

DEPARTMENT OF HEALTH SERVICES

2151 BERKELEY WAY  
BERKELEY, CA 94704



March 31, 1988

Commanding Officer  
Naval Station Treasure Island  
Building I (Code 70)  
San Francisco, CA 94130-5000  
(Attn.: Mr. Kam Tung)

Dear Mr. Tung:

DRAFT QUALITY ASSURANCE PROJECT PLAN - HUNTERS POINT ANNEX

We have reviewed the above draft document dated January 1988.

It should be noted that the Department's Remedial Action Order does not identify the Quality Assurance Project Plan (QAPP) as one of the required submittals. However, from the content of this draft document, it is our interpretation that the Navy intends to satisfy the requirement of a Quality Assurance/Quality Control Plan in a two-step process: a QAPP describing the standard operating procedure and overall data quality goals followed by workplans containing site specific sampling plans and any additional site specific QA/QC procedures. The Department has no objection to this approach as long as all necessary QA/QC goals and procedures are clearly identified prior to the implementation of sampling plans.

Enclosed are our comments regarding the draft QAPP. These comments should be addressed in a revised document before the Department can approve the plan. Pursuant to Section 6.9(b) of the Remedial Action Order, please revise the QAPP by April 29, 1988.

If you have any questions, please contact Chein Kao of this office at (415) 540-3052.

Sincerely,

*Susan Solary for*

Howard K. Hatayama, Chief  
Site Mitigation Unit  
North Coast California Section  
Toxic Substances Control Division

Enclosures

cc: See Next Page

cc: Alex Dong, Navy WESTDIV.  
Roger James, SF RWQCB  
Jerry Clifford, U.S. EPA Region IX  
Scott Lutz, BAAQMD  
Steve Castleman, SF DA  
Dave Wells, SF DPH

**DEB COMMENTS ON QUALITY ASSURANCE PROJECT PLAN  
HUNTERS POINT ANNEX**

At the bottom of the title page, provisions must be made for the signatures of approving personnel. As a minimum, the QAPP must be approved by the following:

1. Organization's Project Manager
2. Organization's responsible QA Official
3. Funding Organization's Project Officer
4. Funding Organization's Quality Assurance Officer

Section 1

The document stresses the need of flexibility to accommodate site specific conditions. The Department feels that one of the objectives of Quality Assurance Project Plan (QAPP) is to develop standard operating procedures in order to assure consistent data quality. We recognize some field conditions may require certain addition or modification of SOPs and will review them on a case by case basis. However, within the context of QAPP, guidance document (QAMS 005/80) clearly indicates the procedures developed in the QAPP should be concise and definitive to achieve data quality goals.

Section 4

1. EPA has found their Certified Lab Program to be 80-85 percent complete on a nationwide basis. The goal of 100% completeness seems unrealistic. A definitive goal of completeness will have to be established prior to the implementation of a sampling plan.
2. Representativeness is mostly concerned with the proper design of the sampling program. The rationale used to determine sampling locations must be explicitly explained.
3. Mg/l should be changed to ug/l for ppb.

Section 5.2.2. Electromagnetic and Resistivity Surveys

Page 5-3: The type of resistivity survey to be conducted needs to be specified (e.g. Schlumberger, Dipole-Dipole).

Section 5.2.3. Seismic Surveys

Page 5-3: In order to improve shallow subsurface data, for any seismic profile equal to or greater than 200 feet in length, in addition to the end shots, an additional shot should also be taken at the center of the spread.

Page 5-4: If explosives are used in the seismic survey, all shots will be conducted by a licensed blaster, and the blasting procedure will be thoroughly documented in the site Health and Safety Plan.

#### Section 5.2.4. Magnetic Surveys

Page 5-5: To reduce the possibility of erroneous measurements due to interference by nearby AC power sources, field personnel should take at least two readings at each survey point, in order to ensure instrument precision.

Since the proton-precession magnetometer measures the total magnetic field, the instrument cannot be used to determine horizontal magnetic gradients. The contractor should specify the instrument they will use to measure horizontal gradients in this section.

#### Section 5.2.5. Geophysical Test Surveys

Page 5-6: The type of DC resistivity soundings to be performed prior to the other geophysical surveys needs to be specified in this section.

#### Section 5.3. Soil Gas Survey

1. Details on the actual methods for sampling and analysis of ambient air, soil gas, and quality assurance/control (QA/QC) samples should be provided. Protocols for Air Quality Sampling and Soil Gas Well and Probe Sampling contained in Sections 10.3 and 10.4 are insufficient to properly review this investigatory technique.
2. Section 5.3 states that 1 to 2 liters of soil gas will be pumped from each well to flush (purge) the probe. Section 10.4 states that 2 probe volumes will be purged from the probe. This discrepancy must be clarified. Two to three probe volumes would be more appropriate.
3. Sources for "organic-free blank samples" must be specified.
4. Identities and the rationale for the selection of "target analytes" to be analyzed for must be provided.
5. Soil gas monitoring is a qualitative, not a quantitative procedure, used to "rapidly evaluate the areal extent of chemical contamination...".

