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FINAL VAPOR INTRUSION SAMPLING WORK PLAN FOR SOLID WASTE MANAGEMENT
UNIT 16 CAST HIGH EXPLOSIVE FILL/B-146 INCINERATOR BUILDING 146 NSA CRANE IN
3/1/2014
TETRA TECH

FINAL
Vapor Intrusion Sampling
Work Plan
FOR
SWMU 16 Cast High Explosive Fill/B-146
Incinerator - Building 146

Naval Support Activity Crane
Crane, Indiana



Naval Facilities Engineering Command
Midwest

Contract Number N62470-08-D-1001

Contract Task Order F276

March 2014

**FINAL
VAPOR INTRUSION
SAMPLING WORK PLAN
FOR
SWMU 16 - CAST HIGH EXPLOSIVE
FILL/B-146 INCINERATOR - BUILDING 146**

**NAVAL SURFACE ACTIVITY
CRANE, INDIANA**

**COMPREHENSIVE LONG-TERM
ENVIRONMENTAL ACTION NAVY (CLEAN) CONTRACT**

**Submitted to:
Naval Facilities Engineering Command Midwest
201 Decatur Avenue
Building IA, Code EV
Great Lakes, Illinois 60088**

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**CONTRACT NUMBER N62470-08-D-1001
CONTRACT TASK ORDER F276**

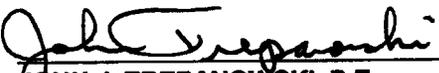
MARCH 2014

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ACRONYMS

1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,1,2-TCA	1,1,2-trichloroethane
ASTM	American Society for Testing and Materials
B-146	Building 146
bgs	below ground surface
cis-1,2-DCE	cis-1,2-dichloroethene
CLEAN	Comprehensive Long-Term Environmental Action Navy
COPC	chemicals of potential concern
CFR	Code of Federal Regulations
CSM	conceptual site model
CTO	Contract Task Order
DCE	dichloroethene
DOD	Department of Defense
DQR	data quality review
DRI	direct reading instrument
EPA	United States Environmental Protection Agency
ER	exception report
FBL	fixed-base laboratory
FD	field duplicate
FOL	Field Operations Leader
ft ²	square feet
GC	gas chromatograph
HASP	Health and Safety Plan
HHRA	Human Health Risk Assessment
HVAC	heating, ventilation, and air conditioning
IAQ	Indoor Air Quality
ID	identification
IDEM	Indiana Department of Environmental Management
IDW	investigation-derived waste
IUPPS	Indiana Underground Plant Protection Services
IURs	inhalation unit risks
LRC	laboratory review checklist
MCS	Media Cleanup Standards
MNA	Monitored Natural Attenuation

MS	Mass spectrometry
$\mu\text{g}/\text{m}^3$	microgram per cubic meter
NAVFAC MW	Naval Facilities Engineering Command Midwest
NSA	Naval Support Activity
OSHA	Occupational Safety and Health Administration
PCE	tetrachloroethene
PEL	permissible exposure limit
ppbv	part per billion by volume
PPE	personal protective equipment
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RSL	Regional Screening Level
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SSO	Site Safety Officer
SWMU	Solid Waste Management Unit
TCE	trichloroethene
TR	target risk
VIM	Voluntary Interim Measure
VC	vinyl chloride
VI	vapor intrusion
VOCs	volatile organic compounds
WP	Work Plan

1.0 INTRODUCTION

This Vapor Intrusion (VI) Sampling Work Plan details the activities that will be performed as part of the indoor air, outdoor, and sub-slab vapor sampling to be conducted at Solid Waste Management Unit (SWMU) 16 - Cast High Explosives Fill/Building 146 (B-146) Incinerator, at the Naval Support Activity (NSA) Crane, located in Crane, Indiana. The Work Plan was prepared for the Department of the Navy (Navy), Naval Facilities Engineering Command Midwest (NAVFAC MW) under Contract Task Order (CTO) F276, Comprehensive Long-Term Environmental Action Navy (CLEAN) Contract No. N62470-08-D-0001.

1.1 BACKGROUND

SWMU 16, approximately 16 acres in size, is located in the north-central portion of NSA Crane (Figure 1-1). B-146 was an explosive fill and washout facility with a trichloroethene (TCE) degreaser present in the northern portion of the building. Discharges from the degreaser entered floor drains and discharged through clay vitreous pipes to sumps located exterior to B-146, to the north and northwest (shown on Figure 1-2). In 1995, voluntary interim measures (VIM) were conducted to remediate TCE which was found in the sumps. The floor drains were sealed at that time to prevent any further discharges to the sumps.

Resource Conservation and Recovery Act (RCRA) Facility Investigations (RFIs) conducted during the early 2000s showed that TCE was present in soils underlying the northern portion of B-146 and exterior to the building, to the north and northwest. The highest TCE concentrations were found in soils underlying the approximate location of the TCE degreaser, and along the path of the pipe that previously discharged to the western sump (Figures 1-2 through 1-4 present summaries of TCE soil data). RFI field investigations also showed that the upper zone of groundwater has been contaminated with explosives and chlorinated volatile organic compounds (VOCs), primarily TCE and 1,1,2-trichloroethane (1,1,2-TCA) and their degradation products. The highest TCE concentrations were found in groundwater wells located to the north and northwest, adjacent to B-146. Figure 1-5 presents a summary of the positive groundwater detections based on data collected during the RFI.

TCE and other chlorinated solvents that are present in groundwater and soil underlying SWMU 16 at elevated concentrations present significant risk for potential future groundwater users. The Navy has determined that interim measures must be conducted to address sources of TCE in soils exterior to B-146 to reduce continuing releases to groundwater. Corrective measures for groundwater will consist of monitored natural attenuation (MNA) with removal of soil sources of chlorinated solvents. The Navy has developed a Remedial Work Plan for the removal of chlorinated-solvent-contaminated soil located beyond

the B-146 footprint. Remediation of contaminated soil beneath the building is not feasible without compromising the building integrity.

VOCs in soil and groundwater can migrate and potentially enter a building through cracks in the foundation and floor, gaps around building pipes, or other openings in the foundation/floor. In 2008, the United States Environmental Protection Agency (EPA) Region 5 recommended that indoor air quality (IAQ) sampling be performed at SWMU 16, B-146, to determine if TCE (present in underlying soil) might be migrating to the indoor air space of B-146. The IAQ sampling study was conducted in 2008 as part of an RFI at NSA Crane (Tetra Tech, 2009). Results of the study indicated that TCE was present in indoor air within three of the five rooms (Bays) sampled, and that the eight-hour concentration in two of these rooms exceeded the Indiana Department of Environmental Management (IDEM) 25-Year Commercial Chronic Action Level [screening level of 1.5 parts per billion by volume (ppbv)].

Since sub-slab vapor sampling was not required as part of IAQ studies at that time, EPA has requested that the indoor air study at B-146 be repeated in conjunction with a sub-slab vapor study. The collection of sub-slab vapor samples in conjunction with indoor air samples will allow an accurate attenuation factor to be established to determine the amount of TCE (and associated degradation products) entering B-146 from the underground source(s).

1.2 OBJECTIVES

The objective of the activities summarized in this Work Plan is to collect information to determine if chlorinated solvent (primarily TCE) and degradation product vapors are entering the B-146 air space at concentrations that present significant risk to human health. If significant risks are occurring, additional corrective measures, such as increasing the air exchange ratios in all or part of B-146, will be required. The sub-slab/indoor air ratio would be used to calculate acceptable air exchange ratios.

1.3 SAMPLING DESIGN AND RATIONALE

The design and rationale for the activities summarized in this Work Plan were developed on the basis of: known TCE contamination in SWMU 16 soil and groundwater (Tetra Tech, 2011); the previous Building 146 indoor air study discussed in Section 1.1 (Tetra Tech, 2009); current VI technical guidance (DOD, 2009; EPA, 2010; Navy, 2011); and an example VI study prepared for EPA Region 5 (CH2MHill, 2009).

The SWMU 16 RFI and Soil Delineation Sampling Data Report identified current TCE concentrations in soil and groundwater (Tetra Tech, 2011; Tetra Tech, 2012). TCE concentrations in surface and subsurface soil are shown on Figures 1-2 through 1-4. In surface soil [0 to 2 feet below ground surface (bgs)], TCE contamination is located under the northern portion of B-146 as indicated on Figure 1-2.

Figures 1-3 and 1-4 for subsurface soil indicate TCE soil contamination is also present in the depth intervals of 2 to 6 feet bgs and 6 to 10 feet bgs.

In 2009, an indoor air quality study was conducted to determine if TCE and associated degradation products are penetrating the building floor from contaminated groundwater located beneath the building. The focus of this field event was to collect air quality samples from the interior of B-146. Results of the study indicated that TCE was present in air only within three of the work areas sampled, at the central and northern portions of B-146. As summarized in Table 1-1, concentrations ranged from 0.83 to 2.1 ppbv, compared to the IDEM Action Level (screening) of 1.5 ppbv. The locations where TEC was detected are consistent with the primary location of TCE contamination in surface and subsurface soil, which is in the north end of the building. A human health risk assessment (HHRA) was completed following the indoor air sampling event at B-146. This study indicated no significant risk is present based on an evaluation of contaminants present in air.

The following factors have been considered in designing the proposed indoor air and sub-slab vapor sampling program:

- The proposed indoor air and sub-slab vapor samples will be collected in an environment that represents the occupational employee exposure, as requested by EPA.
- During the collection of all indoor, outdoor, and sub-slab air samples, the B-146 ventilation system settings will be identical to those used during the receptor's actual work hours.
- The indoor air samples will be collected from a height of 4 to 5 feet above the surface of the floor in order to represent the receptor's breathing zone.
- Since NSA Crane has banned the routine use of chlorinated solvents, none are anticipated to be present in the work area to be sampled; however, this will be verified through discussions with B-146 operating personnel prior to conducting this study. The focus of this VI study is the impact of chlorinated solvent soil contamination (i.e., TCE and degradation products) on the B-146 indoor air quality. Therefore, other solvents (non-chlorinated volatile chemicals) would not present any issues.
- It is important to note that PCE and chlorinated alkanes (1,1,2-TCA and 1,1,2,2-PCA) were also detected in groundwater at SWMU 16. These target analytes and their associated degradation products have also been added to the analytical suite for this project.

All air and sub-slab samples will be collected in accordance with the Standard Operating Procedures (SOPs) provided in Appendix A of this Work Plan.

Details of the proposed field activities are presented in Section 2.

TABLE 1-1

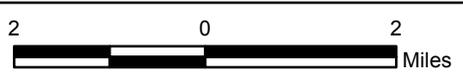
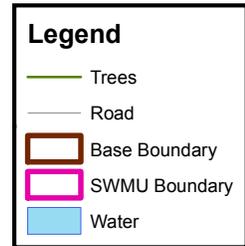
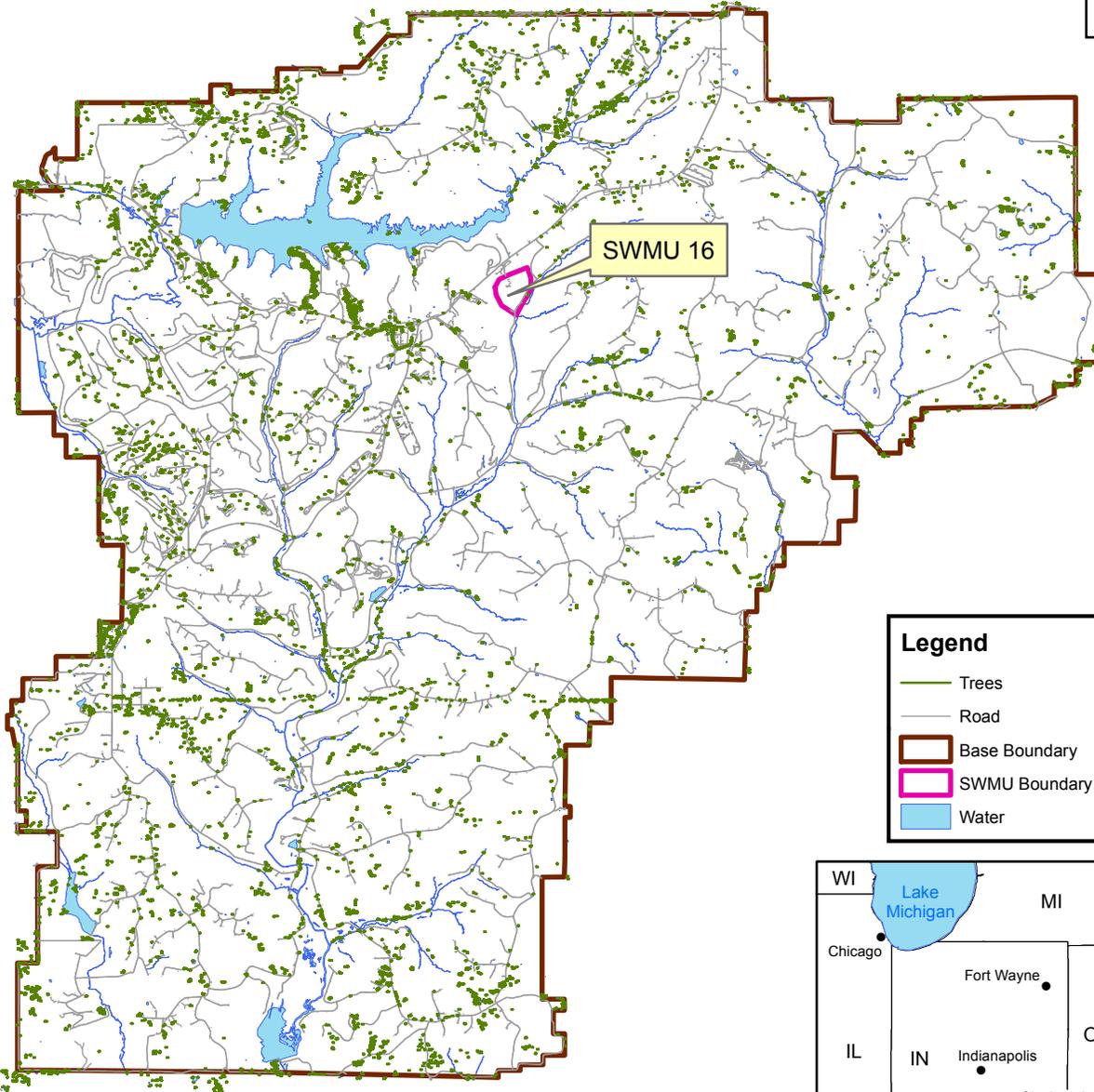
2009 INDOOR AIR QUALITY SAMPLING RESULTS
SWMU 16 - BUILDING 146
NSWC CRANE
CRANE, INDIANA
PAGE 1 OF 2

Location Identification Number	Validated Results (ppbv)	Validated Results ($\mu\text{g}/\text{m}^3$)	Validation Qualifier
1,1-Dichloroethane (CAS: 75-34-3)			
146ASIN01	0.90	3.50	U
146ASIN02	0.90	3.60	U
146ASIN03	0.90	3.60	U
146ASIN04	0.90	3.80	U
146ASIN05	0.90	3.80	U
146ASIN06	0.80	3.30	U
146ASIN06	0.90	3.50	U
146ASIN07	0.90	3.70	U
146ASIN08	0.90	3.70	U
146ASOT01	1.00	4.10	U
1,1-Dichloroethene (CAS: 75-35-4)			
146ASIN01	0.90	3.50	U
146ASIN02	0.90	3.60	U
146ASIN03	0.90	3.60	U
146ASIN04	0.90	3.70	U
146ASIN05	0.90	3.70	U
146ASIN06	0.80	3.20	U
146ASIN06	0.90	0.90	U
146ASIN07	0.90	3.60	U
146ASIN08	0.90	3.60	U
146ASOT01	1.00	4.00	U
Chloroethane (CAS: 75-00-3)			
146ASIN01	0.90	2.30	U
146ASIN02	0.90	2.40	U
146ASIN03	0.90	2.40	U
146ASIN04	0.90	2.50	U
146ASIN05	0.90	2.50	U
146ASIN06	0.80	2.20	U
146ASIN06 ⁽²⁾	0.90	2.30	U
146ASIN07	0.90	2.40	U
146ASIN08	0.90	2.40	U
146ASOT01	1.00	2.70	U
cis-1,2-Dichloroethene (CAS: 156-59-2)			
146ASIN01	0.90	3.50	U
146ASIN02	0.90	3.60	U
146ASIN03	0.90	3.60	U
146ASIN04	0.90	3.70	U
146ASIN05	0.90	3.70	U
146ASIN06	0.80	3.20	U
146ASIN06	0.90	3.40	U
146ASIN07	0.90	3.60	U
146ASIN08	0.90	3.60	U
146ASOT01	1.00	4.00	U

TABLE 1-1

2009 INDOOR AIR QUALITY SAMPLING RESULTS
 SWMU 16 - BUILDING 146
 NSWC CRANE
 CRANE, INDIANA
 PAGE 2 OF 2

Location Identification Number	Validated Results (ppbv)	Validated Results ($\mu\text{g}/\text{m}^3$)	Validation Qualifier
Trichloroethene (CAS: 79-01-6)			
146ASIN01	0.90	5.10	
146ASIN02	0.90	4.80	U
146ASIN03	0.90	4.80	U
146ASIN04	2.10	11.00	
146ASIN05	1.90	10.00	
146ASIN06	1.40	7.40	
146ASIN06	1.40	7.70	
146ASIN07	0.90	4.90	U
146ASIN08	0.80	4.50	J
146ASOT01	1.00	1.00	U
Vinyl Chloride (CAS: 75-01-4)			
146ASIN01	0.90	2.20	U
146ASIN02	0.90	2.30	U
146ASIN03	0.90	2.30	U
146ASIN04	0.90	2.40	U
146ASIN05	0.90	2.40	U
146ASIN06	0.80	2.10	U
146ASIN06	0.90	2.20	U
146ASIN07	0.90	2.30	U
146ASIN08	0.90	2.30	U
146ASOT01	1.00	2.60	U
CAS	Chemical Abstracts Service Registry Number		
ppbv	parts per billion by volume		
$\mu\text{g}/\text{m}^3$	micrograms per cubic meter		
U -	Indicates that the chemical was not detected at the numerical detection limit (sample-specific detection limit) noted.		
J -	Indicates that the chemical was detected; however, the associated numerical result is not a precise representation of the concentration that is actually in the sample. The laboratory-reported concentration is considered to be an estimate of the true concentration.		

