MSD samples should be collected for salt, brackish and fresh water wells to assess matrix effects for each of these scenarios.

Response: Agreed, providing that high conductivity conditions are found in monitoring wells under each of the above conditions (salt, brackish, and fresh water). The text will be expanded accordingly.

27. **Comment**: 4.3.10 Chain of Custody, Field Documentation Responsibilities, Page 4-32, Paragraph 1

"Copies of all field logbooks will be sent to NORTHDIV monthly, to the attention of Lieutenant Jim Conroy."

Copies of the field logbooks must be included as an appendix to the groundwater monitoring report.

Response: Agreed. Copies of all field notes will be provided as part of the Groundwater Monitoring Report as already stated in on Page 6-3 (Appendix C).

28. Comment: 4.3.10 Chain of Custody, Field Documentation Responsibilities, Page 4-32, Paragraph 5

"If necessary, the Project Manager will discuss the change with the pertinent individuals (e.g., Navy Remedial Project Manager, B&R Environmental Quality Assurance Manager) and will provide verbal approval-or denial to the FTL for the proposed change."

The MEDEP and the EPA must be notified of any proposed changes to the work plan prior to field implementation.

Response: The following sentence will be added at the end of Paragraph 5: *"The EPA and MEDEP will be consulted of any scope changes that may occur while field work is ongoing."*

29. Comment: 4.10 Corrective Action, Page 4-41, Paragraph 2

"If warranted by the severity of the problem (for example, if a change in the approved work plan is required), the Navy will be notified in writing and their approval will be obtained prior to implementing any change."

See previous comment.

Response: The following sentence will be added to the end of Paragraph 2. The EPA and MEDEP will be consulted of any scope changes that may occur while fieldwork is ongoing.

30. Comment: 5.1.2 Data Validation, Page 5-1, Paragraph 4

"Although no formal data validation will be conducted, limited analytical data evaluation will be conducted to ensure that only true data points are considered for decision-making purposes."

The MEDEP understands that CLP analytical methods require specified levels of data validation. does the above statement indicate that no independent data validation will be performed?

Response: Data validation (to be conducted by B&R Environmental) is performed independent of laboratory analyses. CLP analytical methods require specified data package deliverables, not necessarily levels of data validation to be performed. (Also refer to EPA comment #14.)

31. Comment: 5.2 Procedures for Determining Significant Increases for Monitored Contaminants and Indicator Parameters, Page 5-3, Paragraph 7

"A project file and computer database will also be kept by PNS with all of the groundwater monitoring data and statistical evaluations."

The MEDEP requests a copy of this database.

Response: The sentence will be revised to read "A project file and computer database will also be kept by PNS *and provided to the EPA and MEDEP* with all of the groundwater monitoring data and statistical evaluations."

32. **Comment**: 5.3 Remedial Action, Page 5-4, Paragraph 1

"A Draft Feasibility Study (FS) has been prepared..."

It seems appropriate a summary should be included that describes what happened after regulatory review of the Draft FS and formats for subsequent FS reports. The description of the modeling effort is too brief.

The purpose of the bulleted items is unclear. They don't appear to relate to the previous paragraph.

Response: The following sentence will be added: *"It is currently planned to develop new feasibility Studies specific to each Operable Unit; therefore, remedial action will be re-evaluated in the future."*

The modeling effort is still in the planning stages, therefore additional discussion is not merited at the current time.

The following sentence was inadvertently deleted and will be reincorporated at the end of the 1st paragraph of Section 5.3 to read: *"If future sampling results reveal evidence of significant contaminant increases in any of the monitored wells, the regulatory authorities will be notified in writing as to:"*

33. **Comment**: 5.3 Remedial Action, Page 5-4, Paragraph 4

"If vertical migration of contaminants is suspected to be a problem, existing deep bedrock monitoring wells DW-7DB at the DRMO and JW-13DB at the JILF will be added to the monitoring program."

Previous results reported for these wells included 160 J µg/L diesel total petroleum at DW-7DB and 8 J µg/L 1,1-dichloroethane and 15 µg/L 1,2-dichloroethylene at JW-13DB.

Response: All existing RFI and RFI Data Gap wells will be sampled during the first and second event sampling. Discussions of additions or deletions of monitoring wells will be held at later point in time, following evaluation of results. Of note; the noted compounds did not warrant development of associated Media Protection Standards (MPSs).

34. **Comment**: Data Management and Reporting, Page 6-2, Paragraph 1

"Records of the groundwater analytical data will be kept in a computer database."

Will field parameters (i.e., pH, specific conductance, temperature, DO, Eh, and turbidity) also be included with this database? The MEDEP strongly urges that they be included if they are not presently being considered as part of the database.

Response: No. Field parameters will only be incorporated as part of the report appendices and not part of the database. Sample log sheets will be provided in the report appendix which includes the requested information. However, pH will be provided in the database as this parameter will be performed by the analytical laboratory.

35. **Comment**: Data Management and Reporting, Page 6-2, Paragraph 6

"Groundwater monitoring reports will be presented in the following format."

Does the Navy intend to prepare groundwater monitoring reports for each of the two initial sampling rounds or only prepare one report covering both sampling rounds?

Response: A single report will be prepared after the second sampling event is completed. The results of the first sampling event will be provided in the form of tables and maps, field notes will also be provided.

36. **Comment**: 7.0 Schedule, Page 7-1

"The pilot test to determine stabilization of field parameters for low-flow purging is planned for May or June of 1996."

Revise the dates for the pilot test.

Response: The sentence will be revised to read "The pilot test to determine stabilization of field parameters for low-flow purging is planned for July or August of 1996."