## Section 6.0. Drilling and Well Installation Procedures

More detailed qualification should be identified for the term "qualified field technician".

### Section 6.1. Drilling Methods

Page 6-1: The objective of performing borings at Hunters Point Annex is to 1) obtain, to the best extent possible, representative records of lithology and hydrogeology, and 2) install monitoring wells to locate and define areas of contaminated ground water. For these reasons, the use of flight augers and direct mud-rotary drilling methods cannot be approved. Additional justification for this action is as follows:

1. Neither flight augers nor mud rotary methods can supply lithologic data of sufficient quality to satisfy our requirements. Both flight auger and mud rotary drilling yield highly disturbed samples that can only be approximately located within the borehole.
2. In mud-rotary methods, a) contaminants can be circulated with the drilling fluid, b) drilling fluid mixes with the formation water and permeates into the formation, c) little information on the locations of water-bearing strata can be gathered during drilling and d) drilling fluids can interfere with the results of chemical analyses.

Since hollow-stem auger (HSA) borings have been successfully completed in unconsolidated sediments as deep as 300 feet, and since this method is ideally suited for undisturbed sampling, HSA boring with continuous coring should be the method of choice. An acceptable second choice would be dual wall reverse-circulation drilling (using air as the drilling fluid), but only under the following conditions: 1) HSAs cannot be successfully used for well completion, due to heaving sediments entering the stem; 2) the borehole is a deep pilot boring that will extend to unweathered bedrock and the hole will also be logged using down-hole geophysics.

Should reverse-circulation drilling be necessary, the use of water or mud as a drilling fluid is only warranted if the hole cannot be kept open using other methods and the hole will be logged using down-hole geophysics. In this case, the Contractor should submit a sample of the drilling mud for chemical analysis, to check for possible interference with soil and ground water analyses.

Section 6.3, 6.5, 6.5.1, 6.5.2

Only a geologist should be allowed to log the bore holes, cores or drill cuttings. The identification/interpretation of the materials observed is the responsibility of a registered geologist. Geologic logging may be done by an unregistered geologist, but then only when under the direct supervision of a registered geologist.

Section 6.4. Borehole Geophysics

Page 6-3: For every boring that will be geophysically logged, a caliper log should also be run.

Section 6.5.1. Single-Casing Wells

1. Copies of unedited field logs shall be sent to the Navy and the regulatory agencies within 7 calendar days after the completion of the monitoring well or completion of the boring if it is not completed as a monitoring well. "Interpretive" or "report-ready" logs have their place in finished reports but are not acceptable for technical review.
2. Surveyed elevations of the measuring points of the monitoring wells shall be submitted to the Navy and the regulatory agencies within 7 calendar days after the completion of the particular phase of the survey.
3. Well design, construction and material selection in the California Site Mitigation Decision Tree process should be considered.
4. Hollow stem auger holes shall be a minimum 8 inches in diameter when using a 4 inch casing. It is necessary to provide a 2 to 3 inch annulus between the casing and the bore hole wall to allow access of a tremie pipe, measuring tape and to prevent bridging of filter pack material or bentonite pallets.

Section 6.5.1 and 6.5.2

1. Only flush-threaded casing is allowed.
2. Casing manufacturer's markings are to be of a non-toxic material that is to be removed during the pre-construction cleaning.
3. The filter pack shall be designed based on the texture of the formation material to be stabilized; the slot size of the screen is to be selected based on the texture of the filter pack material.

4. All materials used to advance the bore hole, construct the monitoring well and develop the well shall be cleaned prior to use and protected from the time it is cleaned until the time it is placed in the hole.
5. Screen lengths should not exceed 5 feet except where necessary to span the expected range of the water table fluctuation. The goal of monitoring is to acquire water quality data at in situ concentrations and to acquire it at discrete depth intervals and to acquire depth-discrete piezometric data. Long screen wells are an expediency that no one can afford; they act to dilute the contaminants by allowing water from many levels into the casing and also are vertical pathways for those contaminants.
6. It is important to specify a time lag after the bentonite pellets have been placed above the filter pack. Using fresh water it may take almost an hour for the pellets to swell enough to seal off the annulus and prevent downward leakage of the grout from the next step in the well construction. Pellets placed below the water table should be 0.5 inch diameter. Formation waters that are saline or brackish may take even longer to cause the pellets to swell. Bentonite placed above the water table should be crushed material, not pellets.

Page 6-7: The bentonite pellet seal should be at least three feet thick. If the seal will be placed below the water table, the seal will be checked for bridging, and any bridges will be broken with a weighted tape, tremie pipe or other similar device.