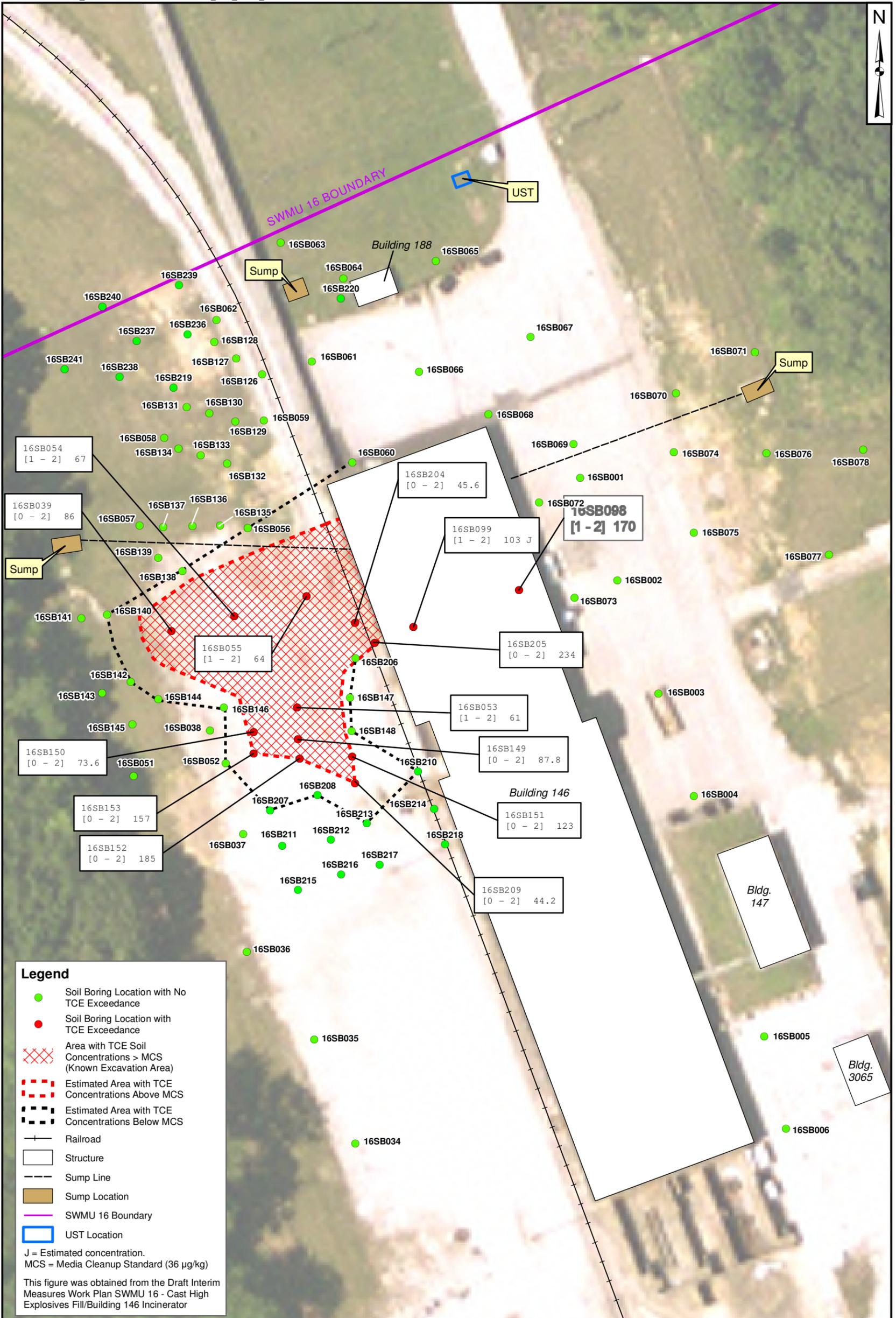


DRAWN BY	DATE
K. MOORE	09/26/08
CHECKED BY	DATE
J. LUCAS	12/21/12
REVISED BY	DATE
SCALE AS NOTED	



BASE AND SITE LOCATION MAP
 SWMU 16 - CAST HIGH EXPLOSIVES FILL /
 B146 INCINERATOR
 NSA CRANE
 CRANE, INDIANA

CONTRACT NUMBER CTO 0377	
OWNER NO.	
APPROVED BY	DATE
FIGURE NO. FIGURE 1-1	REV 0

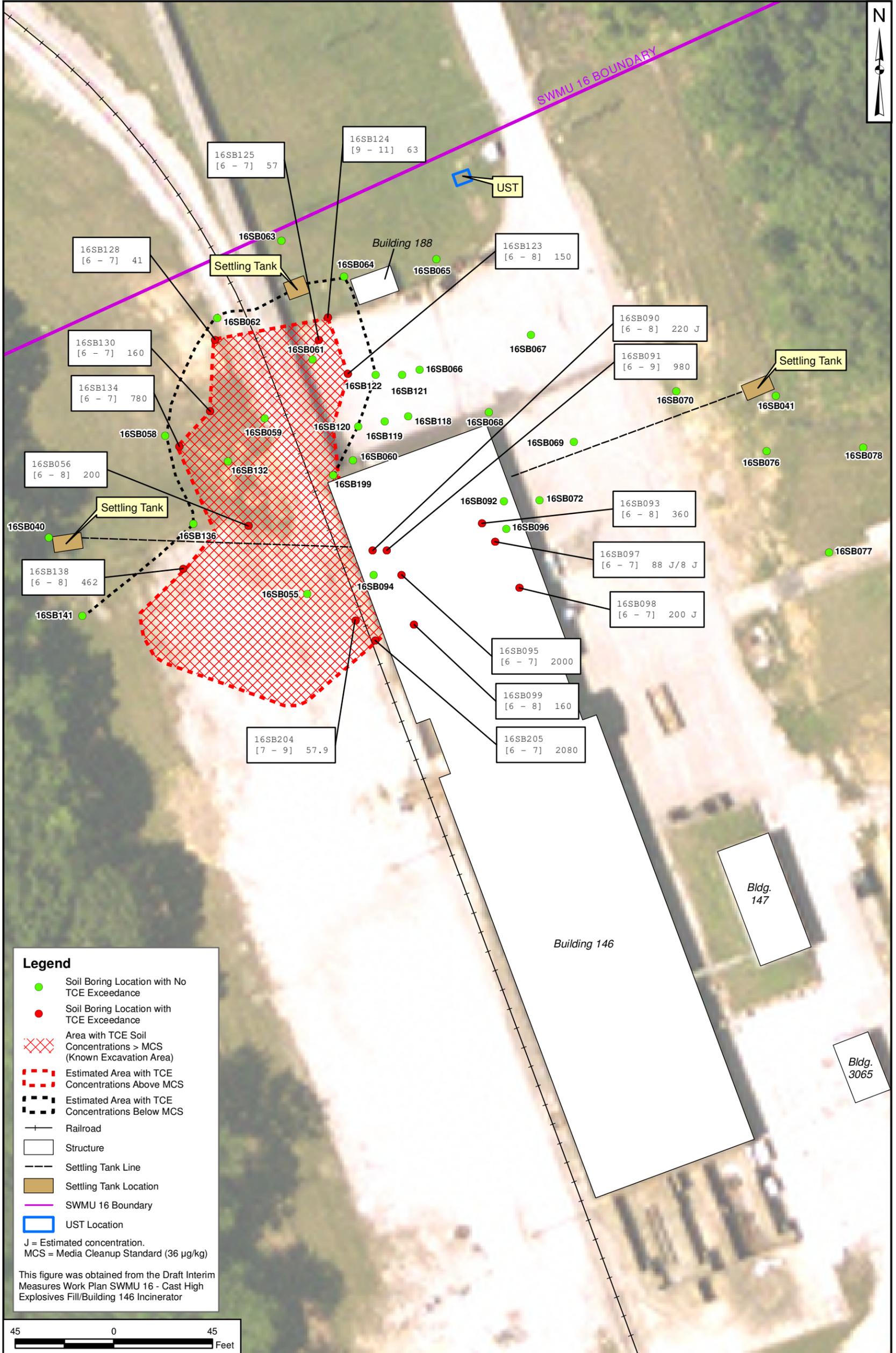


DRAWN BY	DATE
C. TULLEY	01/20/12
CHECKED BY	DATE
J. DUCAR	12/12/12
REVISED BY	DATE
D. COUCH	03/25/13
SCALE	
AS NOTED	



**TCE CONTAMINATION AREA SOIL SAMPLING RESULTS
AND CLEAN BOUNDARY
SURFACE SOIL (0 - 2 FT)
SWMU 16 - CAST HIGH EXPLOSIVES FILL/BLDG. 146 INCINERATOR
NSA CRANE
CRANE, INDIANA**

CONTRACT NUMBER	CTO NUMBER
02127	F277
APPROVED BY	DATE
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APPROVED BY	DATE
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FIGURE NO.	REV
FIGURE 1 - 2	0



Legend

- Soil Boring Location with No TCE Exceedance
- Soil Boring Location with TCE Exceedance
- Area with TCE Soil Concentrations > MCS (Known Excavation Area)
- Estimated Area with TCE Concentrations Above MCS
- Estimated Area with TCE Concentrations Below MCS
- Railroad
- Structure
- Settling Tank Line
- Settling Tank Location
- SWMU 16 Boundary
- UST Location

J = Estimated concentration.
MCS = Media Cleanup Standard (36 µg/kg)

This figure was obtained from the Draft Interim Measures Work Plan SWMU 16 - Cast High Explosives Fill/Building 146 Incinerator

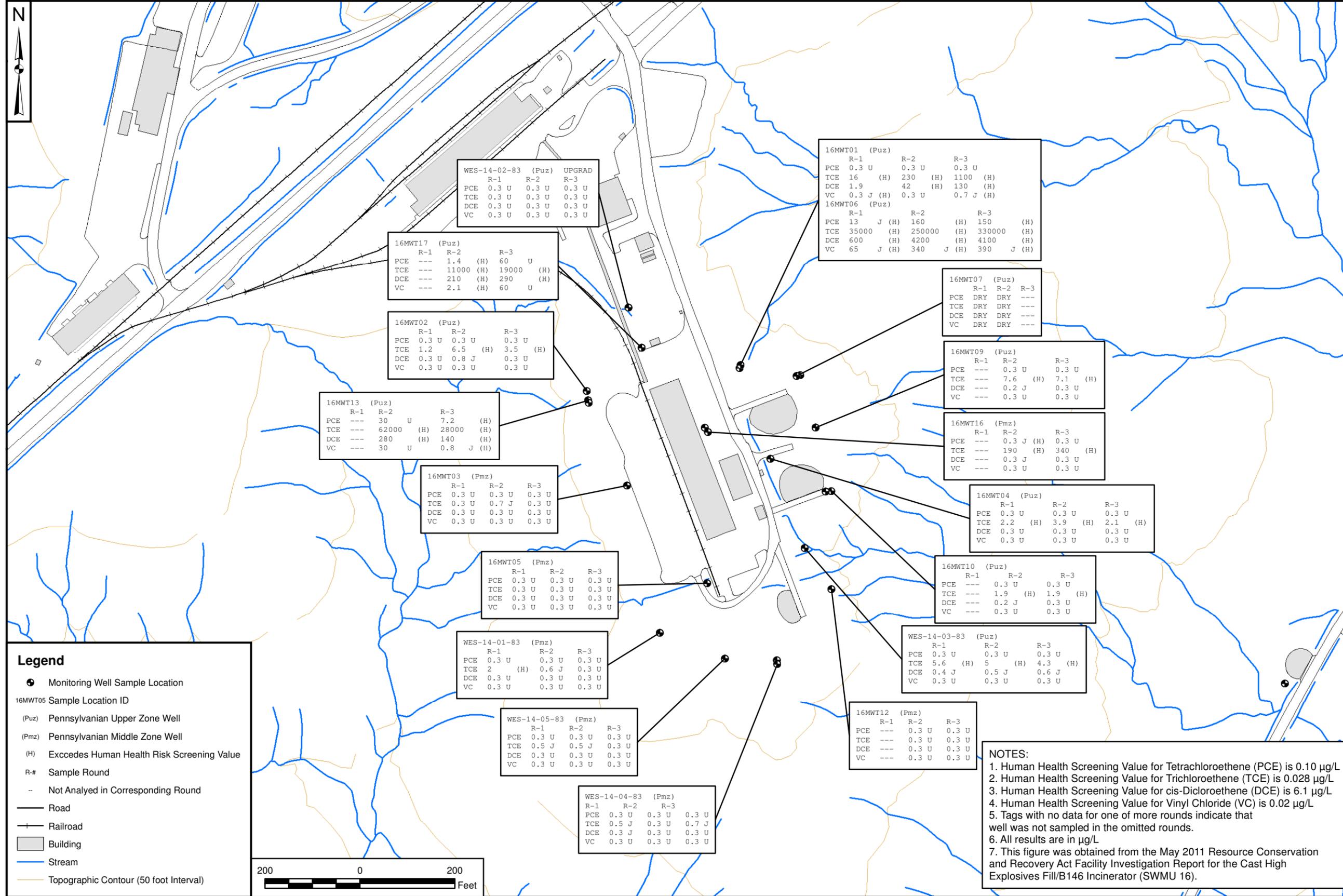


DRAWN BY	DATE
C. TULLEY	01/20/12
CHECKED BY	DATE
R. BARRINGER	03/25/13
REVISED BY	DATE
S. PAXTON	03/25/13
SCALE	
AS NOTED	



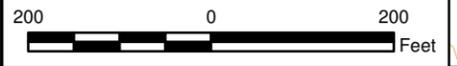
TCE CONTAMINATION AREA SOIL SAMPLING RESULTS AND CLEAN BOUNDARY DEEP SOIL (6 - 10 FT)
SWMU 16 - CAST HIGH EXPLOSIVES FILL/BLDG. 146 INCINERATOR
NSA CRANE
CRANE, INDIANA

CONTRACT NUMBER	CTO NUMBER
02127	F277
APPROVED BY	DATE
APPROVED BY	DATE
FIGURE NO.	REV
FIGURE 1 - 4	0



Legend

- Monitoring Well Sample Location
- 16MWT05 Sample Location ID
- (Puz) Pennsylvanian Upper Zone Well
- (Pmz) Pennsylvanian Middle Zone Well
- (H) Exceeds Human Health Risk Screening Value
- R-# Sample Round
- Not Analyzed in Corresponding Round
- Road
- +— Railroad
- Building
- Stream
- Topographic Contour (50 foot Interval)



NOTES:

1. Human Health Screening Value for Tetrachloroethene (PCE) is 0.10 µg/L
2. Human Health Screening Value for Trichloroethene (TCE) is 0.028 µg/L
3. Human Health Screening Value for cis-Dichloroethene (DCE) is 6.1 µg/L
4. Human Health Screening Value for Vinyl Chloride (VC) is 0.02 µg/L
5. Tags with no data for one of more rounds indicate that well was not sampled in the omitted rounds.
6. All results are in µg/L
7. This figure was obtained from the May 2011 Resource Conservation and Recovery Act Facility Investigation Report for the Cast High Explosives Fill/B146 Incinerator (SWMU 16).

SELECT CHLORINATED ALKENES CONCENTRATIONS (µg/L) IN GROUNDWATER, ROUNDS 1 THROUGH 3, FOR UPPER ZONE AND MIDDLE ZONE WELLS SWMU 16 CAST HIGH EXPLOSIVES FILL / B146 INCINERATOR NSWC CRANE CRANE, INDIANA		CONTRACT NUMBER CTO NUMBER
APPROVED BY J. NOVAK	DATE 04/04/13	DATE 04/10/13
APPROVED BY J. LUCAS	DATE 04/10/13	DATE 04/10/13
SCALE AS NOTED		FIGURE NO. 1-5
		REV 0



2.0 FIELD ACTIVITIES

This section presents a summary of the field activities that will be performed to address the objectives of the vapor intrusion study as discussed in Section 1 of this Work Plan. The proposed locations of the outdoor air, indoor air, and sub-slab vapor samples are shown in Figure 2-1.

2.1 ITINERARY FOR BUILDING STAKEHOLDERS

Prior to the air sampling event, the Navy will identify B-146 stakeholders, which are expected to include:

- The Army (manages B-146)
- B-146 operations personnel
- Army industrial safety personnel

At least two weeks prior to the air sampling event, an itinerary will be developed and presented to the Navy and stakeholders at B-146. The itinerary will indicate the proposed dates of sampling, the proposed locations of each type of sample, and a directive requesting verification that no chlorinated solvents are present, and, if determined to be present, a request that any such solvents be removed prior to the sampling dates.

2.2 BUILDING PREPARATIONS

The VI study is designed to simulate normal inside building conditions when personnel are working in B-146. The routine heating, ventilation, and air conditioning (HVAC) system will remain active during the sampling period to maintain normal air circulation/exchange conditions. For safety reasons, the study will be conducted on a weekend when regular (week day) working personnel are not in the building.

2.3 UTILITY CLEARANCE

At least two weeks prior to the air sampling event, a meeting will be held with the B-146 operations and maintenance personnel to review the proposed sample (drilling) locations against sub-slab utilities location figures (to be provided by B-146 personnel). Any proposed sample location that may present the potential of encountering sub-slab utilities will be re-located, and the final sub-slab sample locations will be marked on the building floor.

2.4 SAMPLE COLLECTION

This VI Sampling Work Plan includes the collection of three types of time-integrated samples: indoor air, sub-slab vapor, and outdoor air. The collection of these sample types is described below, in Sections 2.4.1, 2.4.2, and 2.4.3, respectively. Appendix A contains all SOPs relevant to this work.

The proposed number of locations for indoor air and sub-slab sampling is based, in part, on general VI guidance and on the site-specific conditions at B-146. Technical guidance is currently available from EPA and the Department of Defense (DoD) for conducting VI studies. EPA Region 5 Superfund has developed a Vapor Intrusion Guidebook (October 2010) which advocates the development of a site-specific VI sampling strategy tailored to meet each site's conditions and study objectives, and recommends one sample for sub-slab areas less than or equal to 1,500 square feet (ft²). In addition, the DOD has developed a Vapor Intrusion Handbook (January 2009) which recommends the collection of one sub-slab sample per 1,000 ft². Both references recommend one indoor air sample per enclosed area.

B-146 consists of five divided work bays. Four of the work bays (Bays 1 through 4) are approximately 1,500 ft² in size, while the northernmost bay (Bay 5) measures approximately 2,000 ft². Previous investigations have indicated that TCE contamination is located at the northern portion of B-146 (Tetra Tech, 2011; Tetra Tech, 2012). Because the area of Bay 5 is greater than 1,500 ft² and the majority of the TCE-contaminated area is adjacent to (west of) Bay 5, this Work Plan is recommending the collection of two sub-slab vapor samples in Bay 5, and only one sub-slab sample in each of Bays 1 through 4. A building survey has been conducted to confirm there is no crawl space beneath the floor of B-146 and to confirm preliminary sampling locations.

2.4.1 Indoor Air Sampling

One indoor air sample will be collected in each work bay using evacuated summa canisters at the locations shown in Figure 2-1. Summa canisters will operate continuously for 8 hours and will be shipped to the fixed-base laboratory (FBL) for VOCs analysis at the end of the sampling event. In addition, one duplicate sample will be collected for quality assurance (QA) purposes. Table 2-1 lists the sample identification numbers for the air samples that are proposed for collection, along with their respective general locations. SOP-01 provides a detailed procedure for indoor air sampling using summa canisters (Appendix A).

2.4.2 Sub-Slab Vapor Sampling

Prior to conducting sub-slab vapor sampling, a helium leak test will be conducted at each bore hole to verify the seal of each sampling point. In the event that the seal is compromised, the sampling point will be resealed until it passes the helium leak test. A 3- to 4-hour waiting time will be used before collection of each sample after sample point installation.

New Teflon®-lined tubing will be placed down each bore hole about 2-3 inches below the foundation floor of B-146. Plumber's putty, or a similar VOC-free substance, will be applied to the hole around the tubing to seal the hole, and to minimize disturbance of the sub-slab soil gas concentrations and surface air intrusion. The tubing is attached to a purging pump outside of the hole and three to five tubing volumes are purged into a Tedlar™ bag (to avoid purging into indoor air) to ensure the sample represents subsurface conditions.

A total of six sub-slab vapor samples will be collected using evacuated summa canisters. Based on historical soil and groundwater data, as discussed in Section 1.1, the greatest potential for TCE and chlorinated alkanes (1,1,2-TCA and 1,1,2,2-PCA) in soil is located north, and northwest of Building 146.

As stated for indoor air sampling, summa canisters will operate continuously for 8-hours and will be shipped to the FBL for VOCs analysis following the sampling event. In addition, one duplicate sample will be collected for QA purposes. Table 2-1 lists the sample identification numbers for the sub-slab vapor samples that are proposed for collection, along with their respective general locations. SOP-02 provides a detailed procedure for sub-slab vapor sampling using summa canisters.

At the conclusion of the sub-slab vapor sampling, each indoor air and sub-slab vapor sample location will be triangulated from the corner of each bay area. An updated sample location figure will be provided in the VI report.

2.4.3 Outdoor Air Sampling

The area of TCE contamination in soil and groundwater extends beyond the footprint of Building 146. The RFI has shown that TCE is present in soils exterior to B-146, to the north and northwest. This outside area represents a potential background source of TCE that could possibly bias the indoor air sampling results if outside air cross-contaminated indoor air during the sampling period. The purpose of the indoor air samples being collected for this study is to measure the impact of vapor intrusion via the soil, and not any contribution of VOCs from sources outside B-146.

One outdoor air sample will be collected along the prevailing upwind direction from Building 146 away from any wind obstructions such as trees and buildings and any contaminated soils. On the day scheduled for air sampling, the prevailing wind direction will be determined on the basis of the hourly average wind direction reported at the National Weather Service Bloomington (47401) reporting station. In the event, that hourly wind data is not available from Bloomington, Indianapolis and Terra Haute NWS reporting stations will be used to determine the prevailing wind direction. The outdoor air sampling will begin at least 1-hour prior to the start of indoor air sampling and will continue until at least 30 minutes before indoor air sampling is complete. The wind direction and speed will be recorded for each hour in the log book for the period 1-hour before sampling begins to 1-hour after sampling ends.

2.5 SEQUENCING AND TIMING

All samples will be collected within a 32-hour period. As noted previously, each indoor air and sub-slab vapor sample will be collected over a continuous 8-hour period. Indoor air samples will be collected first, along with one outdoor air (background) sample. Sub-slab vapor samples will be collected after completion of the indoor air and outdoor air sample collection. This sampling sequence is planned in order to minimize any impacts on indoor air samples from the potential release of TCE or degradation products during the drilling activities required for sub-slab vapor sample collection. The sub-slab environment is stable, and TCE concentrations would not be expected to vary significantly within an 8-hour period; whereas, indoor air concentrations would be much more subject to variation due to potential releases during the drilling process, or due to imperfect drill-hole seals following drilling.

2.6 SAMPLE MANAGEMENT

The procedures for proper management of air/vapor samples to be collected throughout the course of the IAQ study are discussed below.

Record-Keeping

The following records will be maintained to document sample collection and handling:

- Sample collection log sheets and/or field logbooks
- Chain-of-custody records
- Freight bills for samples shipped via an overnight carrier
- Analytical reports

All air/vapor samples collected during the course of the IAQ study will be placed in appropriate laboratory-supplied containers for transport to the analytical laboratory.

- Security of the sample during field activities: B-146 will be closed to public access during sampling activities. Upon collection, samples will be in the possession of the sampling crew until shipped to the laboratory via Federal Express (overnight).
- Security of the sample in the laboratory: Samples will be stored in a secure area in the laboratory, with limited access. Upon receipt of the samples, laboratory personnel will check the condition of the samples and the accuracy of the accompanying paperwork.

The following chain-of-custody procedures are intended to document sample possession from the time of sample collection until ultimate disposal of the sample. A sample is considered to be in custody if it is:

- in one's actual possession.
- in view after being in one's possession.
- secured (i.e., locked up) so that no tampering can occur. Or,
- in a secured area, available to authorized personnel only.

A chain-of-custody form will be completed in the field. The original will accompany the samples and copies will be maintained at intermediate steps. The secured shipping container(s) will be delivered to Federal Express for overnight shipment.

Sample Identification

The alpha-numeric (A-N) sample identification system presented below will be used to identify and label all air/vapor samples collected during the field activities. This system corresponds with the nomenclature shown in Table 2-1.

All sample identifiers will begin with "146", referring to B-146, where the samples are to be collected, and "AS", indicating air sample. The other portions of the sample identifier will provide information on the sample sub-category (outdoor air, indoor air, sub-slab vapor, or field duplicate), and each sample will be assigned a unique number. Therefore, each sample identifier will include:

- **146** – to identify Building 146
- **AS** – to identify it as an "Air Sample"
- **AA** – refers to the sub-category of the sample or a QA/QC sample [i.e., outdoor air (**OU**), indoor air (**IN**), sub-slab (**SS**), or field duplicate (**FD**)]

- **NN** – refers to the designated number of the sample (with the first sample collected to be numbered “09” – see below)

Because there were eight previous IAQ samples collected in 2008, the sample identifiers for this IAQ study will begin with the number (NN) “09”. For example, the sample identifier for the **first** sub-slab (“SS”) vapor sample collected from Building 146 would be identified as “146-AS-SS-09.”

This sample identification system will be used on all sample labels and chain-of-custody documents in order to maintain consistency in the labeling process and to allow efficient handling of all samples from different locations.

Field Quality Control

Two sets of field duplicates will be collected during this VI study, one indoor air sample and one sub-slab vapor sample, to monitor the precision of the field sampling process.

Equipment Decontamination

Decontamination is required for any non-dedicated sampling equipment to be re-used, although the use of such equipment is not anticipated for this sampling event. SOP-03 (Appendix A) summarizes the process for decontamination of any non-dedicated sampling equipment, should it be necessary.

Investigation-Derived Waste

Investigation-derived waste (IDW) such as personal protective equipment (PPE), expended air sample tubing, and other consumables related to preparing the sub-slab sampling points is expected to be generated during this sampling event. IDW will be packed into garbage bags and added to the NSA Crane trash disposal system (dumpster) for collection and transport to NSA Crane solid waste treatment plant. SOP-04, located in Appendix A, provides details about IDW.

2.7 HEALTH AND SAFETY

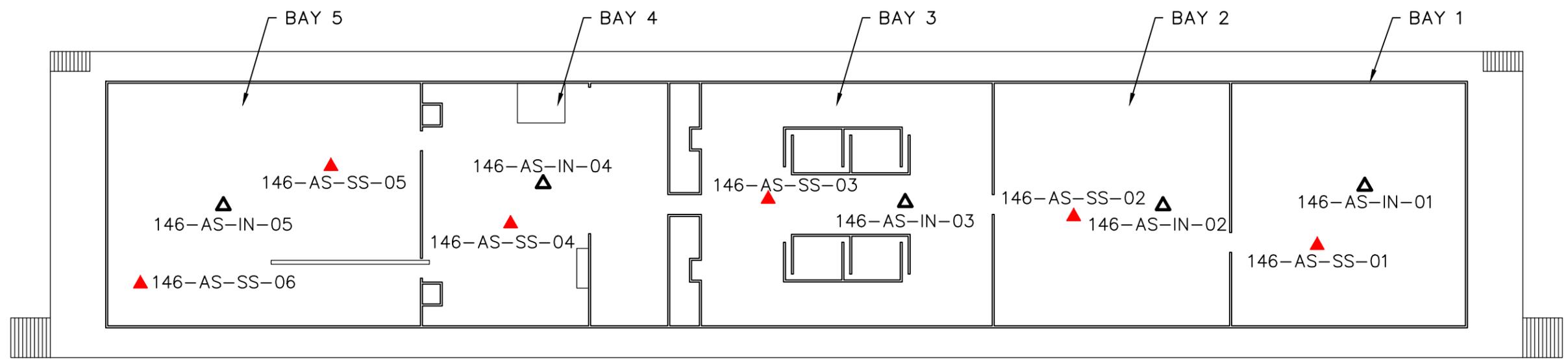
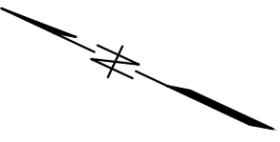
A Health and Safety Plan (HASP) Addendum will be developed in accordance with 29 Code of Federal Regulations (CFR) 1910.120, and will include information such as personnel training requirements, record-keeping, and emergency response procedures. The site safety officer (SSO) will be responsible for ensuring that all field personnel are familiar and work in accordance with the HASP Addendum. The SSO will conduct a safety “tailgate meeting” prior to initiating activities for preparing and repairing the sub-slab holes in the building floor, and prior to each type of air sampling event (indoor air and sub-slab).

TABLE 2-1

**INDOOR AIR, OUTDOOR AIR, AND SUB-SLAB VAPOR
SAMPLE IDENTIFICATION NUMBERS AND LOCATIONS
SWMU 16 - BUILDING 146
NSA CRANE
CRANE, INDIANA**

Sample Type	Sample Identification Number	Sample Location
Indoor Air	146-AS-IN-01	Bay 1
	146-AS-IN-02	Bay 2
	146-AS-IN-03	Bay 3
	146-AS-IN-04	Bay 4
	146-AS-IN-05	Bay 5
Sub-Slab Vapor	146-AS-SS-01	Bay 1
	146-AS-SS-02	Bay 2
	146-AS-SS-03	Bay 3
	146-AS-SS-04	Bay 4
	146-AS-SS-05	Bay 5
	146-AS-SS-06	Bay 5
Outdoor Air	146-AS-OU-01	Outdoor
Field Duplicates	146-AS-FD-01	TBD
	146-AS-FD-02	TBD

TBD- To be determined



146-AS-OU-01

BUILDING 146

LEGEND:

- ▲ INDOOR AIR SAMPLE
146-AS-IN-01
- ▲ SUB-SLAB VAPOR SAMPLE
146-AS-SS-01
- ⊗ OUTDOOR AIR SAMPLE
146-AS-OU-01



PROPOSED LOCATIONS
OF INDOOR, OUTDOOR
AND SUB-SLAB AIR SAMPLING AT
SWMU 16, BUILDING 146

SCALE: 1" = 30'
DATE: 9/25/2008

FIGURE 2-1

3.0 PROJECT QUALITY ASSURANCE

Project requirements related to analytical method, field QC, equipment decontamination, investigation-derived waste (IDW), data validation, and health and safety are presented below.

3.1 ANALYTICAL METHOD

The method of analysis for all outdoor air, indoor air, and sub-slab vapor samples will be Modified EPA Method TO-15 – Volatile Organic Compounds (VOCs) by gas chromatograph (GC)/mass spectrometry (MS) full-scan (provided in Appendix B).

Each canister will be individually certified to provide the highest level of data defensibility. All canisters used in the sampling program will be “certified clean” by the laboratory. The target analytes for each sample will be TCE and TCE degradation products, including: cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride, 1,1-dichloroethane (1,1-DCA), and 1,1-DCE, in addition to PCE and chlorinated alkanes (1,1,2-TCA and 1,1,2,2-PCA) and their associated degradation products.

3.2 DATA VALIDATION

The laboratory will provide an analytical data package for each sample analyzed. The data validation process entails comparing the summarized quality assurance/quality control (QA)/(QC) data for each sample against the established acceptance limits and flagging the noncompliant. Each analytical data package will be evaluated and validated based on applicable EPA data packaging and reporting requirements. A data quality review (DQR) will be provided with the report. The data validation package will include:

- Comparison of the data package to the reporting level requirements to ensure completeness in the analytical data package and compliance with the contract.
- Comparison of the dates of sampling, extraction, and analysis to ensure that samples were extracted and analyzed within the proper holding times.
- Checks of QA/QC samples (laboratory blanks) to evaluate possible contamination sources.

4.0 DATA EVALUATION

This section describes how the validated air quality data will be evaluated to assist in determining risk, if any, to the industrial worker at B-146. All air sample concentrations will be compared to current EPA Regional Screening Levels (RSLs) for Industrial Air and will be evaluated in a HHRA, described further in Section 5.

4.1 INDOOR AIR AND SUB-SLAB VAPOR EVALUATION

As stated previously, each indoor air and sub-slab vapor sample will be analyzed for TCE and TCE degradation products, including: cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride, 1,1-dichloroethane (1,1-DCA), and 1,1-DCE. Multiple lines of evidence will be used to evaluate the magnitude and extent of vapor intrusion at Building 146. Depending on the results of the investigation and a human health risk assessment, it may be determined that either no further action is necessary or that mitigation or remediation may be warranted.

Once the analytical data has been collected, it will be necessary to evaluate the data for site management decision making. The evaluation will utilize a "multiple lines of evidence" approach to assess if the vapor intrusion pathway. The lines of evidence being considered for this project include:

- Near-slab soil gas data
- Indoor air data
- Outdoor air samples collected concurrently with indoor air sample
- Comparison of constituent ratios of chemicals in soil gas and indoor air
- Comparison of analytical results to the USEPA human health project screening levels given in Table 4-1 and determine the level of risk.

All analytical results reported by the laboratory will be provided in units of " $\mu\text{g}/\text{m}^3$ ". As a result, no conversions calculations will be necessary.

4.2 BACKGROUND EVALUATION

Background contributions refer to outdoor air contamination in the ambient air surrounding a structure. Outdoor air can contain numerous VOCs, such as benzene, tetrachloroethene (PCE), and trichloroethene (TCE), as a result of other sources of these VOCs. Depending on building air exchange rates, contaminants from outdoor air may be major contributors to indoor air quality conditions (ITRC, 2007).

The focus of this VI study is on chlorinated solvents. Chlorinated solvents are no longer in use at NSA Crane. The area surrounding NSA Crane is very rural area, where there are no industrial activities that could contribute chlorinated solvents to the outdoor ambient air at B-146. Chlorinated solvents are, however, present in soils and groundwater under and adjacent to the north and northwest corner of B-146, and this contaminated soil and groundwater are a potential outdoor source of chlorinated solvents for air at B-146 if solvents pass through the soil into the atmosphere.

Navy (2011) and DoD (2011) guidance recommend that one background (outdoor) air sample be collected if the study area is potentially influenced by roadways, vehicle parking lots, local industry, or other potential off-site sources of COPCs. In order to evaluate any background contribution from outdoor air to indoor air, one 8-hour outdoor air sample will be collected at the northwest end of B-146 (Figure 2-1), where previous investigations have indicated that surface and subsurface soil is contaminated with TCE concentrations that exceed the Media Cleanup Standards (MCS). The outdoor air sampling will be concurrent with the indoor air sampling.

TABLE 4-1

**REFERENCE LIMITS AND EVALUATION TABLE FOR
INDOOR AIR, OUTDOOR AIR, AND SUB-SLAB VAPOR SAMPLING
SWMU 16 - BUILDING 146
NSA CRANE
CRANE, INDIANA**

Matrix: Indoor Air

Analyte	CAS Number	Project Screening Level (PSL) ⁽¹⁾ (µg/m ³)	Project Screening Level Reference	Project Quantitation Limit Goal (µg/m ³)	Lab Name Chemtech Consulting Group		
					LOQ (µg/m ³)	LOD (µg/m ³)	MDL (µg/m ³)
Trichloroethene (TCE)	79-01-6	3	USEPA VISL	0.29	0.16	0.16	0.16
TCE Degradation Products							
1,1-Dichloroethane	75-34-3	7.7	USEPA VISL	2.57	2.02	0.4	0.16
1,1-Dichloroethene	75-35-4	880	USEPA VISL	29.3	1.98	0.4	0.2
cis-1,2-Dichloroethene ⁽²⁾	156-59-2	260	USEPA VISL	8.7	1.98	0.4	0.22
Vinyl Chloride	75-01-4	2.8	USEPA VISL	0.93	0.08	0.08	0.08
Analyte							
PCE	127-18-4	47	USEPA VISL	6.00	0.2	0.2	0.2
1,1,2,2-PCA	79-34-5	0.21	USEPA VISL	0.070	0.08	0.08	0.08
PCA Degradation Products							
1,1,2-trichloroethane	79-00-5	0.77	USEPA VISL	0.029	2.72	0.54	0.54
1,2-dichloroethane	107-06-2	0.47	USEPA VISL	0.157	2.02	0.4	0.4
Chloroethane	75-00-3	44,000	USEPA VISL	1466.52	1.33	0.27	0.27
Analyte							
1,1,2-TCA	79-00-5	0.77	USEPA VISL	0.029	2.72	0.54	0.54
Chloroform	67-66-3	0.53	USEPA VISL	0.037	2.43	0.49	0.08
Dichlorodifluoromethane	75-71-8	440	USEPA VISL	3.33	2.47	0.49	0.18
Methylene Chloride	75-09-2	1,200	USEPA VISL	21.00	1.74	0.35	0.16
Trichlorofluoromethane	75-69-4	3,100	USEPA VISL	24.33	2.8	0.56	0.22

Matrix: Sub-Slab Vapor

Analyte	CAS Number	Project Screening Level (PSL) ⁽¹⁾ (µg/m ³)	Project Screening Level Reference	Project Quantitation Limit Goal (µg/m ³)	Lab Name Chemtech Consulting Group		
					LOQ (µg/m ³)	LOD (µg/m ³)	MDL (µg/m ³)
Trichloroethene (TCE)	79-01-6	30	USEPA VISL	2.9	0.16	0.16	0.16
TCE Degradation Products							
1,1-Dichloroethane	75-34-3	77	USEPA VISL	25.7	2.02	0.4	0.16
1,1-Dichloroethene	75-35-4	8,800	USEPA VISL	29.3	1.98	0.4	0.2
cis-1,2-Dichloroethene ⁽²⁾	156-59-2	2,600	USEPA VISL	86.7	1.98	0.4	0.22
Vinyl Chloride	75-01-4	28	USEPA VISL	9.3	0.08	0.08	0.08
Analyte							
PCE	127-18-4	470	USEPA VISL	6.00	0.2	0.2	0.2
1,1,2,2-PCA	79-34-5	2.1	USEPA VISL	0.070	0.08	0.08	0.08
PCA Degradation Products							
1,1,2-trichloroethane	79-00-5	7.7	USEPA VISL	0.029	2.72	0.54	0.54
1,2-dichloroethane	107-06-2	4.7	USEPA VISL	0.157	2.02	0.4	0.4
Chloroethane	75-00-3	440,000	USEPA VISL	1466.52	1.33	0.27	0.27
Analyte							
1,1,2-TCA	79-00-5	7.7	USEPA VISL	0.029	2.72	0.54	0.54
Chloroform	67-66-3	5.3	USEPA VISL	0.037	2.43	0.49	0.08
Dichlorodifluoromethane	75-71-8	4,400	USEPA VISL	3.33	2.47	0.49	0.18
Methylene Chloride	75-09-2	12,000	USEPA VISL	21.00	1.74	0.35	0.16
Trichlorofluoromethane	75-69-4	31,000	USEPA VISL	24.33	2.8	0.56	0.22

(1) - PSLs were determined using the United States Environmental Protection Agency (USEPA) Vapor Intrusion Screening Level (VISL) Calculator, Version 3.2.1. November 2013 RSLs in an industrial setting. The selected value was determined based on the lowest of the 1E-06 carcinogenic target risk or hazard index of 1.

(2) - Value is for trans-1,2-dichloroethene.

Abbreviations:

µg/m³ - microgram per cubic meter

LOQ - level of quantitation

LOD - level of detection

MDL - method detection limit

5.0 HUMAN HEALTH RISK ASSESSMENT

A HHRA will be conducted following laboratory analysis and data validation of the collected outdoor air, indoor air, and sub-slab vapor samples. The risk assessment will include:

- The protocol used to select COPCs for the HHRA.
- An exposure assessment providing the methodology used to:
 - Calculate exposure point concentrations (i.e., the concentrations to which the receptor is exposed).
 - Calculate receptor intake under current site-specific (military/industrial) and potential future land use scenarios.
- A toxicity assessment providing the current inhalation toxicity criteria for detected TCE and TCE degradation products in the indoor air and sub-slab vapor samples.
- The development of a site-specific attenuation factor (i.e., the ratio of the concentrations of TCE and TCE degradation products in the indoor air samples versus concentrations in sub-slab vapor samples) based on FBL results.
- If risk is found to be unacceptable, air exchange ratios will be calculated to determine the exchange ratio that would need to be maintained to reduce risks to acceptable levels, while B-146 is occupied.
- Risk characterization results (i.e., cancer and non-cancer risk estimates) for workers exposed to indoor air concentrations under current conditions. For purposes of completeness, risk characterization results for hypothetical buildings/land use scenarios (based on sub-slab vapor concentrations and both site-specific and conservative, default attenuation factors).
- An uncertainty assessment will be conducted to describe the uncertainties related to the HHRA assumptions and conclusions. The uncertainty assessment will include a qualitative assessment of potential future changes in risk which will result as TCE concentrations decrease and the concentrations of more toxic degradation compounds (e.g., vinyl chloride) potentially increase.

- The uncertainty analysis will include an evaluation of the potential risk implications of the degradation of TCE to vinyl chloride in soil/groundwater. This is a relevant issue because vinyl chloride is a more potent carcinogen and is more volatile than TCE. The inhalation unit risks [IURs] for TCE and vinyl chloride are $4.1E-06$ and $4.4E-06$ per $\mu\text{g}/\text{m}^3$ for TCE and vinyl chloride, respectively. The analysis will commence with a simple evaluation of the impact on risk estimates if it is simply assumed that *all* of the TCE in the groundwater is converted to vinyl chloride. This is an extremely conservative assumption, but allows for a theoretical “worst case” analysis. If the results of this simple evaluation suggest a potential for unacceptable risks based on the vinyl chloride concentrations in the groundwater, the analysis will continue with a qualitative discussion of the chemical/physical/hydrogeological factors impacting the vinyl chloride concentrations in the groundwater and the likelihood that unacceptable vinyl chloride concentrations (in terms of the vapor intrusion pathway) will be detected in the groundwater. It should be noted that neither this analysis nor a more quantitative fate-and-transport groundwater modeling analysis will eliminate the need for a long-term monitoring plan to periodically assess groundwater contaminant concentrations and associated risks. However, the results of the suggested analysis may assist the risk management team tasked with making remedial and long-term monitoring decisions for SWMU 16.

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APPENDIX A

FIELD STANDARD OPERATING PROCEDURES

SOP-01

INDOOR AIR QUALITY SUMMA CANISTER AIR SAMPLING PROCEDURE

1.0 PURPOSE

The purpose of this Project Specific Standard Operating Procedure (SOP) is to describe a method for sampling and analysis of Indoor Air Quality (IAQ) with regard to airborne concentrations of volatile organic compounds (VOCs). The method is based on the collection of air samples in subatmospheric stainless steel SUMMA canisters over an 8-hour period. Ambient (outside) air and soil gas samples will also be a part of IAQ assessments conducted.

2.0 SCOPE

This IAQ sampling system described in this SOP was designed specifically to provide analytical support for the assessment of potential health risks from certain volatile organic compounds that may be present in indoor air atmospheres. The sample will be collected using a specially prepared 6-liter, evacuated stainless steel canisters. A controlled flow orifice is used to collect the air sample over an 8-hour period.

Ambient air samples are to be collected concurrently during IAQ sampling. Sub-slab samples are also being collected as part of an IAQ assessment and will be collected sequentially (not concurrently) as soon as possible after IAQ sampling has been completed.

3.0 SAMPLING EQUIPMENT

The following is a list of sampling equipment:

- A clean 6 Liter stainless steel SUMMA Canister fully evacuated to -30 in Hg or greater.
- A pressure gauge within a range of 8 to 12 milliliters/minute (ml/min) and a critical orifice used to control the flow rate into the canister for the 8-hour sampling period (10.4 ml/min).
- SUMMA Canister Air Sampling Field Sample Data Sheet (See Attachment I)
- Logbook

- Digital camera
- Adjustable Wrench
- Teflon tape
- Compressed Air
- Watch
- Pens
- Calculator

4.0 RESPONSIBILITIES

- Field Operations Leader (FOU) – Responsible for overseeing all IAQ sampling events
- Field Crew – Responsible for deploying, checking and retrieving all air quality samples

5.0 HEALTH AND SAFETY

- During sampling, the canister will be attached to a stand, fence, or security cage in the inverted position using hooks and/or zip ties, followed by a bungee cord. The bungee cord is applied to the Base ring (on top when the canister is inverted) to control the canister from falling forward. Care should be exercised when applying the bungee cords as a sudden release may result in the hook striking the body or facial area. When applying bungees, safety glasses must be worn to protect the eyes.
- Do **NOT** attempt to over-stretch the bungee cord as this may result in an accidental release. While striking any other part of the body will result in various levels of pain, significant damage could occur to the facial area (eyes).
- As sub-slab sampling will also be performed in conjunction with IAQ sampling, refer to the project specific SOPs for these sampling activities for health and safety concerns associated with performing these tasks.

6.0 PROCEDURES

The procedures described in this SOP include the following:

- IAQ Sample Collection (Section 6.1)
- Ambient Air Sampling (section 6.2)

6.1 IAQ SAMPLING COLLECTION

Before each IAQ sampling event, each Sample Team will receive SUMMA canisters, pressure gauges, Sample Data Sheets, and labels from Sample Management Team at the Support Site trailer. Each SUMMA canister should be marked indicating that it has been tested and the evacuation is in the acceptable range. Each Sample Team is responsible for checking all sampling materials and confirming the sampling schedule and location prior to leaving the Support Site trailer.

REMINDER

Samplers must exercise extreme caution not to indirectly affect the sample quality. Items that could have a direct/indirect affect include, but not limited to the following:

- Having volatile liquids or conducting decontamination using volatile liquids when a SUMMA Canister is operating. Therefore, no volatile liquids will be transported or used anywhere near the canisters.
- Eliminate the use of perfumes, colognes, after-shaves or similar products when deploying monitoring sample devices as these may affect sample integrity. **This is particularly important with IAQ samples.**
- Do NOT use Sharpies to mark Ziplocs, sampling machines or any other devices in the area of an operating SUMMA Canister.

6.1.1

Upon access to the inside of the building for an IAQ assessment, identify the interior space to be sampled and hang the SUMMA Canister(s) on a stand(s), close to the center of the space. When two IAQ samples are being collected in the same space, the SUMMA Canisters should be side-by-side. For IAQ purposes, air sampling equipment should be mounted to represent breathing zone height of likely occupants in the space approximately 5 to 6 feet above the floor for adults.

6.1.2 Before the start of sampling, check the vacuum integrity using the vacuum/pressure gauge on the orifice assembly as follows:

- a) Make sure the valve is closed and remove the dust cap on the canister.
- b) Attach the pressure gauge/critical orifice assembly using your fingers and an adjustable wrench (finger tight plus 1/8 to X turn).
- c) Attach the dust cap to the critical orifice inlet, open the valve handle and read the vacuum/pressure from the gauge.
- d) Record the initial canister pressure on the Air Sample Data Sheet.
- e) Close the valve after taking the reading and remove the dust cap. Place the dust cap back on the SUMMA Canister.

6.1.3 Once the unit is properly assembled and positioned open the control valve.

6.1.4 Record the meteorological conditions or other factors such as indoor air odors, chemical use, construction activity, open burning outside, etc. that might be pertinent to the collection of this sample on the Sample Data Sheet. In addition, record the date, location, sample ID, canister serial No., initial vacuum pressure, and start time of the sampling event, flow rate, etc.

If possible, interior sampling locations should be isolated (i.e. windows and doors shut) for a period of 12 to 24 hours before the samples are collected. Heating Ventilation and Air Conditioning (HVAC) systems should be operating under normal operating parameters for at least 24 hours prior to and during the scheduled sampling to establish and maintain indoor air temperatures and conditions during typical hours of occupancy. Observations regarding HVAC operation as well as other factors that might affect building pressurization such as exhaust fans must be recorded during the performance of the sampling.

6.1.5 During the sampling event, do not leave the air sampling equipment unattended. The only exception is if the sampling is performed during hours when the building is unoccupied and secured against entry. Check flow rates and proper equipment function at least every hour. During each check, record the pressure gauge reading, temperature, air pressure on the Sample data sheets along with any observations as noted above. Toward the end of the sampling period, increase the number of pressure gauge observations to prevent the canister from reaching equilibrium or zero vacuum.

Photographs should be taken documenting the location of the sampling, in a manner that depicts the general interior space of the building where the samples were collected.

6.2 SAMPLE RETRIEVAL

6.2.1 At the end of the sampling period, record the final vacuum pressure on the Sample Data Sheet and securely tighten the canister valve.

6.2.2 With the valve in the closed position, remove the gauge and replace the dust cap, tighten finger tight then 1/8 to X turn.

6.2.3 Record the end time on your labels and Sample Data Sheet. In this case two labels will be completed. One label will be placed on the base ring of the canister and the other on the outside of the storage/shipping box.

7.0 REFERENCES

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14A, Second Edition, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1997.

Tri-Services Handbook for the Assessment of the Vapor Intrusion Pathway, Rev. 4.0, Final, U.S. Air Force, U.S. Navy, U.S. Army, 15 February 2008.