7. After 24 hours, check for grout shrinkage around the casing at the surface; fill in where needed.
8. The ground water level measuring point shall be clearly marked on each casing or protective cover.
9. The well numbers shall be clearly marked on each casing, cap and on the outside of the protective cover.

#### Section 6.6. Well Development

1. Page 6-10: Swabbing has been known to cause significant damage to monitoring wells and the surrounding filter pack. Therefore, swabbing is not a recommended method of well development.
2. Well development through narrow slots is best done by use of a vented surge block.

## Section 7.0. Soil and Sediment Sampling Procedures

### 1. General Comments on Sampling Procedures:

QAMS 005/80 states that for each major measurement parameter, that the QAPP should include a "description of technique or guidelines used to select sampling sites". This description has not been provided in the QAPP. This description of techniques or "strategies" is particularly important when attempting to determine the spatial distribution of contaminants at a site. It is not necessary to establish where samples are to be taken in the QAPP, but it is necessary to discuss the strategy for locating sampling "points" and the rationale for the selected strategy. If one is looking for evidence of contamination, a different strategy will be used than one for determining the average concentration and quantity of a contaminant in a volume of soil. Also, the sampling strategy will depend on the properties of the contaminant, the nature of contaminant release and dispersal, and what is known about the physical and chemical features of the medium to be sampled. Knowledge of the physical environment will be based upon data obtained during surface geophysical investigations, visual evidence of possible contamination, and research of past site activities.

The distinction between surface and subsurface sampling is not altogether clear. It would be better to differentiate between sampling for the purpose of describing soil physical properties and sampling for the purpose of estimating the concentrations of contaminants.

### 2. Section 7.1. Surface Soil Sampling

Hand trowels are not the best tool for obtaining surface soil samples in that (1) sample volumes are typically inadequate, (2) the dimensions of the sampling unit (depth and diameter) are not easily determined, and (3) the soil may be too hard to penetrate to an appropriate sampling depth. It would be preferable to use stainless steel liner tube sampler for organic volatile samples. Stainless steel trowels could be used for most metals and inorganic analyses. A bucket auger may be appropriate if it is not required to obtain undisturbed soil samples. Procedures for breaking through concrete or asphalt surfaces also need to be briefly discussed.

### 3. Section 7.2

Collecting lithologic samples from the cuttings on a hollow stem auger rig is a poor method of obtaining samples. It is very difficult to determine the particle size distribution of a sample take from cuttings because of mixing and also the uncertainty of the depth that the sample was collected. Lithologic descriptions should be based on a downhole sampling as needed (i.e., 5' intervals may not be sufficient).

Where physically possible, undisturbed soil samples should be obtained from continuous cores or exposed soil faces and should be analyzed for the following physical and chemical properties where appropriate: bulk density, porosity, percent silt (0.05 to 0.002 mm), percent clay (<.002 mm), percent soil moisture (volume/volume), pH, and percent organic carbon (mass/mass). Soil properties to be described in the field should include soil boundaries, soil color, and other physical features that may be visually apparent. It may not be necessary to determine all of the above mentioned soil properties if it can be shown that they are not necessary to model the migration and the fate of contaminants in soils. Soil classification according to the ASTM system does not provide adequate information on soil properties to make an assessment of the potential fate of contaminants in soils and sediments. Details on sampling techniques are provided in Section 3.1.4.a of the California Site Mitigation Decision Tree.

### Section 8.0. Water Sampling Procedure

1. Section 8.1. Sampling Protocol - Label all containers before each sampling round.

Add preservatives before each sampling round.

2. P8-1, bullet 5: In wells which run dry during purging, the samples to be analyzed for volatile compounds should be collected as soon as there is enough water in the well to collect the samples.

bullet 6: Bailers should have an attachment on the bottom (e.g., stopcock) which allow the sample to be decanted from the bottom with minimum of aeration.

3. P8-2, bullet 1: An in-line filtration unit attached to the discharge line of the bladder pump is preferred over decanting samples into a separate filtration assembly.
4. P8-2, bullet 10: The time of purging (beginning and end) should also be noted.

Section 9.9. Water Level Measurement Procedures.

Water level measurements shall be submitted to the Navy and the regulatory agencies within 7 calendar days after the completion of each round of water level measurements.

Section 10. Air Quality Monitoring Procedures.