SOP-02 SUB-SLAB SOIL VAPOR SAMPLING PROCEDURE

1.0 PURPOSE

The purpose of this SOP is to describe a method for sampling and analysis of sub-slab air samples. The method is based on the collection of air samples in sub-atmospheric stainless steel SUMMA canisters over an 8-hour period. The purpose of this procedure is to ensure good quality control in field operations, uniformity between different personnel, and to allow traceability of possible cause of errors in analytical results. A sampling system schematic is presented as Figure 1.

2.0 SCOPE

This procedure describes the methodology to be used for the collection of sub-slab soil vapor samples.

3.0 EQUIPMENT AND MATERIALS

- Hammer Drill with 3/8 inch bit
- 2 Liter Tedlar Bags
- Personal Air Pump - 200 cubic centimeters per minute
- Teflon® tubing
- Swagelok fittings
- Barbed reducing connector
- Tubing Clamp
- 6-Liter Summa Canister
- Regulator – 10.4 milliliters/minute
- Shroud (plastic bucket).
- Barometer
- Modeling Clay
- Helium detector capable of measuring from 1 - 100%
- Laboratory grade helium

4.0 PROCEDURE

4.1 Sampling Apparatus Set-Up

Note: Sampling apparatus should be set up prior to drilling hole in sub-slab.

- 4.1.1 Cut three pieces of 1/4 inch Teflon® tubing about 12 inches in length.
- 4.1.2 Cut two pieces of Teflon® tubing approximately 6 inches in length.
- 4.1.3 Connect one piece of the Teflon® tubing to the regulator on the sampling canister with a Swagelok fitting.
- 4.1.4 Make a "T" out of the three pieces of the Teflon® tubing®.
- 4.1.5 Connect one side of the Teflon® tubing to the Teflon® tubing from the canister.
- 4.1.6 Connect the other side of the Teflon® tubing to the probe. Affix modeling clay around the connection to the probe to seal the connection.
- 4.1.7 Connect the middle piece of the Teflon® tubing to the air pump.
- 4.1.8 Connect the Tedlar purge bag to the pump with a piece of Teflon® tubing.
- 4.1.9 Verify all connections in the sampling apparatus before purging and/or collecting the sample.

4.2 Probe Installation

- 4.2.1 Ensure all sub-slab utilities are marked prior to installation (e.g. gas, water, sewer, refrigerant, and electric).
- 4.2.2 Core hole through cement slab with Hammer drill using a 3/8 inch spline bit. If dust prevention is necessary, cover the location with a towel/cloth and drill through a pre-cut hole in the cloth.
- 4.2.3 Drill approximately 3 inches into the sub-slab soil.
- 4.2.4 Remove the drill and cover the hole with inert material such as modeling clay until the probe is ready to be inserted.
- 4.2.5 Install the sampling apparatus (i.e., commercially available soil vapor point and tubing) so that it "floats" in the slab avoiding obstruction with sub-slab material.
- 4.2.6 Seal the boring by creating an air tight seal around sample probe at ground surface using clay.

4.3 Helium Leak Test

- a. Attach Teflon® tubing' sample tubing to the sample point. This can be accomplished utilizing a number of different methods depending on the sample install (i.e., Swagelok®).
- b. Place the shroud over the sample point and tubing. The size of the shroud should be sufficient to fit over the sub-slab soil-gas point. It is worth noting that using a smaller shroud obviously uses less helium as well; this may be important when projects require a number of helium tracer tests. The shroud will need to have three small holes in it. These holes will include one on the top (to accommodate the sample tubing), and two on the side (one for the helium detector probe, and one for the helium line).
- c. Pull the tubing through hole in top of shroud. Seal opening with modeling clay.
- d. Place weight on top of shroud to help maintain a good seal with the ground.
- e. Insert helium tubing into hole in side of shroud, seal with modeling clay to prevent leaks.
- f. Fill shroud with helium. While filling shroud allow atmospheric air to escape either by leaving a crack with the surface or by providing a release valve on the side of the shroud.
- g. Use the helium detector to test level of helium gas from the bottom of the shroud
- h. Purge the sample point through the sample tubing into a Tedlar bag using a hand held sampling pump. The sample pump should be operating at a rate of 0.2 liter per minute (lpm) (the purge rate should not exceed the sample collection rate). Use a stand-alone flow sensor to monitor purge flow-rate during purge. Test the air in the Tedlar® bag for helium using portable helium detector. If the sample point has been installed properly there should be zero helium in purge air. **Note: DO NOT open the Summa canister valve at this time; it will remain closed throughout the purging process.**
- i. If > 5% helium is noted in purge air, add more clay or other material to the seal the sample port at the surface and repeat the testing procedure. If the seal cannot be fixed, re-install sample point.
- j. Monitor and record helium level in shroud before, during and after tracer test.
- k. Monitor and record helium level in purge exhaust at the end of purging.
- l. At successful completion of tracer test and sample point purging, the soil-gas sample can be collected (if the helium shroud must be removed prior to sample collection be mindful not disturb the sample tubing and any established seals).

4.4 Soil Vapor Collection

- 4.4.1 Record location, date, time, weather, atmospheric pressure, approximate depth of sub-slab vapor samples on Soil Vapor Sample Log Sheet.

- 4.4.2 Without opening the canisters, purge the probe and tubing by filling a Tedlar bag (filled bags to be emptied outdoors) connected to the air pump. Purge rate should be approximately 200 cubic centimeters per minute for 10 minutes.
- 4.4.3 Record purge date and time on Soil Vapor Sample Log sheet.
- 4.4.4 After purging, place a clamp on the piece of tubing leading to the pump.
- 4.4.5 Check vacuum in canister prior to sampling. Record start time and pressure on the Soil Vapor Sample Log sheet.
- 4.4.6 Collect sub-slab vapor sample by opening the evacuated certified 6-L Summa canister equipped with regulator to control intake at a rate of 10.4 liters per minute. Turn the canister off by closing the valve after 8 hours. At least 4 liters of air will be collected in the canister for analysis.
- 4.4.7 Record end time and pressure on the Soil Vapor Sample Log sheet.
- 4.4.8 Remove sampling apparatus and seal the borehole annulus with an appropriate sealant (such as Modeling Clay) to the original surface grade.

4.5 Replicate Soil Vapor Collection

- 4.5.1 Note replicate sample location on the Soil Vapor Sample Log sheet.
- 4.5.2 Replicate samples will be collected using a replicate tee to connect to the parent canister.5 The replicate tee will connect to the tubing and probe apparatus the same as in Section 4.2.
- 4.5.3 Open the replicate canister simultaneously with the parent canister when sample collection begins.
- 4.5.4 Record all information including starting and ending pressure on the Soil Vapor Sample Log sheet.

5.0 RECORDS

A record of all field procedures, tests, and observation must be recorded in the field logbook. Entries should include all pertinent data regarding the soil vapor sampling. The use of sketches, photographs, and field landmarks will help to supplement the investigation and evaluation. In addition, laboratory accession procedures must be followed including field documentation, chain-of-custody, field blanks, field sample replicates and laboratory duplicates, as appropriate.

Appropriate QA/QC protocols will be followed for sample collection and laboratory analysis, such as use of certified clean sample devices, meeting sample holding times and temperatures, sample

accession, and chain of custody. Samples will be delivered to the analytical laboratory as soon as possible after collection.

The sampling team will avoid actions (e.g., using permanent marking pens, and wearing freshly dry-cleaned clothing or personal fragrances) which can cause sample interference. The field team will document conditions during sampling to aid in the interpretation of the sampling results. The uses of possible VOCs (paints, solvents, consumer products) will be identified, as well as any heating or air conditioning systems. Floor plan sketches will be drawn that include the floor layout with sample locations, chemical storage areas, garages, doorways, stairways, location of basement sumps or subsurface drains and utility perforations through building foundations, HVAC system air supply and return registers, compass orientation (north), and any other pertinent information. If possible, photographs will accompany floor plan sketches. Significant weather conditions (e.g., precipitation, indoor/outdoor temperature, and barometric pressure) and ventilation conditions (e.g., heating system active and windows closed) will also be reported. Any pertinent observations (such as spills, floor stains, and organic odors) will be recorded.

SOP-03 - DECONTAMINATION OF FIELD SAMPLING EQUIPMENT

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedures to be followed when decontaminating non-dedicated field sampling equipment during the field investigations.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

- Writing utensil (preferably black pen with indelible ink)
- Non-latex rubber or plastic gloves
- Cotton gloves
- Field logbook
- Potable water
- Deionized water
- Isopropanol (optional)
- Liqui-Nox® or Alconox® detergent
- Brushes, spray bottles, paper towels, etc.
- Container to collect and transport decontamination fluids

3.0 DECONTAMINATION PROCEDURES

- 3.1 Don non-latex and/or cotton gloves and decontaminate sampling equipment (in accordance with the following steps) prior to field sampling and between samples.
- 3.2 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.
- 3.3 Wash the equipment with a solution of Liqui-Nox® or Alconox® detergent. Prepare the detergent wash solution in accordance with the instructions on the detergent container. Collect the wash solution into a container. Use brushes or sprays as appropriate for the equipment. If oily residue has accumulated on the sampling equipment, remove the residue with an isopropanol wash and repeat the detergent wash.
- 3.4 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.

- 3.5 Rinse the equipment with deionized water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the deionized water rinsate into a container.
- 3.6 Remove excess water by air drying and shaking or by wiping with paper towels as necessary.
- 3.7 Document decontamination by recording it in the field logbook.

SOP-04 - MANAGEMENT OF INVESTIGATION-DERIVED WASTE

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes how investigation-derived waste (IDW) will be collected, segregated, classified, and managed during the field investigations at Naval Support Activity (NSA) Crane. The following types of IDW may be generated during this investigation:

- Decontamination solutions
- Personal protective equipment (PPE) and clothing
- Miscellaneous trash and incidental items

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

- Health and safety equipment (with PPE)
- Bucket (with collected development/purge water)
- Decontamination equipment
- Field logbook
- Writing utensil (preferably black pen with indelible ink)
- Plastic sheeting and/or tarps
- 55-gallon drums with sealable lids
- IDW labels for drums
- Plastic garbage bags

3.0 PROCEDURES

Management of IDW includes the collection, segregation, temporary storage, classification, final disposal, and documentation of the waste-handling activities if necessary.

3.1 Liquid Wastes

Liquid wastes that may be generated during the site activities include decontamination solutions from sampling equipment. These wastes will be collected and containerized in a central location at NSA Crane for proper disposal.

3.2 PPE and Incidental Trash

All PPE wastes and incidental trash materials (e.g., wrapping or packing materials from supply cartons, waste paper, etc.) will be decontaminated (if contaminated), double bagged, securely tied shut, and placed in a designated waste receptacle at NSA Crane.

APPENDIX B

**U.S. EPA TEST METHOD
METHOD TO-15**

**Compendium of Methods
for the Determination of
Toxic Organic Compounds
in Ambient Air**

Second Edition

Compendium Method TO-15

**Determination Of Volatile Organic
Compounds (VOCs) In Air Collected In
Specially-Prepared Canisters And
Analyzed By Gas Chromatography/
Mass Spectrometry (GC/MS)**

**Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268**

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DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.

- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures.*
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology).*

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990*, U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogenes are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after “aging” for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate ($\pm 10\%$) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2- μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carboxpack B (60/80 mesh) and 50 mg Carboxieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1 Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2 Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r , from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z , along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g., 1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

7.3.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.

T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

[Note: The sampling system should be contained in an appropriate enclosure.]

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

8.3.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within $\pm 10\%$. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

8.3.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

8.3.8 The canister valve and vacuum/pressure gauge valve are opened.

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

8.3.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

8.4.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.4.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

Air released/evacuated from canisters should be diverted to a fume hood.

8.4.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.4.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

8.4.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.4.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.4.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.4.3 Zero Air Certification.

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]

8.4.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocused on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocused prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.4.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

8.4.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.4.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d₅, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.}) (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10 \text{ ppm})(1 \text{ mL/min})(1000 \text{ ppb/1 ppm})}{(1000 \text{ mL/min}) + (1 \text{ mL/min})} = 10 \text{ ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, μL .

d = Density of the liquid neat standard, $\text{mg}/\mu\text{L}$.

V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(\text{mL})(d)}{\text{MW}}$$

where:

- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap

Adsorbent Trap

Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[*Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.*]

10.1.2 Desorption Conditions

Cryogenic Trap

Desorb Temperature	120°C
Desorb Flow Rate	~ 3 mL/min He
Desorb Time	<60 sec

Adsorbent Trap

Desorb Temperature	Variable
Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap

Initial bakeout	120°C (24 hrs)
Variable (24 hrs)	
After each run	120°C (5 min)

Adsorbent Trap

Initial bakeout	
After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

<u>Item</u>	<u>Condition</u>
Carrier Gas:	Helium
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer
Temperature Program:	Initial Temperature: -50°C
	Initial Hold Time: 2 min
	Ramp Rate: 8° C/min
	Final Temperature: 200°C
	Final Hold Time: Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

<u>Item</u>	<u>Condition</u>
-------------	------------------

Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤ 20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB 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. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$\text{RRF} = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
 A_x = Area of the primary ion for the compound to be measured, counts.
 A_{is} = Area of the primary ion for the internal standard, counts.
 C_{is} = Concentration of internal standard spiking mixture, ppbv.
 C_x = Concentration of the compound in the calibration standard, ppbv.

[*Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.*]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^n \frac{x_i}{n}$$

where: \overline{RRF} = Mean relative response factor.
 x_i = RRF of the compound at concentration i .
 n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^N \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).
 RRF_i = Relative response factor at a concentration level i .
 \overline{RRF} = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds
 RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times (\overline{RRT}). Calculate the mean of the relative retention times (\overline{RRT}) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{\text{RRT}} = \sum_{i=1}^n \frac{\text{RRT}}{n}$$

where: $\overline{\text{RRT}}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response (\bar{Y}) for Internal Standard. Calculate the mean area response (\bar{Y}) for each internal standard compound over the initial calibration range using the following equation:

$$\bar{Y} = \sum_{i=1}^n \frac{Y_i}{n}$$

where: \bar{Y} = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{\text{RT}}$). Calculate the mean of the retention times ($\overline{\text{RT}}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{\text{RT}} = \sum_{i=1}^n \frac{\text{RT}_i}{n}$$

where: $\overline{\text{RT}}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]

10.5.5.2 The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response \bar{Y} over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF}_i}{\overline{RRF}_i} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

\overline{RRF}_i = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ± 30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ± 40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ± 0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary

in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port valve is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked 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.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} RRF}$$

where: C_x = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

\overline{RRF} = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 μ L) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ± 0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- 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.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ± 40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤ 0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where:

- x_1 = First measurement value.
- x_2 = Second measurement value.
- \bar{x} = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER
MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.**COMMENT ON CANISTER CLEANING PROCEDURES**

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.

LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF
SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

**TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--
MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs**

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH ₃ Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C ₂ H ₃ Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH ₂ N ₂	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH ₂ O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C ₄ H ₆	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl ₂ O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	15.8	1.1 x 10	107		
Ethylene oxide; C ₂ H ₄ O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	31.7	500	97	X	X
Propylene oxide; C ₃ H ₆ O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH ₃ I	74-88-4	42.4	400	141.9		
Methylene chloride; CH ₂ Cl ₂	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS ₂	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	55.2	249	86		
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C ₄ H ₅ Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	63.0	163	72		
Chloroform; CHCl ₃	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	63	157.0	60.0		
Hexane; C ₆ H ₁₄	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	74.1	100	133.4	X	X
Methanol; CH ₄ O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl ₄	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	79.6	77.5	72		X
Benzene; C ₆ H ₆	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	83.5	61.5	99	X	X
Triethylamine; C ₆ H ₁₅ N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH ₆ N ₂	60-34-4	87.8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C ₈ H ₁₈	540-84-1	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	104	30.0	115		
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	100	29.3	100		
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	112	27.8	111	X	X
Toluene; C ₇ H ₈	108-88-3	111	22.0	92	X	X
Trichloroethylene; C ₂ HCl ₃	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	124	10.0	103		
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	120	10.0	89		
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C ₈ H ₁₀	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	142	6.7	106.2	X	X
Styrene; C ₈ H ₈	100-42-5	145	6.6	104	X	X
p-Xylene; C ₈ H ₁₀	106-42-3	138	6.5	106.2	X	X
m-Xylene; C ₈ H ₁₀	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr ₃	75-25-2	149	5.6	252.8		
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	146	5.0	167.9	X	X
o-Xylene; C ₈ H ₁₀	95-47-6	144	5.0	106.2	X	X
Dimethylcarbonyl chloride; C ₃ H ₆ ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	152	3.7	74		
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	153	3.2	120		
Acrylic acid; C ₃ H ₄ O ₂	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C ₃ H ₇ NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C ₃ H ₆ O ₃ S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C ₈ H ₈ O	98-86-2	202	1.0	120		
Dimethyl sulfate; C ₂ H ₆ O ₄ S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C ₄ H ₈ Cl ₂ O	111-44-4	178	0.71	143		
Chloroacetic acid; C ₂ H ₃ ClO ₂	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C ₆ H ₇ N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	51-79-6	183	0.54	89		
Acrylamide; C ₃ H ₅ NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C ₈ H ₁₁ N	121-69-7	192	0.50	121		
Hexachloroethane; C ₂ Cl ₆	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	215	0.40	260.8	X	X
Isophorone; C ₉ H ₁₄ O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	59-89-2	225	0.32	116.1		
Styrene oxide; C ₈ H ₈ O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C ₄ H ₁₀ O ₄ S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture); C ₇ H ₈ O	1319-77-3	202	0.26	108		
o-Cresol; C ₇ H ₈ O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	240	0.22	110		
Phenol; C ₆ H ₆ O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg) ¹	MW ¹	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	240	0.22	110		
Phenol; C ₆ H ₆ O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	213	0.18	181.5	X	X
nitrobenzene; C ₆ H ₅ NO ₂	98-95-3	211	0.15	123		

¹Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:

(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;

(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and

(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

**TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING
THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS**

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH ₃ Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-88-1	60	62
Vinyl chloride (chloroethene); C ₂ H ₃ Cl	75-01-4	62	64
Diazomethane; CH ₂ N ₂	334-88-3	42	41
Formaldehyde; CH ₂ O	50-00-0	29	30
1,3-Butadiene; C ₄ H ₆	106-99-0	39	54
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	94	96
Phosgene; CCl ₂ O	75-44-5	63	65
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	106	108
Ethylene oxide; C ₂ H ₄ O	75-21-8	29	44
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	64	66
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	61	96
Propylene oxide; C ₃ H ₆ O	75-56-9	58	57
Methyl iodide (iodomethane); CH ₃ I	74-88-4	142	127
Methylene chloride; CH ₂ Cl ₂	75-09-2	49	84, 86
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	76	41, 78
Carbon disulfide; CS ₂	75-15-0	76	44, 78
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	73	41, 53
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C ₄ H ₅ Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	42	41, 72
Chloroform; CHCl ₃	67-66-3	83	85, 47
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	42	43
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	60	45, 59
Hexane; C ₆ H ₁₄	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	97	99, 61
Methanol; CH ₄ O	67-56-1	31	29
Carbon tetrachloride; CCl ₄	56-23-5	117	119
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C ₆ H ₆	71-43-2	78	77, 50
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	62	64, 27
Triethylamine; C ₆ H ₁₅ N	121-44-8	86	58, 101
Methylhydrazine; CH ₆ N ₂	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C ₈ H ₁₈	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	88	58
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	79	49, 81
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	55	73
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-6	41	69, 100
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	75	39, 77
Toluene; C ₇ H ₈	108-88-3	91	92
Trichloethylene; C ₂ HCl ₃	79-01-6	130	132, 95
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	97	83, 61
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	166	164, 131
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	107	109
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	60	44, 103
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	43	41
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	112	77, 114
Ethylbenzene; C ₈ H ₁₀	100-41-4	91	106
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	91	106
Styrene; C ₈ H ₈	100-42-5	104	78, 103
p-Xylene; C ₈ H ₁₀	106-42-3	91	106
m-Xylene; C ₈ H ₁₀	108-38-3	91	106
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr ₃	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	83	85
o-Xylene; C ₈ H ₁₀	95-47-6	91	106
Dimethylcarbanyl chloride; C ₃ H ₆ ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	74	42
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	42	43
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	105	120
Acrylic acid; C ₃ H ₄ O ₂	79-10-7	72	45, 55
N,N-Dimethylformamide; C ₃ H ₇ NO	68-12-2	73	42, 44
1,3-Propane sultone; C ₃ H ₆ O ₃ S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C ₈ H ₈ O	98-86-2	105	77, 120
Dimethyl sulfate; C ₂ H ₆ O ₄ S	77-78-1	95	66, 96
Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C ₄ H ₈ Cl ₂ O	111-44-4	93	63, 95
Chloroacetic acid; C ₂ H ₃ ClO ₂	79-11-8	50	45, 60
Aniline (aminobenzene); C ₆ H ₇ N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	146	148, 111
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	51-79-6	31	44, 62
Acrylamide; C ₃ H ₅ NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C ₈ H ₁₁ N	121-69-7	120	77, 121
Hexachloroethane; C ₂ Cl ₆	67-72-1	201	199, 203
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	225	227, 223
Isophorone; C ₉ H ₁₄ O	78-59-1	82	138
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	59-89-2	56	86, 116
Styrene oxide; C ₈ H ₈ O	96-09-3	91	120
Diethyl sulfate; C ₄ H ₁₀ O ₄ S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C ₇ H ₈ O	1319-77-3		
o-Cresol; C ₇ H ₈ O	95-48-7	108	107
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	110	64
Phenol; C ₆ H ₆ O	108-95-2	94	66
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	180	182, 184
Nitrobenzene; C ₆ H ₅ NO ₂	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria ¹
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

¹All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)¹

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	--	--
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	--	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	--
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	--
1,1-Dichloroethene	--	0.22
cis-1,2-Dichloroethene	--	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	--
cis-1,3-Dichloropropene	0.36	--
trans-1,3-Dichloropropene	0.22	--
Ethylbenzene	0.27	0.05
Chloroethane	0.19	--
Trichlorofluoromethane	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane	--	--
1,2-Dichloro-1,1,2,2-tetrafluoroethane	--	--
Dichlorodifluoromethane	--	--
Hexachlorobutadiene	--	--
Bromomethane	0.53	--
Chloromethane	0.40	--
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	--	--
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	--
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	--	--
1,3,5-Trimethylbenzene	--	--
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

¹Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

**TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP)
FROM EPA NETWORK OPERATIONS¹**

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59 ²	1.1	8.7	47	0.2 ²
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

¹Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.

²Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

**TABLE 6. AUDIT ACCURACY (AA) VALUES¹ FOR SELECTED
COMPENDIUM METHOD TO-14A COMPOUNDS**

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

¹Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

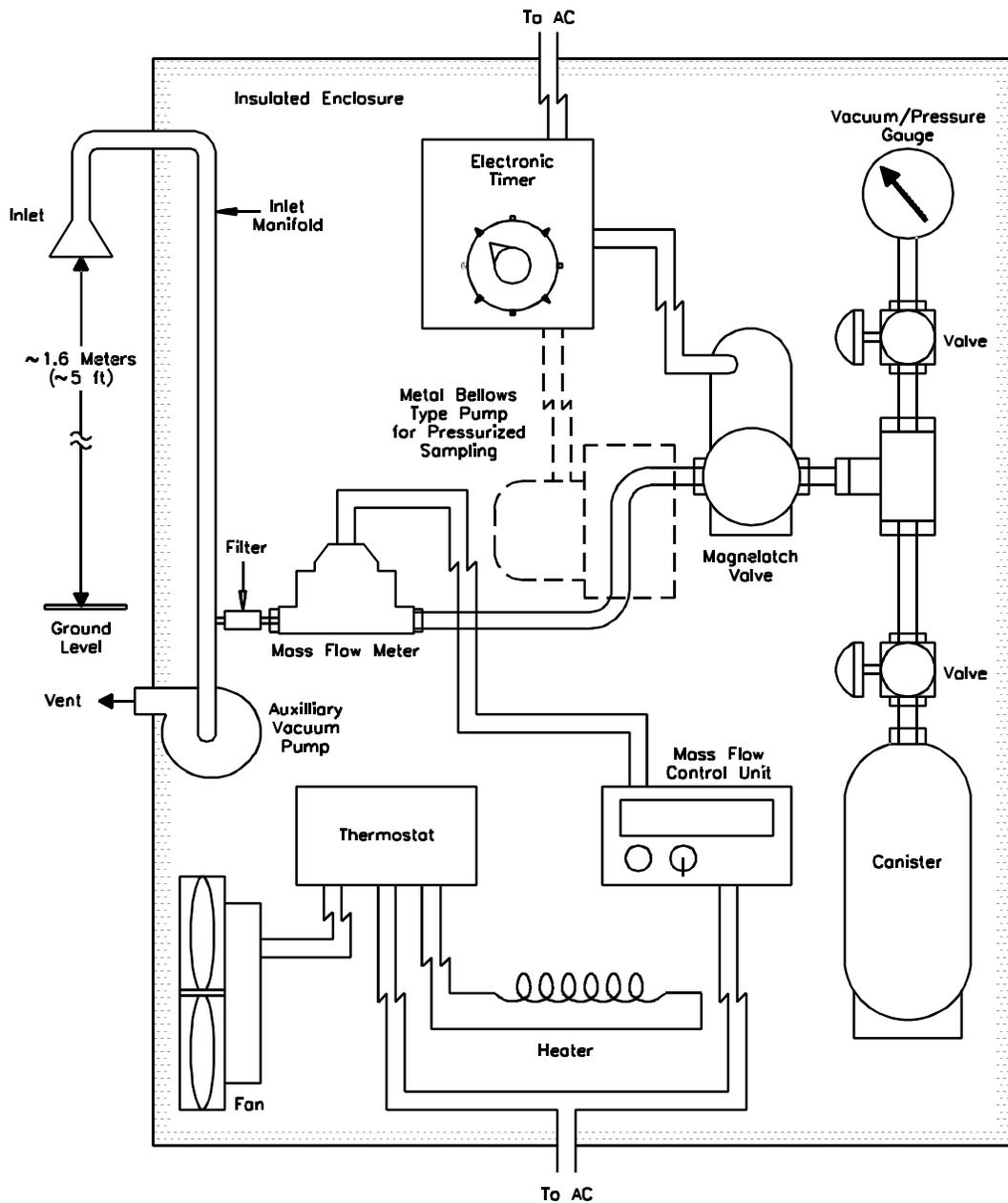
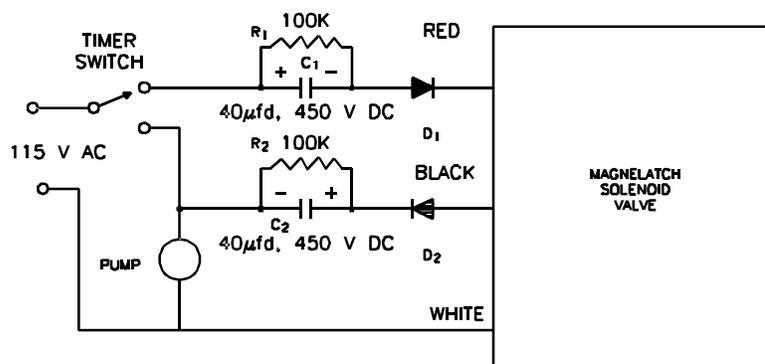
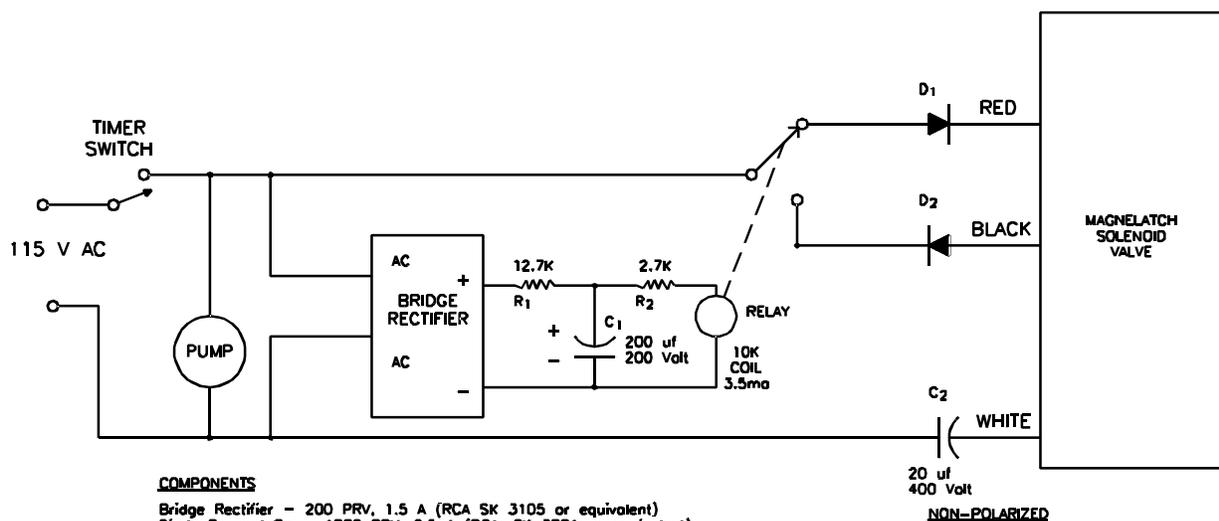


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.

**COMPONENTS**

Capacitor C₁ and C₂ - 40 µf, 450 VDC (Sprague Atom TVA 1712 or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3061 or equivalent)

(a). Simple Circuit for Operating Magnelatch Valve

**COMPONENTS**

Bridge Rectifier - 200 PRV, 1.5 A (RCA SK 3105 or equivalent)
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3061 or equivalent)
 Capacitor C₁ - 200 µf, 250 VDC (Sprague Atom TVA 152B or equivalent)
 Capacitor C₂ - 20 µf, 400 VDC Non-Polarized (Sprague Atom TVAN 1652 or equivalent)
 Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

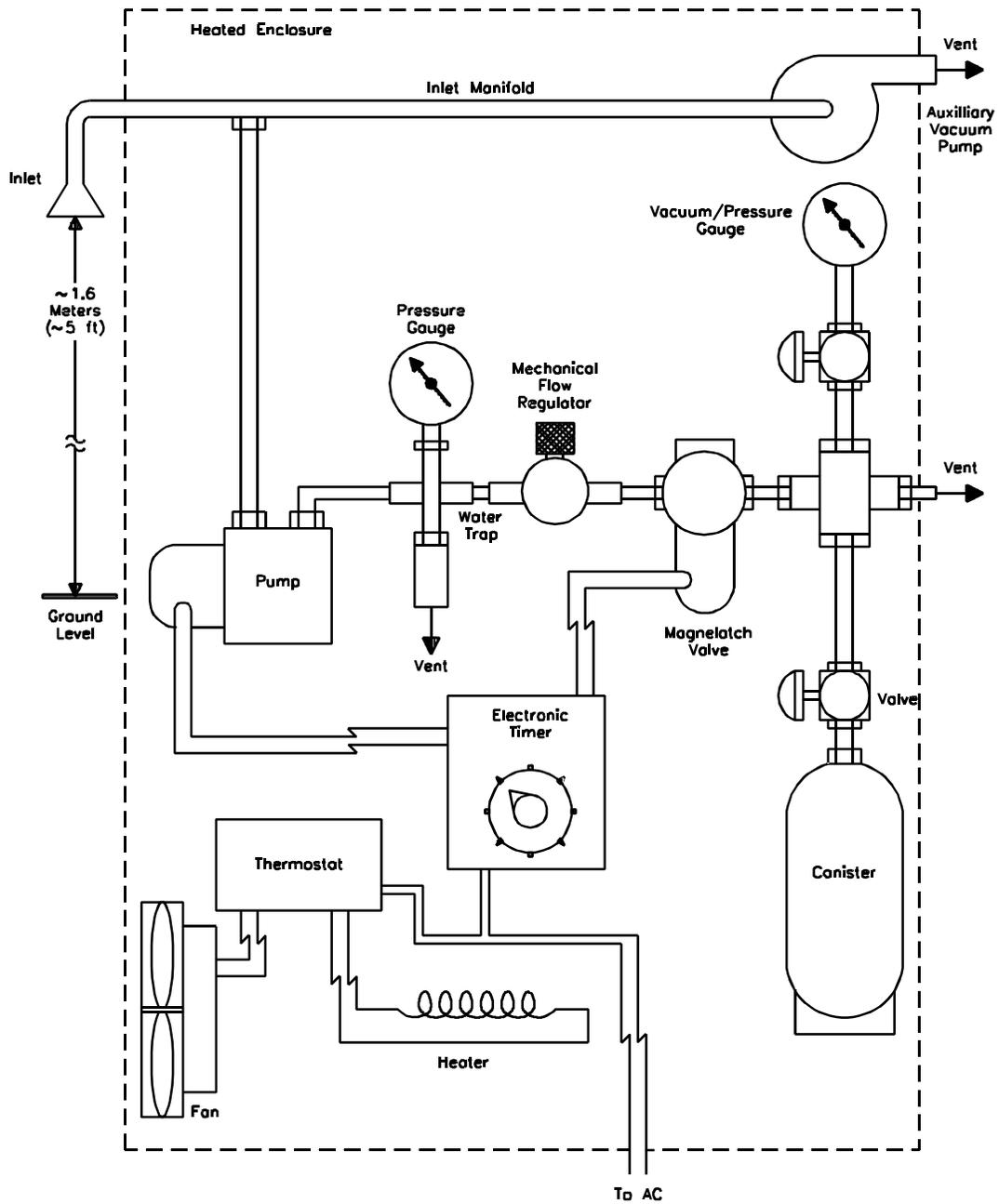


Figure 3. Alternative sampler configuration for pressurized canister sampling.

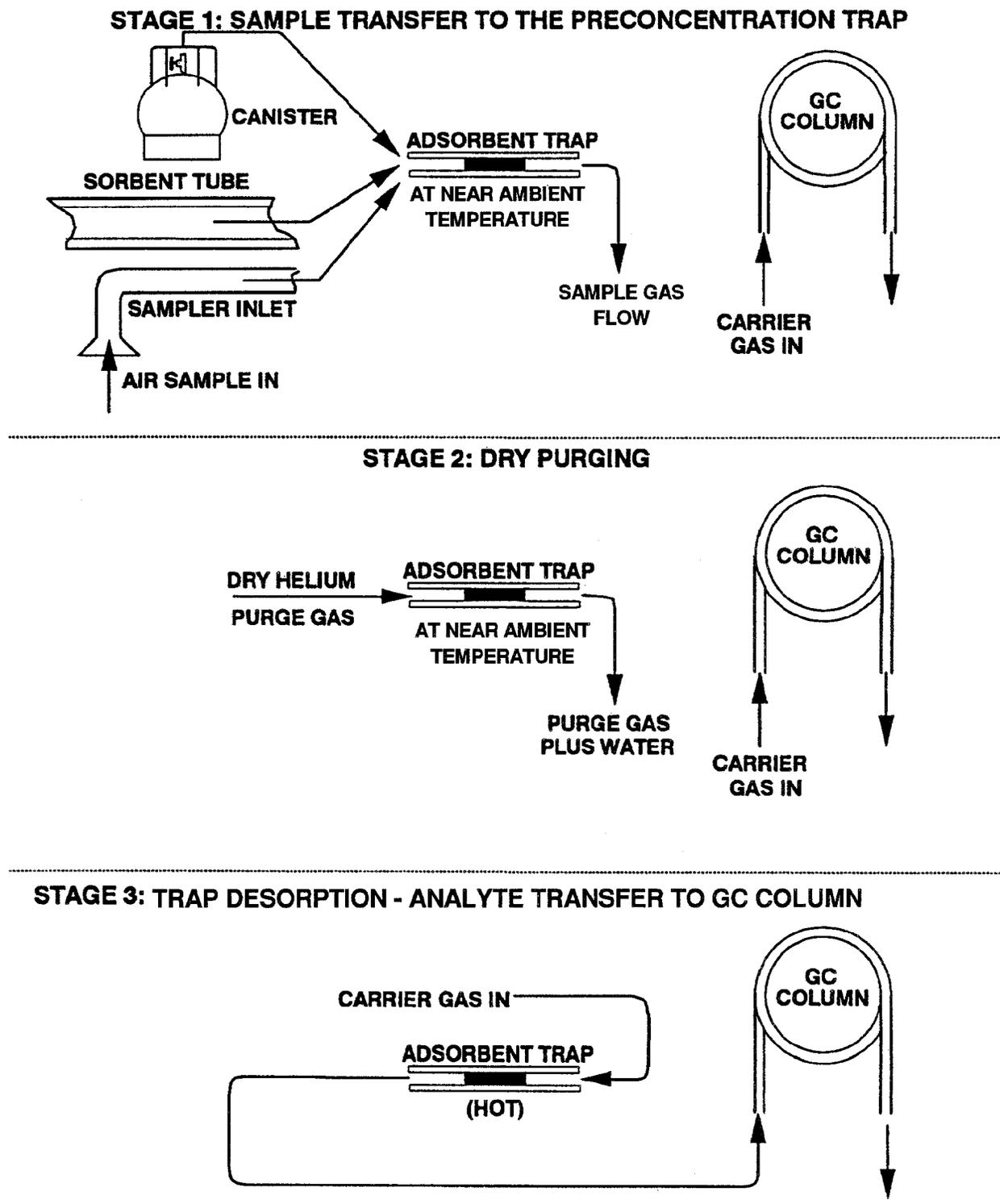


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

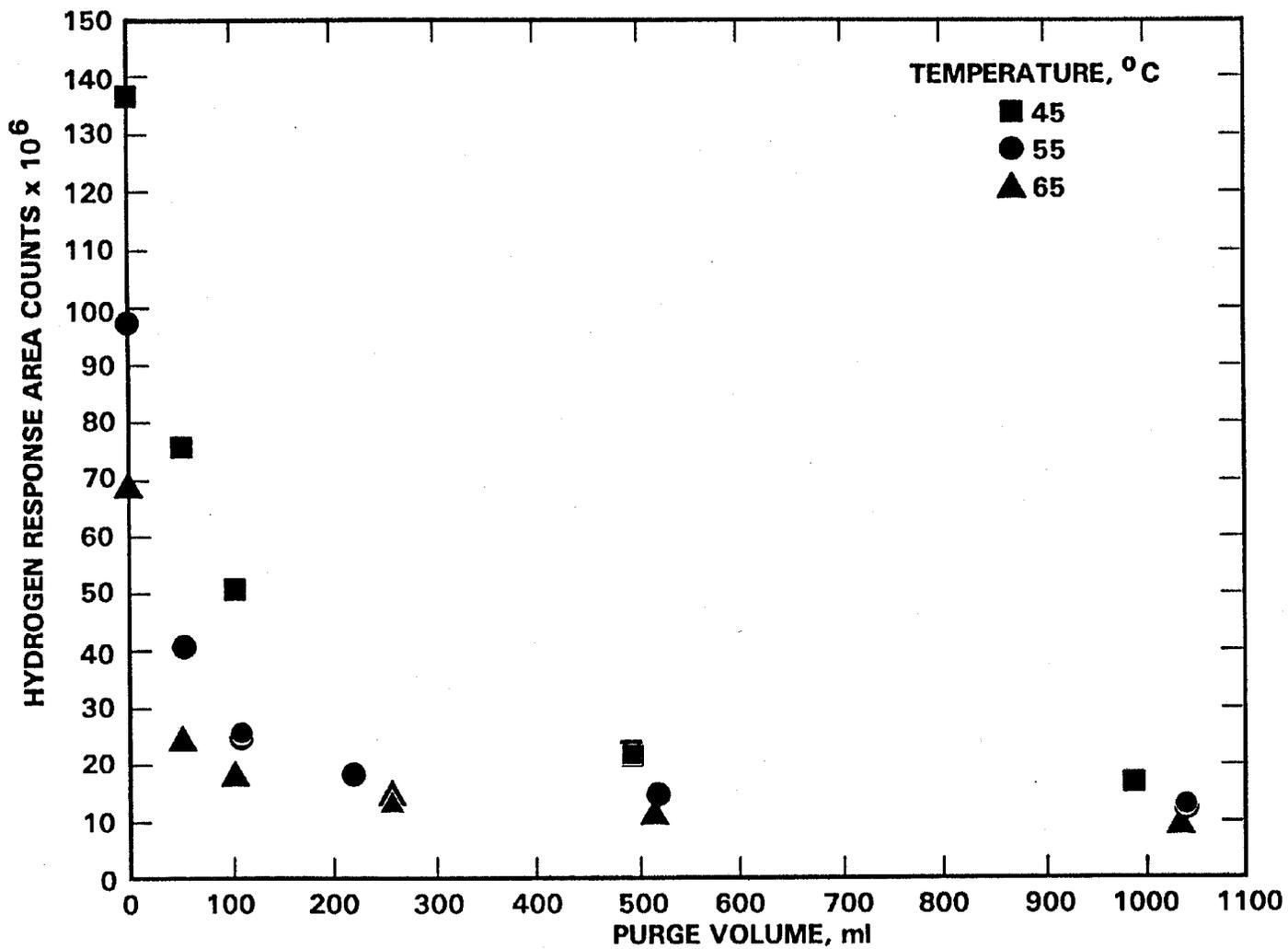


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

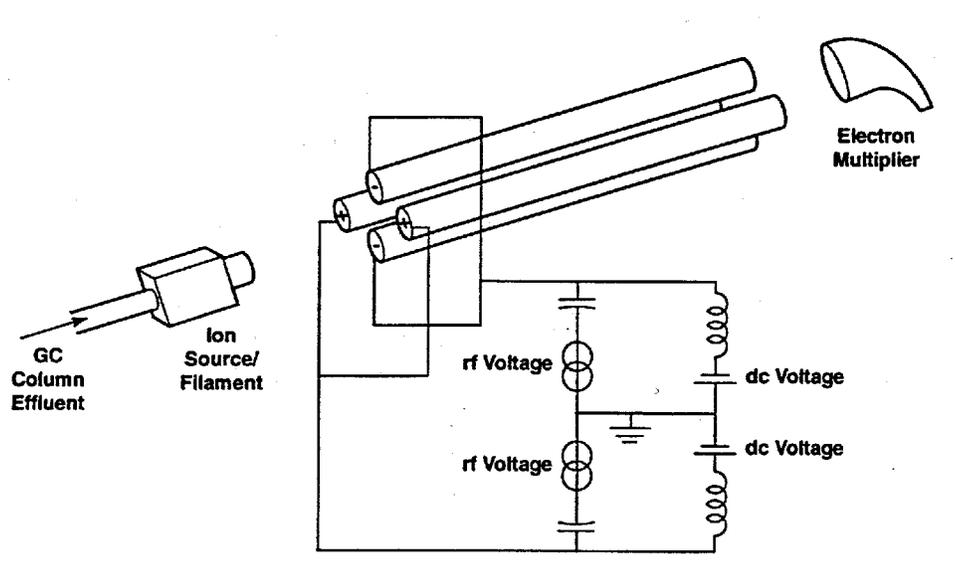


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

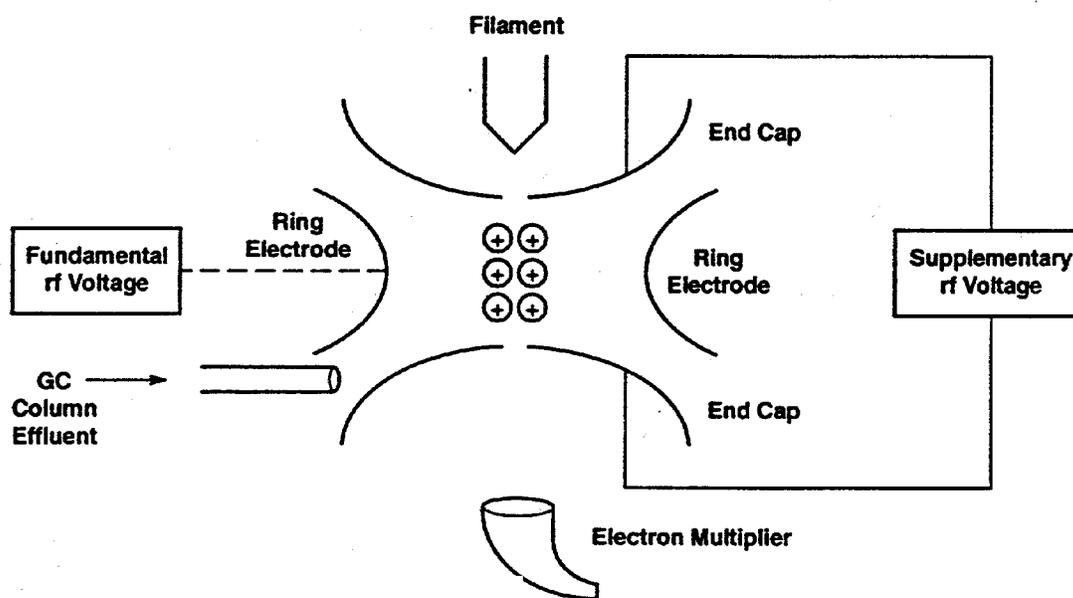


Figure 7. Simplified diagram of an ion trap mass spectrometer.

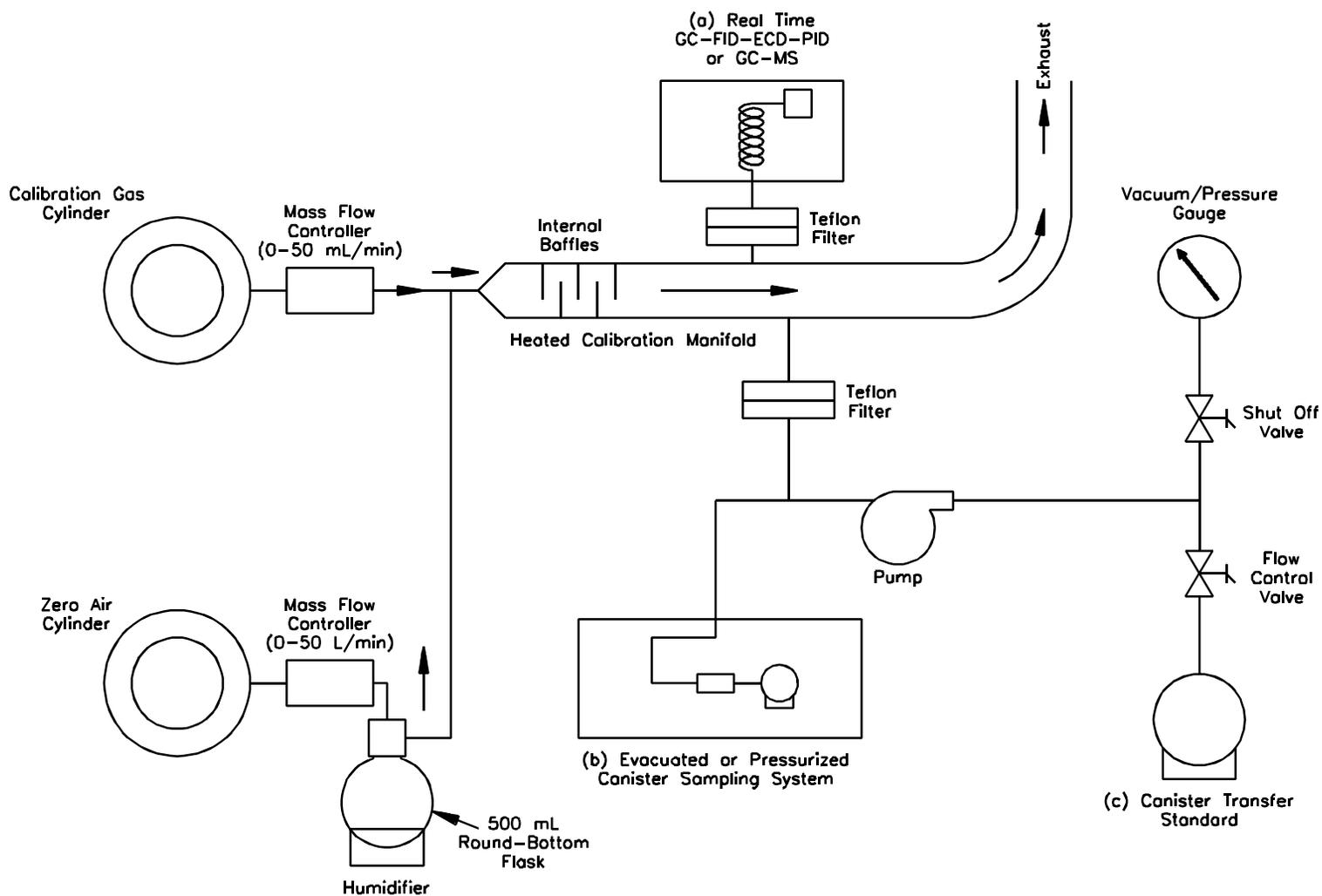


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

**COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET**

A. GENERAL INFORMATION

SITE LOCATION: _____
 SITE ADDRESS: _____

 SAMPLING DATE: _____

SHIPPING DATE: _____
 CANISTER SERIAL NO.: _____
 SAMPLER ID: _____
 OPERATOR: _____
 CANISTER LEAK
 CHECK DATE: _____

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES	
	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES		
MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
 QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
 RECEIVED BY: _____
 INITIAL PRESSURE: _____
 FINAL PRESSURE: _____
 DILUTION FACTOR: _____

ANALYSIS
 GC-FID-ECD DATE: _____
 GC-MSD-SCAN DATE: _____
 GC-MSD-SIM DATE: _____

RESULTS*: _____

 GC-FID-ECD: _____
 GC-MSD-SCAN: _____
 GC-MSD-SIM: _____

 SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

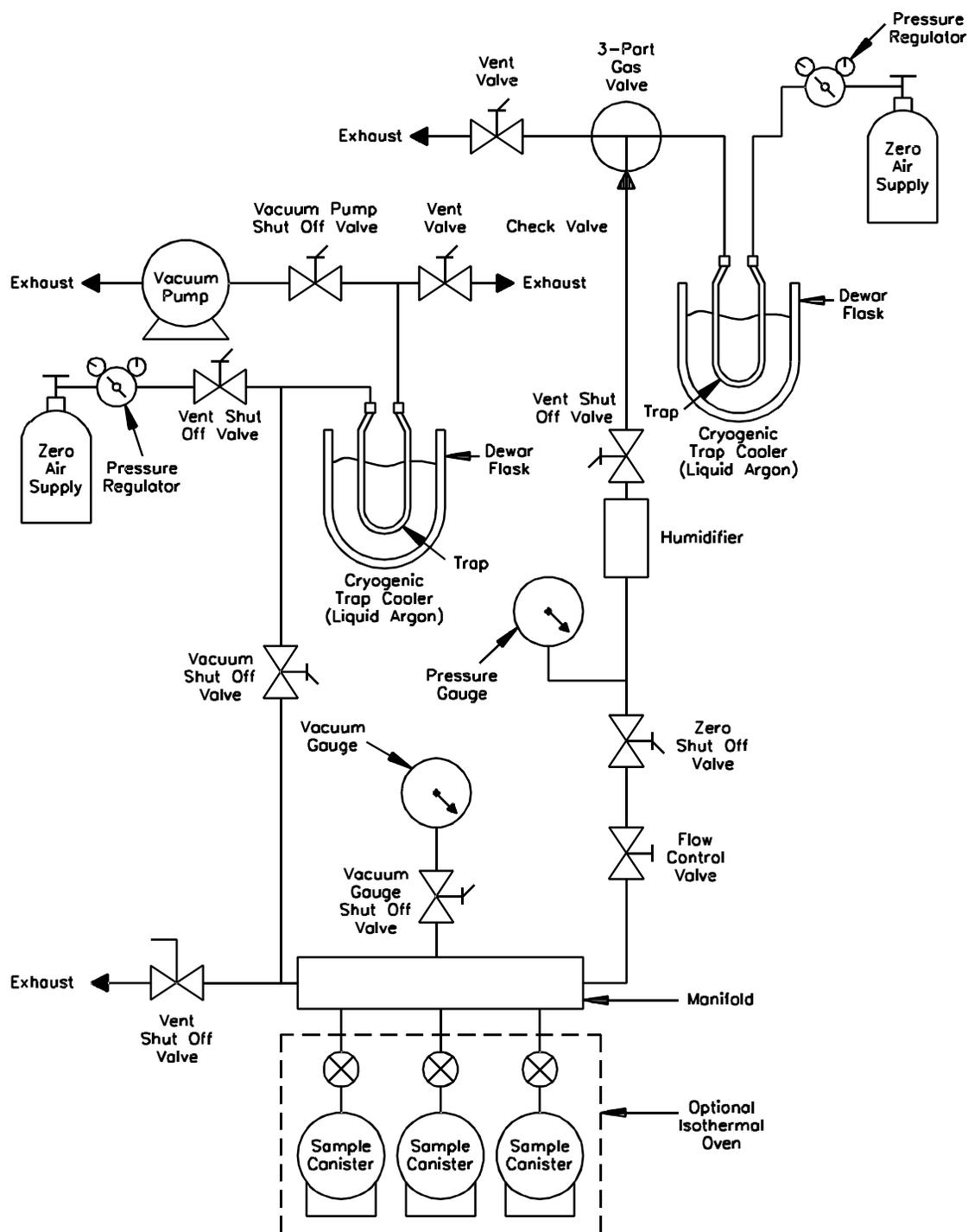


Figure 10. Canister cleaning system.

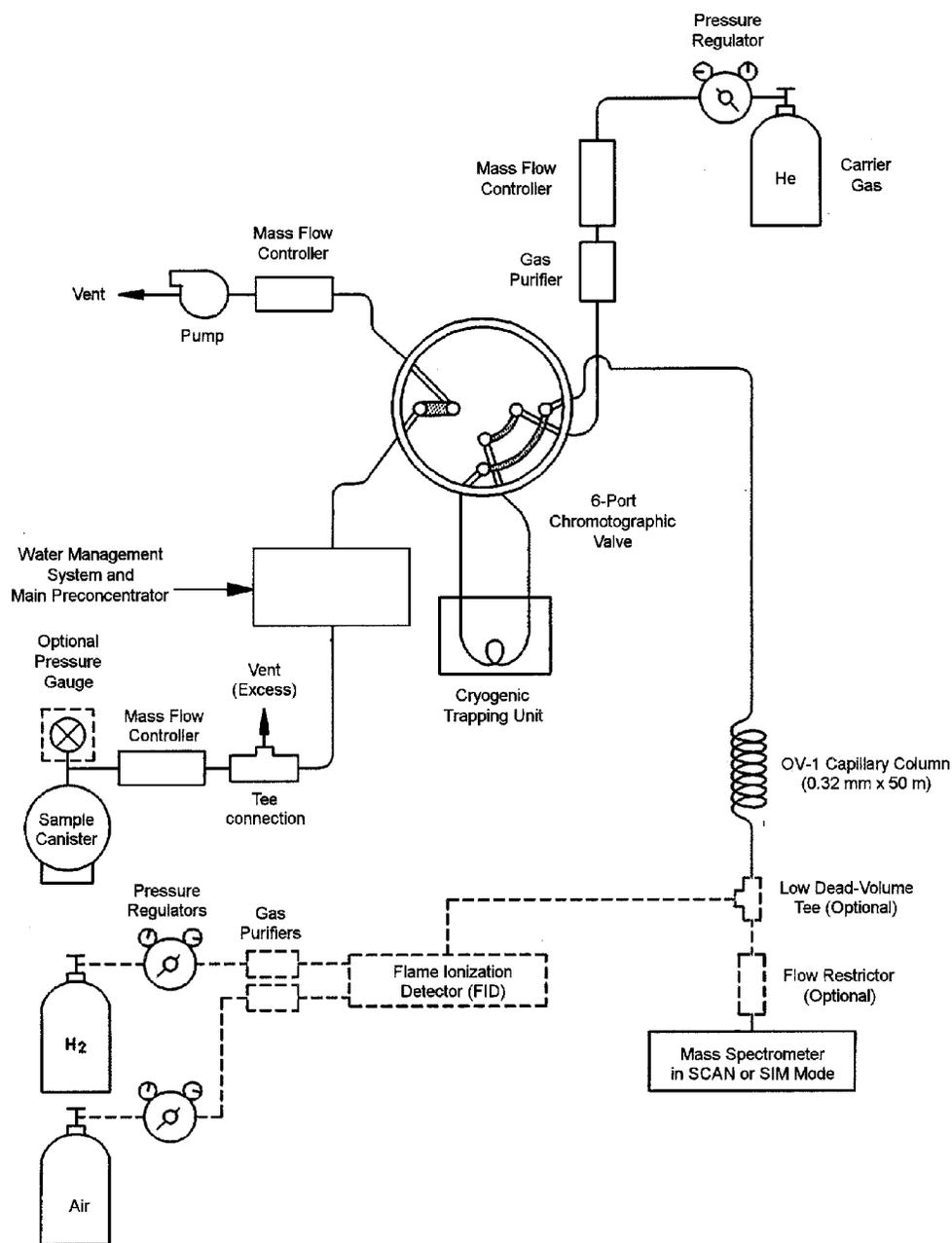
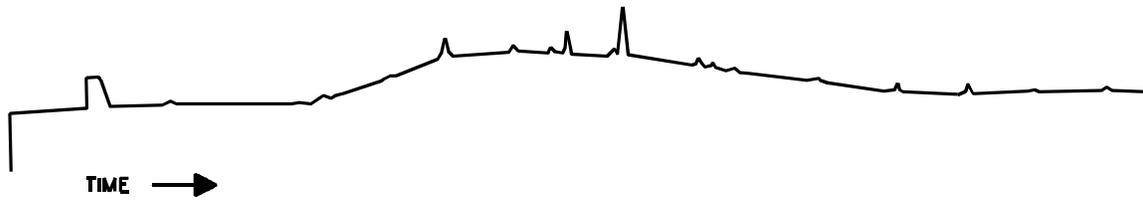
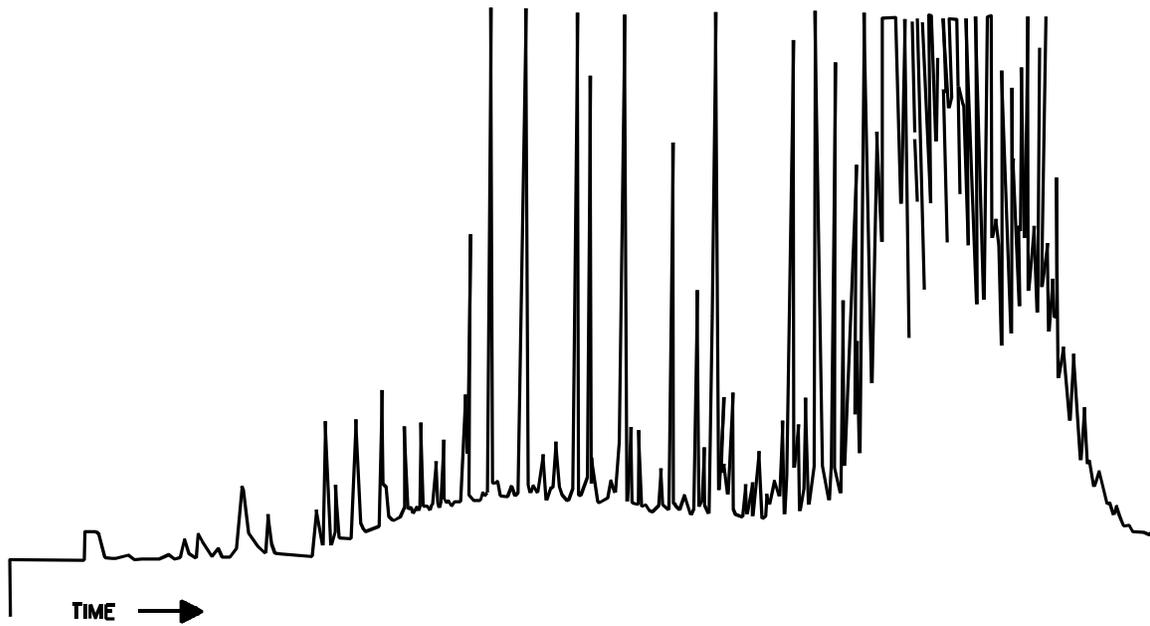


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]



(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

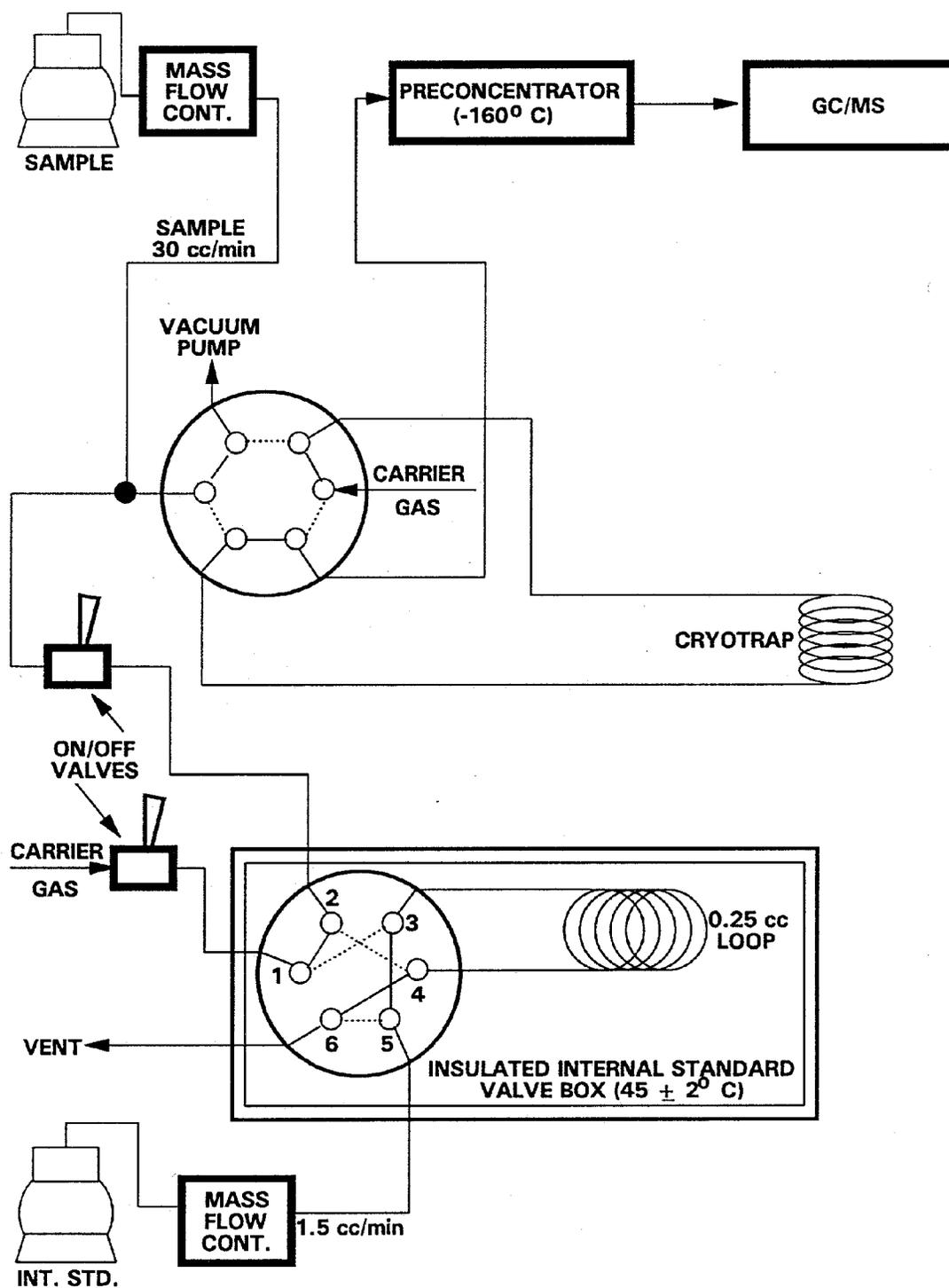


Figure 13. Diagram of design for internal standard addition.

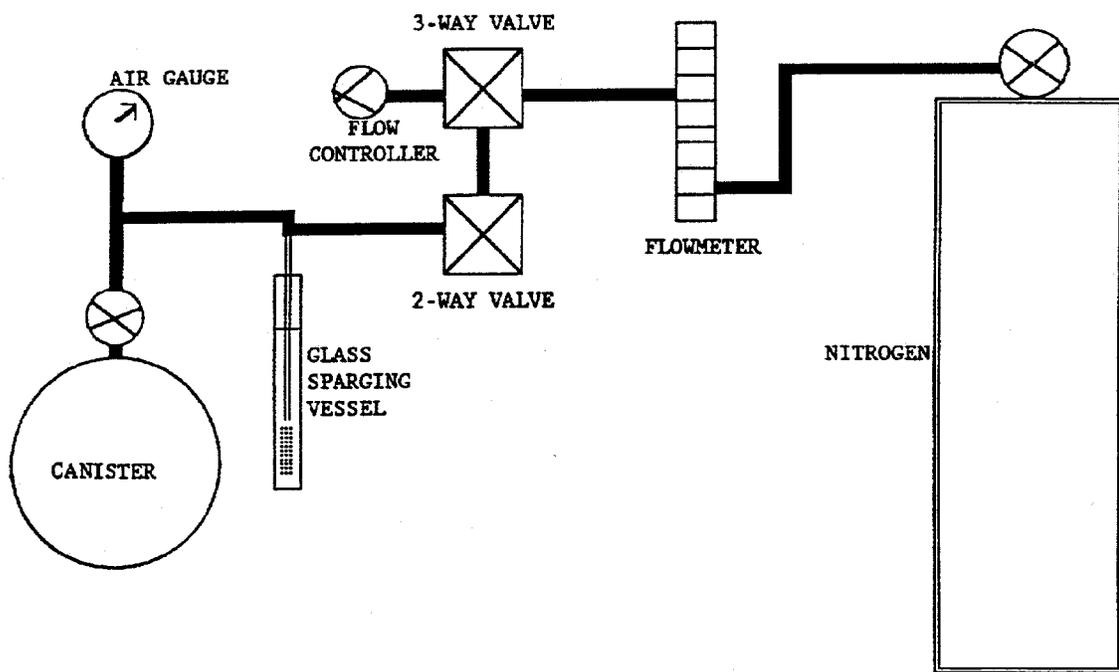


Figure 14. Water method of standard preparation in canisters.