1. There is no mention of air sampling for semi-volatile organics. Semi-volatile organics should be sampled in vapor phase and trapped on particulates. A high volume sampler with backup absorbent can be used.
2. Detection limits for ARB/ADD L002 methods should be 1 ppb.
3. Air sampling form should include volumetric flow rate being used and should have identification of sampling station. The above comments also apply to integrated sample forms. Ambient temperature and pressure should also be on forms.
4. The QAPP mentions tedlar bags to collect ambient air samples. If the bags are to be reused, there should be a section on preparation, purification, storage, and handling of the bags.
5. At least 10 percent of ambient air samples taken should be collocated samples. Spiked tedlar bags should be taken into the field to determine losses.
6. Air samples collected in tedlar bags should be analyzed within 72 hours.
7. Prior to collecting air samples on absorbents, the breakthrough volume of various chemicals have to be determined in order to use the correct flow rate. There is a minimum and maximum flow rate within which solid absorbents can be used.
8. If solid absorbents are used, EPA's method should be preferred over NIOSH's.
9. The flow rate shall be calibrated using a flow meter traceable to NBS.
10. Air samples collected on solid absorbents should be analyzed within the time limit specified in EPA's "Compendium of Methods for the Determination Toxin Organic Compounds in Ambient Air". Solid absorbents not listed by EPA should follow NIOSH methods.

## Section 11. Decontamination Procedures

### P11-2, bullet 2:

Frequent equipment blanks should be collected. Usually, equipment for collecting samples containing metals is rinsed in 1:1 nitric acid and that for samples containing organic materials, such as oil and grease, is cleaned with a spectroscopic grade solvent such as isopropanol. These rinses are the preferred decontamination method and if they are omitted, the adequacy of the alternate procedures should be demonstrated with frequent blanks.

## Section 14.0. Analytical Procedures

Not all of the labs listed here are certified by DHS to perform all of the analytical procedures that will be required at the site. Care should be taken to insure that analyses are requested only from those labs that are certified for those particular analyses. TMA/Norcal is the only lab listed that is certified for asbestos analysis.

## Section 15.0. Data Reduction, Validation, and Reporting

1. Specific standard mathematical and/or statistical procedures for data reduction should be identified and an example should be given here.
2. Section 15.3. The following should be added to the reporting requirements.
  - "o Presentation of all QC data (e.g. all blanks, internal duplicates and RPD, spikes and percent recovery, field duplicates and RPD) with related Calculations".
  - "o Any corrective actions".

## Section 16. Quality Control Checks

1. Section 16.1. Field QC Checks

There is no list showing "The matrix and analysis specific description and frequency of field external QC samples" as indicated in the text.

2. Section 16.2. The check standards used should preferably be obtained from a standard setting agency such as the EPA, NBS, etc. If such standards are not available, then, a second standard may be obtained from a different manufacturer (or a different lot number of the same manufacturer).

Section 19

1. Section 19.1. If HLA will not eliminate data, then data that do not meet certain QC performance standards should be identified and rationale given for not eliminating the data.

It is stated that "sample recollection and analysis will only be used in extreme cases of QC problems". Please define "extreme cases of QC problems". Sample recollection and analysis should be done whenever it is necessary to achieve QA goals.

2. Duplicates. Field duplicates for analyses, except volatile organics, should be thoroughly mixed so that a homogenous mixture results and duplicates should be taken from this mixture.
3. Section 19.1.2. Duplicates. The statistical analysis should stop at the calculation of the RPD. The RPD for each parameter should be compared to precision objectives in Table 1.
4. Section 19.1.3. Spikes. The statistics analysis should stop at calculation of percent recovery for each parameter. The percent recovery for each parameter can then be compared to accuracy objectives in Table 1.
5. Pg 19-5. Since a general percent recovery limit of 75% to 125% has been set for spike recoveries a similar general precision limit should be set as a precision measure for the duplicates.
6. QC charts should be plotted to see if data are within acceptable limits.
7. Pg 20-1. If QC criteria (precision and accuracy) specified are not met, then these samples should be subjected to corrective action.

Table 1

1. Precision goals of 50% or greater set for some analytes are too wide. We suggest, at maximum, 40% for VOC and 20% for all others.
2. Quality Assurance goals in the table must be clearly distinguished from actual QC criteria. The certified laboratories listed in page 14-1, should have QC criteria based on actual data for laboratory measurements. These QC criteria should be used to implement corrective action when necessary.

3. RPD should be reported for base/neutral/acid organics (semi-volatiles) and pesticides/PCBs in air, and the sources for this data should be given.
4. Table II should read "Acceptable Percent Recovery" not Acceptable RPD. Percent recovery should be reported for semi-volatiles and pesticides/PCBs in air, and the sources for this data should be given.
5. Analysis of Surrogates. This table should also read "Acceptable Percent Recovery" not acceptable RPD.

#### Table 2

1. Analytical methods for semi-volatiles and pesticides/PCBs in air should be identified.
2. Reference 7, provided for TPH analysis, is incorrect. As far as can be determined, the document referenced, "Recommended Methods of Analysis for the Organic Compounds Required for AB 1803" does not contain these methods. The proper reference should be "Leaking Underground Fuel Tank (LUFT) Field Manual". A copy of this document is enclosed for your use (See Attachment A).
3. Please specify the precision and accuracy for the PQLs cited in the table (see reference 2).
4. Reference methods for Anions/Cations should be EPA 300 series/200 series rather than EPA 200/300.