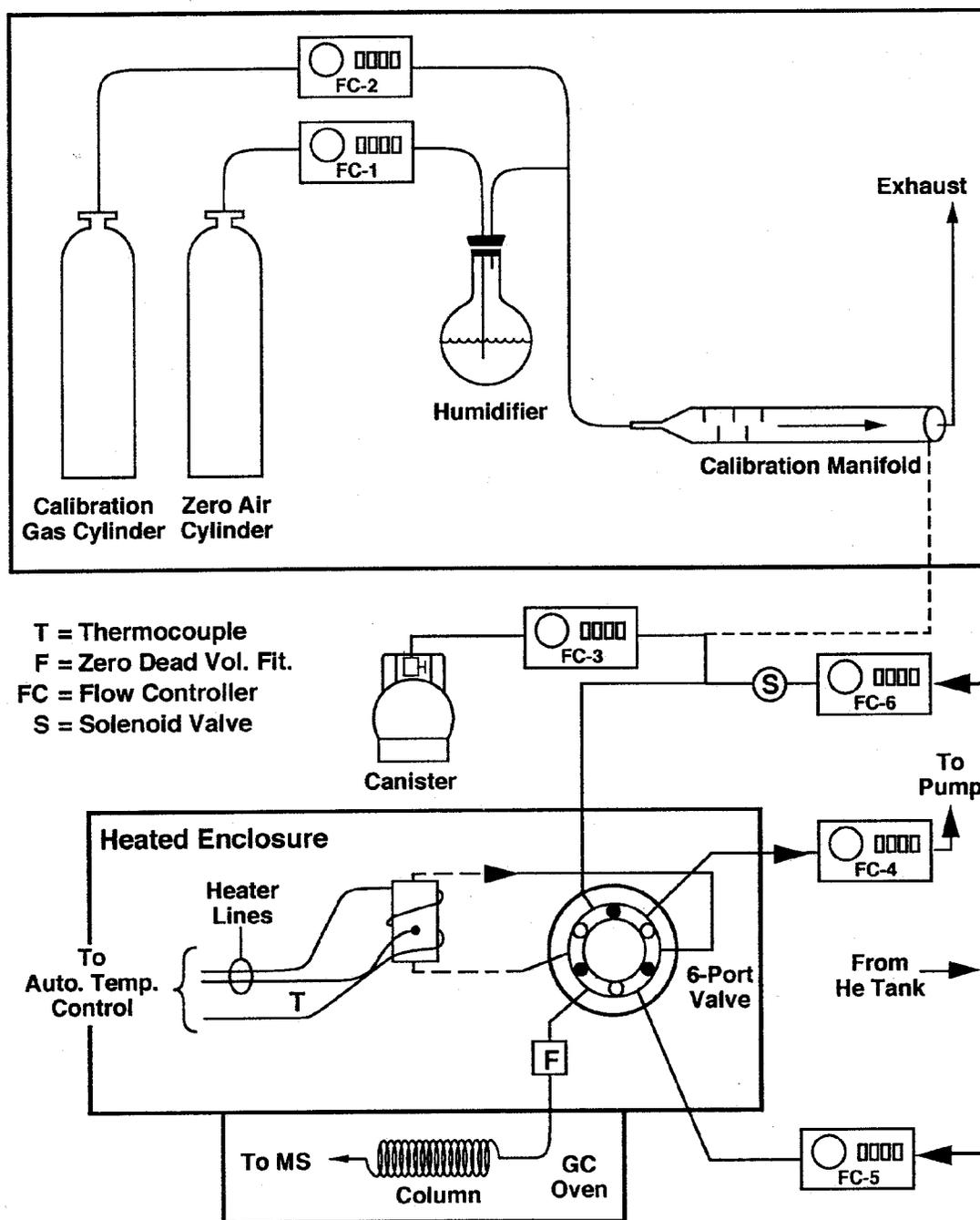


Figure 15. Diagram of the GC/MS analytical system.

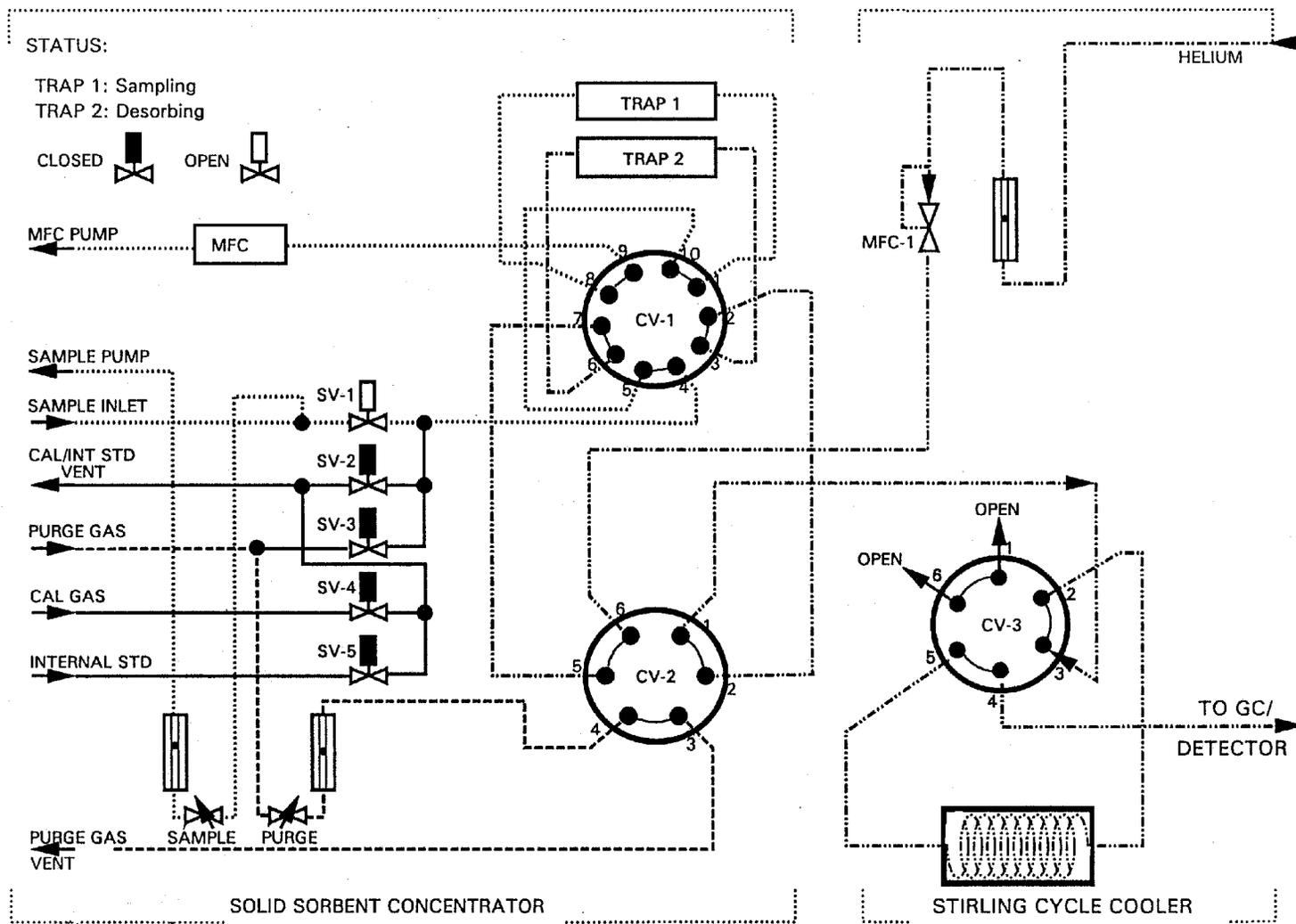


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

APPENDIX C

**U.S. EPA REGIONAL SCREENING LEVEL (RSL)
INDUSTRIAL AIR SUPPORTING TABLE (NOVEMBER 2013)**

Key: I = IRIS; P = PPRTV; A = ATSDR; C = Cal EPA; X = PPRTV Appendix; H = HEAST; J = New Jersey; O = EPA Office of Water; E = Environmental Criteria and Assessment Office; S = see user guide Section 5; L = see user guide on lead; M = mutagen; V = volatile; F = See FAQ; R = RBA applied (See User Guide for Arsenic notice); c = cancer; * = where n SL < 100X c SL; ** = where n SL < 10X c SL; n = noncancer; m = Concentration may exceed ceiling limit (See User Guide); s = Concentration may exceed Csat (See User Guide); SSL values are based on DAF=1

Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RF _C (mg/m ³)	k v o l u t a g e n	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
5.1E-06	C				ALAR	1596-84-5	2.4E+00	
2.2E-06	I	9.0E-03	I	V	Acephate	30560-19-1		
					Acetaldehyde	75-07-0	5.6E+00	3.9E+01
		3.1E+01	A	V	Acetochlor	34256-82-1		
		2.0E-03	X	V	Acetone	67-64-1		1.4E+05
					Acetone Cyanohydrin	75-86-5		8.8E+00
		6.0E-02	I	V	Acetonitrile	75-05-8		2.6E+02
1.3E-03	C			V	Acetophenone	98-86-2		
					Acetylaminofluorene, 2-	53-96-3	9.4E-03	
		2.0E-05	I	V	Acrolein	107-02-8		8.8E-02
1.0E-04	I	6.0E-03	I		Acrylamide	79-06-1	1.2E-01	2.6E+01
		1.0E-03	I		Acrylic Acid	79-10-7		4.4E+00
6.8E-05	I	2.0E-03	I	V	Acrylonitrile	107-13-1	1.8E-01	8.8E+00
		6.0E-03	P		Adiponitrile	111-69-3		2.6E+01
					Alachlor	15972-60-8		
					Aldicarb	116-06-3		
					Aldicarb Sulfone	1646-88-4		
					Aldicarb sulfoxide	1646-87-3		
4.9E-03	I				Aldrin	309-00-2	2.5E-03	
		1.0E-04	X		Allyl	74223-64-6		
					Allyl Alcohol	107-18-6		4.4E-01
6.0E-06	C	1.0E-03	I	V	Allyl Chloride	107-05-1	2.0E+00	4.4E+00
		5.0E-03	P		Aluminum	7429-90-5		2.2E+01
					Aluminum Phosphide	20859-73-8		
6.0E-03	C				Amdro	67485-29-4		
					Ametryn	834-12-8		
					Aminobiphenyl, 4-	92-67-1	2.0E-03	
					Aminophenol, m-	591-27-5		
					Aminophenol, p-	123-30-8		
					Amityaz	33089-61-1		
		1.0E-01	I		Ammonia	7664-41-7		4.4E+02
		3.0E-03	X	V	Ammonium Sulfamate	7773-06-0		
					Amyl Alcohol, tert-	75-85-4		1.3E+01
1.6E-06	C	1.0E-03	I		Aniline	62-53-3	7.7E+00	4.4E+00
					Anthraquinone, 9,10-	84-65-1		
					Antimony (metallic)	7440-36-0		
					Antimony Pentoxide	1314-60-9		
					Antimony Potassium Tartrate	11071-15-1		
					Antimony Tetroxide	1332-81-6		
		2.0E-04	I		Antimony Trioxide	1309-64-4		8.8E-01
7.1E-06	I				Apollo	74115-24-5	1.7E+00	
					Aramite	140-57-8		
4.3E-03	I	1.5E-05	C		Arsenic, Inorganic	7440-38-2	2.9E-03	6.6E-02
		5.0E-05	I		Arsine	7784-42-1		2.2E-01
					Assure	76578-14-8		
2.5E-04	C				Asulam	3337-71-1	4.9E-02	
					Atrazine	1912-24-9		
					Auramine	492-80-8		
3.1E-05	I			V	Avermectin B1	65195-55-3	4.0E-01	
		5.0E-04	H		Azobenzene	103-33-3		
					Barium	7440-39-3		2.2E+00
					Baygon	114-26-1		
					Bayleton	43121-43-3		
					Baythroid	68359-37-5		
					Benefin	1861-40-1		
					Benomyl	17804-35-2		
					Bentazon	25057-89-0		
7.8E-06	I	3.0E-02	I	V	Benzaldehyde	100-52-7	1.6E+00	1.3E+02
					Benzene	71-43-2		
					Benzenediamine-2-methyl sulfate, 1,4-	6369-59-1		
6.7E-02	I			V	Benzenethiol	108-98-5	1.8E-04	
				M	Benzidine	92-87-5		
					Benzoic Acid	65-85-0		
					Benzotrithloride	98-07-7		
4.9E-05	C	1.0E-03	P	V	Benzyl Alcohol	100-51-6	2.5E-01	4.4E+00
					Benzyl Chloride	100-44-7		
2.4E-03	I	2.0E-05	I		Beryllium and compounds	7440-41-7	5.1E-03	8.8E-02
					Bidrin	141-66-2		
					Bifenox	42576-02-3		
		4.0E-04	X	V	Biphenthrin	82657-04-3		
1.0E-05	H			V	Biphenyl, 1,1'-	92-52-4	1.2E+00	1.8E+00
					Bis(2-chloro-1-methylethyl) ether	108-60-1		
3.3E-04	I			V	Bis(2-chloroethoxy)methane	111-91-1	3.7E-02	
6.2E-02	I			V	Bis(2-chloroethyl)ether	111-44-4	2.0E-04	
					Bis(chloromethyl)ether	542-88-1		

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Toxicity and Chemical-specific				Contaminant		Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1		
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	v o l u t i l e n c e	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
		2.0E-02	H			Bisphenol A	80-05-7		
		2.0E-02	P			Boron And Borates Only	7440-42-8		8.8E+01
						Boron Trichloride	10294-34-5		8.8E+01
		1.3E-02	C			Boron Trifluoride	7637-07-2		5.7E+01
6.0E-04	X				V	Bromate	15541-45-4	2.0E-02	
						Bromo-2-chloroethane, 1-	107-04-0		
		6.0E-02	I	V		Bromobenzene	108-86-1		2.6E+02
		4.0E-02	X	V		Bromochloromethane	74-97-5		1.8E+02
3.7E-05	C				V	Bromodichloromethane	75-27-4	3.3E-01	
1.1E-06	I					Bromoform	75-25-2	1.1E+01	
		5.0E-03	I	V		Bromomethane	74-83-9		2.2E+01
						Bromophos	2104-96-3		
						Bromoxynil	1689-84-5		
3.0E-05	I	2.0E-03	I	V		Bromoxynil Octanoate	1689-99-2		
						Butadiene, 1,3-	106-99-0	4.1E-01	8.8E+00
						Butanol, N-	71-36-3		
						Butyl Benzyl Phthlate	85-68-7		
		3.0E+01	P			Butyl alcohol, sec-	78-92-2		1.3E+05
						Butylate	2008-41-5		
5.7E-08	C					Butylated hydroxyanisole	25013-16-5	2.2E+02	
						Butylated hydroxytoluene	128-37-0		
					V	Butylbenzene, n-	104-51-8		
					V	Butylbenzene, sec-	135-98-8		
					V	Butylbenzene, tert-	98-06-6		
1.8E-03	I	1.0E-05	A			Cacodylic Acid	75-60-5		
1.8E-03	I	1.0E-05	A			Cadmium (Diet)	7440-43-9		
						Cadmium (Water)	7440-43-9	6.8E-03	4.4E-02
		2.2E-03	C			Caprolactam	105-60-2		9.6E+00
4.3E-05	C					Captaol	2425-06-1	2.9E-01	
6.6E-07	C					Captan	133-06-2	1.9E+01	
						Carbaryl	63-25-2		
						Carbofuran	1563-66-2		
		7.0E-01	I	V		Carbon Disulfide	75-15-0		3.1E+03
6.0E-06	I	1.0E-01	I	V		Carbon Tetrachloride	56-23-5	2.0E+00	4.4E+02
						Carbosulfan	55285-14-8		
						Carboxin	5234-68-4		
		9.0E-04	I			Ceric oxide	1306-38-3		3.9E+00
						Chloral Hydrate	302-17-0		
						Chloramben	133-90-4		
1.0E-04	I	7.0E-04	I			Chloranil	118-75-2		
4.6E-03	C					Chlordane	12789-03-6	1.2E-01	3.1E+00
						Chlordecone (Kepone)	143-50-0	2.7E-03	
						Chlorfenviphos	470-90-6		
						Chlorimuron, Ethyl-	90982-32-4		
		1.5E-04	A			Chlorine	7782-50-5		6.4E-01
		2.0E-04	I			Chlorine Dioxide	10049-04-4		8.8E-01
						Chlorite (Sodium Salt)	7758-19-2		
		5.0E+01	I	V		Chloro-1,1-difluoroethane, 1-	75-68-3		2.2E+05
3.0E-04	I	2.0E-02	I	V		Chloro-1,3-butadiene, 2-	126-99-8	4.1E-02	8.8E+01
						Chloro-2-methylaniline HCl, 4-	3165-93-3		
7.7E-05	C					Chloro-2-methylaniline, 4-	95-69-2	1.6E-01	
					V	Chloroacetaldehyde, 2-	107-20-0		
		3.0E-05	I			Chloroacetic Acid	79-11-8		
						Chloroacetophenone, 2-	532-27-4		1.3E-01
		5.0E-02	P	V		Chloroaniline, p-	106-47-8		
3.1E-05	C					Chlorobenzene	108-90-7	4.0E-01	2.2E+02
						Chlorobenzilate	510-15-6		
		3.0E-01	P	V		Chlorobenzoic Acid, p-	74-11-3		
					V	Chlorobenzotrifluoride, 4-	98-56-6		1.3E+03
					V	Chlorobutane, 1-	109-69-3		
		5.0E+01	I	V		Chlorodifluoromethane	75-45-6		2.2E+05
2.3E-05	I	9.8E-02	A	V		Chloroethanol, 2-	107-07-3	5.3E-01	4.3E+02
						Chloroform	67-66-3		
		9.0E-02	I	V		Chloromethane	74-87-3		3.9E+02
6.9E-04	C				V	Chloromethyl Methyl Ether	107-30-2	1.8E-02	
		1.0E-05	X			Chloronitrobenzene, o-	88-73-3		4.4E-02
		6.0E-04	P			Chloronitrobenzene, p-	100-00-5		2.6E+00
					V	Chlorophenol, 2-	95-57-8		
		4.0E-04	C	V		Chloropicrin	76-06-2		1.8E+00
8.9E-07	C				V	Chlorothalonil	1897-45-6	1.4E+01	
					V	Chlorotoluene, o-	95-49-8		
					V	Chlorotoluene, p-	106-43-4		
6.9E-02	C					Chlorozotocin	54749-90-5	1.8E-04	
						Chlorpropham	101-21-3		
						Chlorpyrifos	2921-88-2		

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1		
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k v o l u t a g e n	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)	
					Chlorpyrifos Methyl Chlorsulfuron Chlorthiophos	5598-13-0 64902-72-3 60238-56-4			
8.4E-02	S	1.0E-04	I	M	Chromium(III), Insoluble Salts Chromium(VI) Chromium, Total	16065-83-1 18540-29-9 7440-47-3	1.5E-04	4.4E-01	
9.0E-03 6.2E-04	P I	6.0E-06	P M		Cobalt Coke Oven Emissions Copper	7440-48-4 8007-45-2 7440-50-8	1.4E-03 2.0E-02	2.6E-02	
		6.0E-01	C		Cresol, m-	108-39-4		2.6E+03	
		6.0E-01	C		Cresol, o-	95-48-7		2.6E+03	
		6.0E-01	C		Cresol, p-	106-44-5		2.6E+03	
		6.0E-01	C		Cresol, p-chloro-m-	59-50-7		2.6E+03	
			V		Cresols	1319-77-3		2.6E+03	
		4.0E-01	I	V	Crotonaldehyde, trans-	123-73-9		2.6E+03	
6.3E-05	C				Cumene Cupferron Cyanazine	98-82-8 135-20-6 21725-46-2	1.9E-01	1.8E+03	
					Cyanides				
					~Calcium Cyanide	592-01-8			
					~Copper Cyanide	544-92-3			
		8.0E-04	S	V	~Cyanide (CN-)	57-12-5		3.5E+00	
			V		~Cyanogen	460-19-5		3.5E+00	
			V		~Cyanogen Bromide	506-68-3		3.5E+00	
			V		~Cyanogen Chloride	506-77-4		3.5E+00	
		8.0E-04	I	V	~Hydrogen Cyanide	74-90-8		3.5E+00	
					~Potassium Cyanide	151-50-8		3.5E+00	
					~Potassium Silver Cyanide	506-61-6		3.5E+00	
					~Silver Cyanide	506-64-9		3.5E+00	
					~Sodium Cyanide	143-33-9		3.5E+00	
					~Thiocyanates	NA		3.5E+00	
					~Thiocyanic Acid	463-56-9		3.5E+00	
					~Zinc Cyanide	557-21-1		3.5E+00	
		6.0E+00	I	V	Cyclohexane	110-82-7		2.6E+04	
		7.0E-01	P		Cyclohexane, 1,2,3,4,5-pentabromo-6-chloro-	87-84-3		3.1E+03	
		1.0E+00	X	V	Cyclohexanone	108-94-1		4.4E+03	
					Cyclohexene	110-83-8		4.4E+03	
					Cyclohexylamine	108-91-8		4.4E+03	
					Cyhalothrin/karate	68085-85-8		4.4E+03	
6.9E-05	C				Cypermethrin	52315-07-8	1.8E-01		
					Cyromazine	66215-27-8			
					DDD	72-54-8			
9.7E-05	C				DDE, pp'	72-55-9	1.3E-01		
9.7E-05	I				DDT	50-29-3	1.3E-01		
					Dacthal	1861-32-1			
					Dalapon	75-99-0			
					Decabromodiphenyl ether, 2,2',3,3',4,4',5,5',6,6'-(BDE-209)	1163-19-5			
					Demeton	8065-48-3			
					Di(2-ethylhexyl)adipate	103-23-1			
					Diallate	2303-16-4			
					Diazinon	333-41-5			
			V		Dibenzothiophene	132-65-0			
6.0E-03	P	2.0E-04	I	V	M	Dibromo-3-chloropropane, 1,2-	96-12-8	2.0E-03	8.8E-01
					Dibromobenzene, 1,4-	106-37-6		8.8E-01	
2.7E-05	C		V		Dibromochloromethane	124-48-1	4.5E-01		
6.0E-04	I	9.0E-03	I	V	Dibromoethane, 1,2-	106-93-4	2.0E-02	3.9E+01	
		4.0E-03	X	V	Dibromomethane (Methylene Bromide)	74-95-3		1.8E+01	
					Dibutyltin Compounds	NA			
					Dicamba	1918-00-9			
4.2E-03	P		V		Dichloro-2-butene, 1,4-	764-41-0	2.9E-03		
4.2E-03	P		V		Dichloro-2-butene, cis-1,4-	1476-11-5	2.9E-03		
4.2E-03	P		V		Dichloro-2-butene, trans-1,4-	110-57-6	2.9E-03		
					Dichloroacetic Acid	79-43-6			
		2.0E-01	H	V	Dichlorobenzene, 1,2-	95-50-1		8.8E+02	
1.1E-05	C	8.0E-01	I	V	Dichlorobenzene, 1,4-	106-46-7	1.1E+00	3.5E+03	
3.4E-04	C				Dichlorobenzidine, 3,3'	91-94-1	3.6E-02		
					Dichlorobenzophenone, 4,4'	90-98-2		4.4E+02	
1.6E-06	C	1.0E-01	X	V	Dichlorodifluoromethane	75-71-8	7.7E+00		
			V		Dichloroethane, 1,1-	75-34-3		4.4E+02	
2.6E-05	I	7.0E-03	P	V	Dichloroethane, 1,2-	107-06-2	4.7E-01	3.1E+01	
		2.0E-01	I	V	Dichloroethylene, 1,1-	75-35-4		8.8E+02	
			V		Dichloroethylene, 1,2- (Mixed Isomers)	540-59-0		8.8E+02	
			V		Dichloroethylene, 1,2-cis-	156-59-2		2.6E+02	
		6.0E-02	P	V	Dichloroethylene, 1,2-trans-	156-60-5		2.6E+02	
					Dichlorophenol, 2,4-	120-83-2		2.6E+02	