#### Table 3

1. Holding times for air samples should be listed.
2. VOC samples should be collected in special VOA vials that can be purchased as certified clean.
3. Certified clean containers can be purchased for other organic analyses or the container should be cleaned as described below:
  - 1) Thoroughly washed with nonphosphate detergent and hot tap water.
  - 2) Rinsed 3 times with tap water.
  - 3) Rinsed with nitric acid (1:1).
  - 4) Rinsed 3 times with ASTM Type I water.
  - 5) Rinsed with methylene chloride.
  - 6) Oven dried.
  - 7) Baked at 400 degrees C (when required).

Containers for metals should be:

- 1) Thoroughly washed with nonphosphate detergent and hot tap water.
  - 2) Rinsed 3 times with tap water.
  - 3) Rinsed with nitric acid (1:1).
  - 4) Rinsed 3 times with ASTM Type I Water
  - 5) Oven dried.
4. From table 3, it appears that soil samples may be sent to the lab in brass sleeves. If this is the case, there should be a written procedure describing how the "core" will be handled in the lab. Special care in obtaining samples for VOC analysis seems appropriate.

Draft Method\*  
for  
Total Petroleum Hydrocarbons  
and  
Total Organic Lead

Hazardous Materials Laboratory  
California Department of Health Services  
2151 Berkeley Way  
Berkeley, CA 94704  
(415) 540-3003

February, 1988



\* The draft methods are reproduced from: LEAKING UNDERGROUND FUEL TANK (LUFT) FIELD MANUAL, California State Water Resources Control Board, Division of Water Quality, December 17, 1987. Complete copies of LUFT field manual are available from Ms. Diane Edwards at (916)324-9088. The draft methods for Total Petroleum Hydrocarbons and Total Organic Lead may be replaced by future revisions.

## APPENDIX B

### SAMPLE COLLECTION, TRANSPORT AND LABORATORY ANALYSIS

#### A. Sample Collection

##### 1. Field Notebook

The field investigator should keep a field notebook (preferably bound with pages numbered) to record sample collection procedures, dates, laboratory identification, sample collection location, and the name of the sampler. This is important for later recall or legal challenge.

##### 2. Soil Samples

- a. Hydrocarbons: Soil samples collected from a backhoe or from the ground should be collected in a thin-walled stainless steel or brass cylinder at least three inches long by one inch in diameter that has been prepared by the laboratory doing the analysis or the project consultant. About one inch of soil should be removed from the immediate surface area where the sample is to be taken and the cylinder then pounded into the soil with a wooden mallet. No headspace should be present in the cylinder once the sample is collected. When the sample is collected, each end of the cylinder should be covered with aluminum foil and then capped with a polyethylene lid, taped, and labeled. The sample should then be immediately placed in an ice chest containing dry ice and kept frozen for delivery to the laboratory. Care should be taken throughout to avoid contamination of both the inside and outside of the cylinder and its contents (1).

Samples should be kept frozen at the laboratory until they are analyzed. Holding time should not exceed 14 days from the time of collection. Frozen soil cores should be removed from the cylinders by spot heating the cylinder and immediately extruding the sample (or a portion of it). A portion of the frozen sample should be removed and prepared for analysis according to approved EPA methods.

In situations where the above procedure is inappropriate, i.e. semi-solid samples, glass vials (properly prepared by contract laboratory or consultant) with Teflon seal and screw cap should be used, and maintained at 4°C until analysis.

- b. Organolead: Tetraethyl/tetramethyl-lead are volatile; therefore, soil samples should be collected in cylinders and frozen as described for volatile hydrocarbons above.

Water samples should be collected in vials or containers specifically designed to prevent loss of volatile constituents from the sample. These vials should be provided by an analytical laboratory, and preferably, the laboratory conducting the analysis. No headspace should be present in the sample container once the container has been capped. This can be checked by inverting the bottle, once the sample is collected, and looking for bubbles. Sometimes it is not possible to collect a sample without air bubbles, particularly if water is aerated. In these cases, the investigator should record the problem and account for probable error. Cooling samples may also produce headspace (bubbles), but these will disappear once the sample is warmed for analysis.

Samples should be placed in an ice chest maintained at 4°C with blue ice (care should be taken to prevent freezing of the water and bursting of the glass vial). A thermometer with a protected bulb should be carried in each ice chest.

- c. Surface water: Grab samples should be collected in appropriate glass containers supplied by the laboratory. The sample should be collected in such a manner that air bubbles are not entrapped. Semisolid samples should be collected the same way. The collected samples should be refrigerated (blue ice, 4°C) for transport and analyzed within 14 days of collection.

TABLE 3-3

## HOLDING TIME FOR SOIL SAMPLES 1/

Analyte	Holding Time for Soil
Benzene, toluene, xylenes	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as gasoline	Analyze as soon as possible (maximum 14 days)
Total Petroleum Hydrocarbons, as diesel	Extract within 14 days, analyze within 40 days

1/ Results from samples not meeting the listed holding times should be considered minimum values. That is, the actual concentration is equal to or greater than the concentration determined after the holding time has expired.

#### C. Recommended Analytical Methods

Recommended analytical procedures are summarized in Table 3-4. The Department of Health Services may approve an alternate method which has at least equivalent detection limits, precision, and accuracy as the referenced methods. For example, a cryogenic gas chromatography/mass spectrometry (GC/MS) system may be used instead of a gas chromatography (GC) system, provided the GC/MS system can produce data which are equal or better than data provided by the referenced GC system in terms of detection limits, precision, and accuracy for an identical sample matrix.

Total Petroleum Hydrocarbons (TPH) arising from gasoline or diesel and total organic lead can be analyzed by the attached Department of Health Services (DHS) methods. The investigator should alert the laboratories to the procedures given in Table 3-4 and supply the laboratories with copies of the TPH and total organic lead methods, if necessary.

## Detection Limits for LUFT Investigations

Minimum detection limits for key analytes are listed in Table 3-5. The detection limits for benzene, toluene, and xylene are consistent with the experience of several commercial laboratories under optimal conditions. The detection limits for benzene, toluene, and xylene in soil assume the direct purging of a soil-water mixture and subsequent gas chromatography-photoionization detection (GC-PID). Lower detection limits are achievable with available technology by using: modifications of reference methods, a larger sample or additional concentration techniques. Detection limits may be significantly higher in samples with interfering organics or matrix effects. The readily obtainable 0.3 ppm detection limit cited on page 20 takes into account potential sample interferences.

TABLE 3-5

### DETECTION LIMITS FOR COMMONLY ANALYZED FUEL PRODUCTS

Analyte	Water µg/l	Soil µg/kg	Method
Benzene	0.3	5	EPA 602, 8020
Toluene	0.3	5	EPA 602, 8020
Xylenes, total	0.6	15	EPA 602, 8020
Total Petroleum Hydrocarbons	500.0	10,000	DHS: GC-FID

#### D. Recommended DHS Analytical Methods

##### Total Petroleum Hydrocarbons (TPH) Analysis -- Gasoline and Diesel

###### 1. Scope and Application

- a. This method is for the determination of gasoline and diesel in contaminated ground water, sludges, and soil.
- b. This method is recommended for use by, or under the supervision of, analysts experienced in the operation of GC and in the interpretation of chromatograms.

- b. Vial with cap: 40 milliliter (ml) capacity screw cap (Pierce number 14070 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C before use.
- c. Septum: Teflon-300-3 silicone (Pierce number 12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C for 30 minutes before use.
- d. Separatory funnel: 5-liter with Teflon stopcock.
- e. Kuderna-Danish (K-D) apparatus.
- f. Boiling chips: Solvent extracted approximately 10/40 mesh.
- g. Water bath: Heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.
- h. GC: Analytical system completed with programmable GC suitable for on-column injection and all required accessories, including FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.
- i. GC column: 6 feet by 1/8 inch ID glass column packed with 5% SP-2100 on Supelcoport 60/80 mesh.
- j. Detector: FID.
- k. Microsyringes: 10 µl, 100 µl, 200 µl.
- l. Erlenmeyer flask: Pyrex, 250 ml capacity with a screw cap.
- m. Mechanical shaker.

## 5. Reagents

- a. Stock diesel standard solutions: Prepare a commercial diesel standard in carbon disulfide. Place 9 ml of CS<sub>2</sub> into a 10 ml glass-stoppered volumetric flask. Allow to stand for a few minutes. Weigh the flask to the nearest 0.1 mg. Using a 100 µl syringe, immediately add an amount of diesel to the flask, then reweigh. Be sure that the liquid falls directly into the CS<sub>2</sub> without contacting the neck of the flask. Dilute to volume, stopper, mix by inverting the flask several times. Calculate the concentration in µg/l from the net gain in weight. Secondary working standards can be prepared from the stock standards.
- b. Stock gasoline standard solutions: Gasoline stock standards can be prepared as above using commercial gasoline as standard in dodecane.

- (9) Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 5 ml with the solvent to be used in instrument analyses.

c. Soil and Sludges

- (1) Weigh 20.0 gram (g) sample into a 250 ml screw cap Erlenmeyer flask. Add 80 ml of solvent.
- (2) Cap the flask and shake on a mechanical shaker for at least four hours.
- (3) After the extraction is completed, filter the extract and dry it by passing through a column of anhydrous sodium sulfate.
- (4) Collect the dried extract in K-D flask, fitted with a 10 ml concentrator tube and a three-ball Snyder column. Wash the extractor flask and the sodium sulfate with a portion of carbon disulfide and collect it into the K-D flask.
- (5) Add one or two clean boiling chips and concentrate the extract to 5 ml as discussed in steps (8) and (9) (page 63).

d. GC Conditions

The recommended GC column and operating conditions are:

Column: 6 feet by 1/8 inch ID glass column packed with 5% SP-2100 on Supelcoport, 60/80 mesh with nitrogen carrier gas at 20 ml/minute flow rate. Column temperature is set at 40°C at the time of injection, hold for 4 minutes, and programmed at 10°C/minute to a final temperature of 265°C for 10 minutes.

e. Calibration

- (1) Establish GC operating parameters as specified in d. above. By injecting secondary standards, adjust the sensitivity of the analytical system for the analysis of gasoline and diesel in environmental samples. Detection limits for the extraction method and the headspace method are listed in Table 3-6 (page 61). Calibrate the chromatographic system with the external standard technique. At least three concentration levels should be used for the preparation of the calibration curve. One of the external standards should be at a concentration near, but above, the method detection limit. The other standard should

- (f) Analyze the standard and adjust instrument sensitivity to give minimum response of at least two times the background. Record and sum up all peak areas of the gasoline standard.
- (g) Analyze the spike sample in the same manner. Record all peak areas.
- (h) Analyze the undosed sample in (g) above.
- (i) Small sample size should be used if the concentration is found to be outside the concentration range of the instrument.

g. Standard laboratory quality control practices should be used with this method.

## Determination of Organolead -- DHS Method

### 1. Discussion

Organolead compounds constitute the largest single industrial application of organo-metallic chemistry. Estimates indicate that about 1,450 organolead compounds were known in 1968, and the number has increased with synthesis of about 130 new compounds each year. The widespread presence of toxic, volatile, lipophilic organolead compounds in the environment can lead to serious public health effects and damage to the aquatic biota. With the phasing out of leaded fuels, substantial amounts of lead compounds from petroleum sludges are being discharged into waste streams. There is also evidence to suggest that the more toxic organoleads such as tetramethyl-lead can be synthesized from lead salts and simple chemical reagents in aqueous solutions.

Caution: Some organolead compounds are volatile and toxic. Process the samples in a well-ventilated hood.

### 2. Scope

The method describes the determination of organolead compounds in various types of hazardous material samples. In this method, a rapid organic extraction technique is applied to separate the organo Pb from a matrix with xylene, followed by reaction with 1% Aliquat 336/MIBK on I<sub>2</sub> solution. The extract is then analyzed by a flame atomic absorption spectrophotometer. The detection limit for organolead is 0.05 ppm as lead.

### 3. Reagents

3.1 (MIBK) methyl-isobutyl ketone (4-methyl-2-pentanone).

5.4 Pipet 0.1 ml of I<sub>2</sub> solution into the flask and mix for about one minute.

5.5 Pipet 5 ml of 1% Aliquat 336 in MIBK and mix.

5.6 Dilute to volume with MIBK and mix.

## 6. Standard and Blank Preparation

Prepare appropriate working standards and blank from 100 g/ml Pb standard.

6.1 Add approximately 20 ml of xylene to 50 ml volumetric flask. Pipet the correct amount of the 100 µg/ml Pb standard into the flask to prepare the right standard.

6.2 Add immediately 0.1 ml of I<sub>2</sub> solution and mix well.

6.3 Add 5 ml of 1% Aliquat 336/MIBK and mix well.

6.4 Dilute to volume with MIBK and mix well.

6.5 Blank xylene/MIBK (40% xylene) should be treated as the working standard solutions.

## 7. Analysis

7.1 Set up the AA according to the manufacturer's instructions. Use background correction to decrease broad band absorption interference.

7.2 Aspirate H<sub>2</sub>O into the flame and adjust the acetylene flow to 8.5 l/min and the air flow to 25 l/min.

7.3 Aspirate MIBK containing 40% xylene into the flame.

7.4 Reduce the acetylene flow to about 4.8 l/min and make fine adjustments in the acetylene flow to produce an even flame with no yellow luminescence to obtain optimum conditions.

7.5 Aspirate into the flame blank, working standards, and sample to measure the absorbencies. Estimate the concentrations of organolead in sample.

## 8. Calculations

Solids:

$$\frac{100 \text{ ml}}{50 \text{ g}} \quad \frac{50 \text{ ml}}{20 \text{ ml}} \quad \frac{\mu\text{g/l}}{1000 \text{ ml/l}} \quad \times F = \mu\text{g/g organolead calculated as Pb.}$$

where F = dilution factor.

Figure III-4



United States  
Environmental Protection  
Agency

Region 10  
1001 South Avenue  
Seattle, WA 98101

CHAIN OF CUSTODY RECORD

PROJECT				SAMPLERS: <i>(Signature)</i>							
LAB #	STATION	DATE	TIME	SAMPLE TYPE						NUMBER OF CONTAINERS	REMARKS
				WATER	SEDIMENT	TISSUE	AIR	OIL	OTHER		
RELINQUISHED BY: <i>(Signature)</i>			RECEIVED BY: <i>(Signature)</i>					DATE/TIME			
RELINQUISHED BY: <i>(Signature)</i>			RECEIVED BY: <i>(Signature)</i>					DATE/TIME			
RELINQUISHED BY: <i>(Signature)</i>			RECEIVED BY: <i>(Signature)</i>					DATE/TIME			
RELINQUISHED BY: <i>(Signature)</i>			REC'VD BY MOBILE LAB FOR FIELD ANAL: <i>(Signature)</i>					DATE/TIME			
DISPATCHED BY: <i>(Signature)</i>		DATE/TIME		RECEIVED FOR LAB BY: <i>(Signature)</i>			DATE/TIME				
METHOD OF SHIPMENT:											

Distribution: Original - Accompany Shipment  
One Copy - Survey Coordinator Field Files

U.S. EPA Chain of Custody Form

Table 3-7

## A General Guide for Collection of Field QC Samples (7)

Sample	Description and Purpose	Number of QC Samples
Trip or Travel Blank (Mandatory for volatile organics)	A sample container filled in the laboratory with organic-free water and carried unopened during the sampling trip. It must be prepared by the laboratory supplying sample containers. It is used to identify contamination introduced from the originating laboratory. The trip blank remains with the collected samples and is analyzed along with the field samples to check residual contamination. Trip blanks are mandatory for volatile hydrocarbon analysis in water.	<ol style="list-style-type: none"> <li>1. One per sample set.</li> <li>2. Greater than 20 samples per set: 5 percent trip blank analysis should be done. Statistical need and cost effectiveness should be considered where large numbers of samples are involved.</li> </ol>
Field Blank (optional)	A sample container filled with organic-free water that is taken on the field trip. It is opened and exposed at the sampling site to detect contamination from air exposure. The water sample may be poured into appropriate containers to simulate actual sampling conditions. Contamination from air exposure can vary considerable from site to site therefore, the need for this sample should be evaluated relative to the sampling situation. Reference material (i.e., chemically defined soil) can be used in lieu of organic-free water as dictated by the sampling needs.	<ol style="list-style-type: none"> <li>1. One for each team per trip or</li> <li>2. One for each relevant sample type or</li> <li>3. One per day at a single site</li> <li>4. The need for field blanks should be made relative to site specific conditions and sampling requirements.</li> </ol>
Blind Sample (optional)	A sample whose composition or source is known to the submitter but not known by the person logging in samples or the analyst. It is submitted along with the regular field sample set. When both the anticipated sample composition and the blind status of the sample are not known to the analyst, the sample is called a "double blind" sample. A blind sample is used to check analytical performance and proficiency.	<ol style="list-style-type: none"> <li>1. One per sample set up to 10 samples.</li> <li>2. 10-14 samples: 5 percent blind sample analysis. &gt;40 samples: requirements should be based on the needs of the project.</li> </ol>
Field Duplicate (optional except required for volatile analysis (VOA))	A second field sample collected identically to and immediately after the first sample. This provides a measure of analytical precision and second sample confirmation. It provides a means of determining random error when adequate numbers of duplicates are collected. Field duplicates may also be collected as splits. Duplicates can also serve as blind field samples.	<ol style="list-style-type: none"> <li>1. The need to collect duplicates is determined by project objectives.</li> <li>2. The number of sample duplicates required is determined by project objectives and QC requirements.</li> </ol>
Split Sample <sup>1/</sup> (optional)	The goal in obtaining splits is to obtain subsamples that do not differ significantly from each other or from the original sample. These are used to compare performance between/among laboratories.	<ol style="list-style-type: none"> <li>1. 10 percent</li> <li>2. Need for these is determined by project objectives.</li> </ol>

<sup>1/</sup> Split sample collection has critical limitations. See special instructions in the following section.

## REFERENCES

1. D. B. Cohen, D. Gilmore, C. Fischer, and G. W. Bowes. 1983. Water Quality and Pesticides: 1,2-Dichloropropane (1,2-D) and 1,2-Dichloropropene (1,3-D). Special Projects Report No. 83-8SP. California State Water Resources Control Board, Sacramento, CA.
2. U. S. EPA. 1982. Test Methods for Evaluating Solid Waste; Physical/Chemical Methods. SW-846. Second Edition. Office of Solid Waste and Emergency Response, U. S. EPA, Washington, D.C. (A third edition is available now, but because of extensive changes that were made, U. S. EPA has not incorporated the third edition into RCRA regulations at this time.)
3. U. S. EPA. 1982. Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA 600/4-82-057, U. S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH.
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