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	v o l u t i l i t y	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
1.0E-05	C	4.0E-03	I	V	Dichlorophenoxy Acetic Acid, 2,4-Dichlorophenoxybutyric Acid, 4-(2,4-Dichloropropane, 1,2-	94-75-7 94-82-6 78-87-5	1.2E+00	1.8E+01
				V	Dichloropropane, 1,3-Dichloropropanol, 2,3-Dichloropropene, 1,3-	142-28-9 616-23-9 542-75-6	3.1E+00	8.8E+01
4.0E-06	I	2.0E-02	I	V	Dichlorvos	62-73-7	1.5E-01	2.2E+00
8.3E-05	C	5.0E-04	I		Dicyclopentadiene	77-73-6	3.1E-01	3.1E+01
4.6E-03	I	7.0E-03	P	V	Dieldrin	60-57-1	2.7E-03	
3.0E-04	C	5.0E-03	I		Diesel Engine Exhaust	NA	4.1E-02	2.2E+01
		2.0E-04	P		Diethanolamine	111-42-2		8.8E-01
		1.0E-04	P		Diethylene Glycol Monobutyl Ether	112-34-5		4.4E-01
		3.0E-04	P		Diethylene Glycol Monoethyl Ether	111-90-0		1.3E+00
1.0E-01	C				Diethylformamide	617-84-5	1.2E-04	
					Diethylstilbestrol	56-53-1		
		4.0E+01	I	V	Difenzoquat	43222-48-6		
				V	Diflubenzuron	35367-38-5		
1.3E-05	C			V	Difluoroethane, 1,1-	75-37-6	9.4E-01	1.8E+05
		7.0E-01	P	V	Dihydrosafrole	94-58-6		
				V	Diisopropyl Ether	108-20-3		3.1E+03
				V	Diisopropyl Methylphosphonate	1445-75-6		
					Dimethipin	55290-64-7		
					Dimethoate	60-51-5		
					Dimethoxybenzidine, 3,3'-	119-90-4		
1.3E-03	C				Dimethyl methylphosphonate	756-79-6	9.4E-03	
					Dimethylamino azobenzene [p-]	60-11-7		
					Dimethylaniline HCl, 2,4-	21436-96-4		
				V	Dimethylaniline, 2,4-	95-68-1		
					Dimethylaniline, N,N-	121-69-7		
					Dimethylbenzidine, 3,3'-	119-93-7		
		3.0E-02	I		Dimethylformamide	68-12-2		1.3E+02
1.6E-01	C	2.0E-06	X		Dimethylhydrazine, 1,1-Dimethylhydrazine, 1,2-	57-14-7 540-73-8	7.7E-05	8.8E-03
					Dimethylphenol, 2,4-	105-67-9		
					Dimethylphenol, 2,6-	576-26-1		
					Dimethylphenol, 3,4-	95-65-8		
1.3E-05	C			V	Dimethylvinylchloride	513-37-1	9.4E-01	
					Dinitro-o-cresol, 4,6-	534-52-1		
					Dinitro-o-cyclohexyl Phenol, 4,6-	131-89-5		
					Dinitrobenzene, 1,2-	528-29-0		
					Dinitrobenzene, 1,3-	99-65-0		
					Dinitrobenzene, 1,4-	100-25-4		
					Dinitrophenol, 2,4-	51-28-5		
8.9E-05	C				Dinitrotoluene Mixture, 2,4/2,6-Dinitrotoluene, 2,4-	NA 121-14-2	1.4E-01	
					Dinitrotoluene, 2,6-	606-20-2		
					Dinitrotoluene, 2-Amino-4,6-	35572-78-2		
					Dinitrotoluene, 4-Amino-2,6-	19406-51-0		
					Dinitrotoluene, Technical grade	25321-14-6		
5.0E-06	I	3.0E-02	I		Dinoseb	88-85-7	2.5E+00	1.3E+02
					Dioxane, 1,4-	123-91-1		
1.3E+00	I				Dioxins	NA	9.4E-06	
3.8E+01	C	4.0E-08	C		**Hexachlorodibenzo-p-dioxin, Mixture **TCDD, 2,3,7,8-	1746-01-6	3.2E-07	1.8E-04
					Diphenamid	957-51-7		
					Diphenyl Sulfone	127-63-9		
					Diphenylamine	122-39-4		
2.2E-04	I				Diphenylhydrazine, 1,2-	122-66-7	5.6E-02	
					Diquat	85-00-7		
2.1E-03	C				Direct Black 38	1937-37-7	5.8E-03	
2.1E-03	C				Direct Blue 6	2602-46-2	5.8E-03	
1.9E-03	C				Direct Brown 95	16071-86-6	6.5E-03	
					Disulfoton	298-04-4		
				V	Dithiane, 1,4-	505-29-3		
					Diuron	330-54-1		
					Dodine	2439-10-3		
				V	EPTC	759-94-4		
					Endosulfan	115-29-7		
					Endothall	145-73-3		
					Endrin	72-20-8		
1.2E-06	I	1.0E-03	I	V	Epichlorohydrin	106-89-8	1.0E+01	4.4E+00
		2.0E-02	I	V	Epoxybutane, 1,2-	106-88-7		8.8E+01
					Ethephon	16672-87-0		
					Ethion	563-12-2		
		6.0E-02	P		Ethoxyethanol Acetate, 2-	111-15-9		2.6E+02

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k v o l u t a g e n	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
2.0E-01	I				Ethoxyethanol, 2-	110-80-5		
7.0E-02	P		V		Ethyl Acetate	141-78-6		8.8E+02
			V		Ethyl Acrylate	140-88-5		3.1E+02
1.0E+01	I		V		Ethyl Chloride (Chloroethane)	75-00-3		4.4E+04
			V		Ethyl Ether	60-29-7		
3.0E-01	P		V		Ethyl Methacrylate	97-63-2		1.3E+03
2.5E-06	C	1.0E+00	I	V	Ethyl-p-nitrophenyl Phosphonate	2104-64-5	4.9E+00	4.4E+03
					Ethylbenzene	100-41-4		
					Ethylene Cyanohydrin	109-78-4		
4.0E-01	C				Ethylene Diamine	107-15-3		1.8E+03
1.6E+00	I				Ethylene Glycol	107-21-1		7.0E+03
					Ethylene Glycol Monobutyl Ether	111-76-2		
8.8E-05	C	3.0E-02	C	V	Ethylene Oxide	75-21-8	1.4E-01	1.3E+02
1.3E-05	C				Ethylene Thiourea	96-45-7	9.4E-01	
1.9E-02	C			V	Ethyleneimine	151-56-4	6.5E-04	
					Ethylphthalyl Ethyl Glycolate	84-72-0		
					Express	101200-48-0		
					Fenamiphos	22224-92-6		
					Fenpropathrin	39515-41-8		
1.3E-02	C				Fluometuron	2164-17-2		5.7E+01
					Fluoride	16984-48-8		
1.3E-02	C				Fluorine (Soluble Fluoride)	7782-41-4		5.7E+01
					Fluridone	59756-60-4		
					Flurprimidol	56425-91-3		
					Flutolanil	66332-96-5		
					Fluvalinate	69409-94-5		
					Folpet	133-07-3		
1.3E-05	I	9.8E-03	A		Fomesafen	72178-02-0		4.3E+01
					Fonofos	944-22-9		
					Formaldehyde	50-00-0	9.4E-01	1.3E+00
3.0E-04	X				Formic Acid	64-18-6		
					Fosetyl-AL	39148-24-8		
					Furans			
				V	~Dibenzofuran	132-64-9		
				V	~Furan	110-00-9		
2.0E+00	I		V		~Tetrahydrofuran	109-99-9		8.8E+03
4.3E-04	C	5.0E-02	H		Furazolidone	67-45-8		2.2E+02
					Furfural	98-01-1		
8.6E-06	C				Furium	531-82-8	2.9E-02	
					Furmecycloz	60568-05-0	1.4E+00	
8.0E-05	C				Glufosinate, Ammonium	77182-82-2		3.5E-01
					Glutaraldehyde	111-30-8		
1.0E-03	H				Glycidyl	765-34-4		4.4E+00
					Glyphosate	1071-83-6		
					Goal	42874-03-3		
1.0E-02	A				Guthion	86-50-0		4.4E+01
					Haloxyp, Methyl	69806-40-2		
					Harmony	79277-27-3		
1.3E-03	I				Heptachlor	76-44-8	9.4E-03	
2.6E-03	I				Heptachlor Epoxide	1024-57-3	4.7E-03	
					Hexabromobenzene	87-82-1		
4.6E-04	I				Hexabromodiphenyl ether, 2,2',4,4',5,5'- (BDE-153)	68631-49-2		
2.2E-05	I				Hexachlorobenzene	118-74-1	2.7E-02	
					Hexachlorobutadiene	87-68-3	5.6E-01	
1.8E-03	I				Hexachlorocyclohexane, Alpha-	319-84-6	6.8E-03	
5.3E-04	I				Hexachlorocyclohexane, Beta-	319-85-7	2.3E-02	
3.1E-04	C				Hexachlorocyclohexane, Gamma- (Lindane)	58-89-9	4.0E-02	
5.1E-04	I				Hexachlorocyclohexane, Technical	608-73-1	2.4E-02	
		2.0E-04	I		Hexachlorocyclopentadiene	77-47-4		8.8E-01
1.1E-05	C	3.0E-02	I		Hexachloroethane	67-72-1	1.1E+00	1.3E+02
					Hexachlorophene	70-30-4		
					Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4		
1.0E-05	I		V		Hexamethylene Diisocyanate, 1,6-	822-06-0		4.4E-02
					Hexamethylphosphoramide	680-31-9		
7.0E-01	I		V		Hexane, N-	110-54-3		3.1E+03
					Hexanedioic Acid	124-04-9		
3.0E-02	I		V		Hexanone, 2-	591-78-6		1.3E+02
4.9E-03	I	3.0E-05	P		Hexazinone	51235-04-2		
					Hydrazine	302-01-2	2.5E-03	1.3E-01
4.9E-03	I				Hydrazine Sulfate	10034-93-2	2.5E-03	
		2.0E-02	I		Hydrogen Chloride	7647-01-0		8.8E+01
		1.4E-02	C		Hydrogen Fluoride	7664-39-3		6.1E+01
		2.0E-03	I		Hydrogen Sulfide	7783-06-4		8.8E+00
					Hydroquinone	123-31-9		
					Imazalil	35554-44-0		

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	v o l u t a g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
					Imazaquin	81335-37-7		
					Iodine	7553-56-2		
					Iprodione	36734-19-7		
2.0E+00			C		Iron	7439-89-6		
					Isobutyl Alcohol	78-83-1		
					Isophorone	78-59-1		8.8E+03
7.0E+00			C		Isopropalin	33820-53-0		
					Isopropanol	67-63-0		3.1E+04
					Isopropyl Methyl Phosphonic Acid	1832-54-8		
3.0E-01			A	V	Isoxaben	82558-50-7		
					JP-7	NA		1.3E+03
					Kerb	23950-58-5		
8.0E-05			C		Lactofen	77501-63-4		
					Lead Compounds			
					~Lead acetate	301-04-2	1.5E-01	
1.1E-05			C		~Lead and Compounds	7439-92-1		
					~Lead subacetate	1335-32-6	1.1E+00	
					~Tetraethyl Lead	78-00-2		
					Linuron	330-55-2		
					Lithium	7439-93-2		
					Londax	83055-99-6		
					MCPA	94-74-6		
					MCPB	94-81-5		
					MCPP	93-65-2		
7.0E-04			C		Malathion	121-75-5		
					Maleic Anhydride	108-31-6		3.1E+00
					Maleic Hydrazide	123-33-1		
					Malononitrile	109-77-3		
					Mancozeb	8018-01-7		
					Maneb	12427-38-2		
5.0E-05			I		Manganese (Diet)	7439-96-5		
5.0E-05			I		Manganese (Non-diet)	7439-96-5		2.2E-01
					Mephosfolan	950-10-7		
3.0E-04			S		Mepiquat Chloride	24307-26-4		
					Mercury Compounds			
					~Mercuric Chloride (and other Mercury salts)	7487-94-7		1.3E+00
3.0E-04			I	V	~Mercury (elemental)	7439-97-6		1.3E+00
					~Methyl Mercury	22967-92-6		
					~Phenylmercuric Acetate	62-38-4		
					Merphos	150-50-5		
					Merphos Oxide	78-48-8		
					Metaxyl	57837-19-1		
3.0E-02			P	V	Methacrylonitrile	126-98-7		1.3E+02
					Methamidophos	10265-92-6		
2.0E+01			I		Methanol	67-56-1		8.8E+04
1.4E-05			C		Methidathion	950-37-8		
					Methomyl	16752-77-5	8.8E-01	
					Methoxy-5-nitroaniline, 2-	99-59-2		
1.0E-03			P		Methoxychlor	72-43-5		
					Methoxyethanol Acetate, 2-	110-49-6		4.4E+00
2.0E-02			I		Methoxyethanol, 2-	109-86-4		8.8E+01
				V	Methyl Acetate	79-20-9		
2.0E-02			P	V	Methyl Acrylate	96-33-3		8.8E+01
5.0E+00			I	V	Methyl Ethyl Ketone (2-Butanone)	78-93-3		2.2E+04
1.0E-03	X	2.0E-05	X		Methyl Hydrazine	60-34-4	1.2E-02	8.8E-02
		3.0E+00	I	V	Methyl Isobutyl Ketone (4-methyl-2-pentanone)	108-10-1		1.3E+04
		1.0E-03	C	V	Methyl Isocyanate	624-83-9		4.4E+00
7.0E-01			I	V	Methyl Methacrylate	80-62-6		3.1E+03
					Methyl Parathion	298-00-0		
					Methyl Phosphonic Acid	993-13-5		
4.0E-02			H	V	Methyl Styrene (Mixed Isomers)	25013-15-4		1.8E+02
2.8E-05			C		Methyl methanesulfonate	66-27-3	4.4E-01	
2.6E-07		3.0E+00	I	V	Methyl tert-Butyl Ether (MTBE)	1634-04-4	4.7E+01	1.3E+04
2.4E-03			C		Methyl-1,4-benzenediamine dihydrochloride, 2-	615-45-2		
					Methyl-5-Nitroaniline, 2-	99-55-8		
					Methyl-N-nitro-N-nitrosoguanidine, N-	70-25-7	5.1E-03	
3.7E-05			C		Methylaniline Hydrochloride, 2-	636-21-5	3.3E-01	
					Methylarsonic acid	124-58-3		
					Methylbenzene,1,4-diamine monohydrochloride, 2-	74612-12-7		
6.3E-03			C		Methylbenzene-1,4-diamine sulfate, 2-	615-50-9		
1.0E-08		6.0E-01	I	V	Methylcholanthrene, 3-	56-49-5	1.9E-03	
				M	Methylene Chloride	75-09-2	1.2E+03	2.6E+03
4.3E-04			C		Methylene-bis(2-chloroaniline), 4,4'-	101-14-4	2.9E-02	
1.3E-05			C		Methylene-bis(N,N-dimethyl) Aniline, 4,4'-	101-61-1	9.4E-01	
4.6E-04		2.0E-02	C		Methylenebisbenzenamine, 4,4'-	101-77-9	2.7E-02	8.8E+01

Toxicity and Chemical-specific						Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	v o l u t i l i t y	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
6.0E-04	I				V	Methylenediphenyl Diisocyanate	101-68-8		2.6E+00
						Methylstyrene, Alpha-Metolachlor	98-83-9 51218-45-2		
5.1E-03	C				V	Metribuzin	21087-64-9		
						Mineral oils	8012-95-1	2.4E-03	
						Mirex	2385-85-5		
						Molinate	2212-67-1		
						Molybdenum	7439-98-7		
						Monochloramine	10599-90-3		
						Monomethylaniline	100-61-8		
						N,N'-Diphenyl-1,4-benzenediamine	74-31-7		
						Naled	300-76-5		
1.0E-01	P				V	Naphtha, High Flash Aromatic (HFAN)	64724-95-6		4.4E+02
0.0E+00	C					Naphthylamine, 2-Napropamide	91-59-8 15299-99-7		
1.4E-05	C					Nickel Carbonyl	13463-39-3		6.1E-02
2.0E-05	C					Nickel Oxide	1313-99-1		8.8E-02
2.4E-04	I	1.4E-05	C			Nickel Refinery Dust	NA	5.1E-02	6.1E-02
2.6E-04	C	9.0E-05	A			Nickel Soluble Salts	7440-02-0	4.7E-02	3.9E-01
4.8E-04	I	1.4E-05	C			Nickel Subulfide	12035-72-2	2.6E-02	6.1E-02
						Nitrate	14797-55-8		
						Nitrate + Nitrite (as N)	NA		
5.0E-05	X					Nitrite	14797-65-0		
						Nitroaniline, 2-	88-74-4		2.2E-01
6.0E-03	P					Nitroaniline, 4-	100-01-6		2.6E+01
4.0E-05	I	9.0E-03	I	V		Nitrobenzene	98-95-3	3.1E-01	3.9E+01
						Nitrocellulose	9004-70-0		
3.7E-04	C					Nitrofurantoin	67-20-9		
						Nitrofurazone	59-87-0	3.3E-02	
						Nitroglycerin	55-63-0		
8.8E-06	P	5.0E-03	P	V		Nitroguanidine	556-88-7	1.4E+00	2.2E+01
2.7E-03	H	2.0E-02	I	V		Nitromethane	75-52-5	4.5E-03	8.8E+01
						Nitropropane, 2-	79-46-9		
7.7E-03	C				M	Nitroso-N-ethylurea, N-	759-73-9	1.6E-03	
3.4E-02	C				M	Nitroso-N-methylurea, N-	684-93-5	3.6E-04	
1.6E-03	I				V	Nitroso-di-N-butylamine, N-	924-16-3	7.7E-03	
2.0E-03	C					Nitroso-di-N-propylamine, N-	621-64-7	6.1E-03	
8.0E-04	C					Nitrosodiethanolamine, N-	1116-54-7	1.5E-02	
4.3E-02	I				M	Nitrosodimethylamine, N-	55-18-5	2.9E-04	
1.4E-02	I	4.0E-05	X		M	Nitrosodimethylamine, N-	62-75-9	8.8E-04	1.8E-01
2.6E-06	C					Nitrosodiphenylamine, N-	86-30-6	4.7E+00	
6.3E-03	C					Nitrosomethylethylamine, N-	10595-95-6	1.9E-03	
1.9E-03	C					Nitrosomorpholine [N-]	59-89-2	6.5E-03	
2.7E-03	C					Nitrosopiperidine [N-]	100-75-4	4.5E-03	
6.1E-04	I					Nitrosopyrrolidine, N-	930-55-2	2.0E-02	
						Nitrotoluene, m-	99-08-1		
						Nitrotoluene, o-	88-72-2		
						Nitrotoluene, p-	99-99-0		
2.0E-02	P				V	Nonane, n-	111-84-2		8.8E+01
						Norfurazon	27314-13-2		
						Nustar	85509-19-9		
						Octabromodiphenyl Ether	32536-52-0		
						Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691-41-0		
						Octamethylpyrophosphoramide	152-16-9		
						Oryzalin	19044-88-3		
						Oxadiazon	19666-30-9		
						Oxamyl	23135-22-0		
						Pacllobutrazol	76738-62-0		
						Paraquat Dichloride	1910-42-5		
						Parathion	56-38-2		
						Pebulate	1114-71-2		
						Pendimethalin	40487-42-1		
						Pentabromodiphenyl Ether	32534-81-9		
						Pentabromodiphenyl ether, 2,2',4,4',5- (BDE-99)	60348-60-9		
						Pentachlorobenzene	608-93-5		
						Pentachloroethane	76-01-7		
5.1E-06	C					Pentachloronitrobenzene	82-68-8	2.4E+00	
						Pentachlorophenol	87-86-5		
						Pentaerythritol tetranitrate (PETN)	78-11-5		
1.0E+00	P				V	Pentane, n-	109-66-0		4.4E+03
						Perchlorates			
						~Ammonium Perchlorate	7790-98-9		
						~Lithium Perchlorate	7791-03-9		
						~Perchlorate and Perchlorate Salts	14797-73-0		
						~Potassium Perchlorate	7778-74-7		

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	muta- c gen	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
6.3E-07	C				~Sodium Perchlorate ~Permethrin ~Phenacetin	7601-89-0 52645-53-1 62-44-2	1.9E+01	
2.0E-01	C				~Phenmedipham ~Phenol ~Phenothiazine	13684-63-4 108-95-2 92-84-2		8.8E+02
3.0E-04	I V				~Phenylphenol, 2- ~Phorate ~Phosgene	90-43-7 298-02-2 75-44-5		1.3E+00
					~Phosmet Phosphates, Inorganic ~Aluminum metaphosphate	732-11-6 13776-88-0		
					~Ammonium polyphosphate ~Calcium pyrophosphate ~Diammonium phosphate	68333-79-9 7790-76-3 7783-28-0		
					~Dicalcium phosphate ~Dimagnesium phosphate ~Dipotassium phosphate	7757-93-9 7782-75-4 7758-11-4		
					~Disodium phosphate ~Monoaluminum phosphate ~Monoammonium phosphate	7558-79-4 13530-50-2 7722-76-1		
					~Monocalcium phosphate ~Monomagnesium phosphate ~Monopotassium phosphate	7758-23-8 7757-86-0 7778-77-0		
					~Monosodium phosphate ~Polyphosphoric acid ~Potassium tripolyphosphate	7558-80-7 8017-16-1 13845-36-8		
					~Sodium acid pyrophosphate ~Sodium aluminum phosphate (acidic) ~Sodium aluminum phosphate (anhydrous)	7758-16-9 7785-88-8 10279-59-1		
					~Sodium aluminum phosphate (tetrahydrate) ~Sodium hexametaphosphate ~Sodium polyphosphate	10305-76-7 10124-56-8 68915-31-1		
					~Sodium trimetaphosphate ~Sodium tripolyphosphate ~Tetrapotassium phosphate	7785-84-4 7758-29-4 7320-34-5		
					~Tetrasodium pyrophosphate ~Trialuminum sodium tetra decahydrogenoctaorthophosphate (dihydrate) ~Tricalcium phosphate	7722-88-5 15136-87-5 7758-87-4		
3.0E-04	I				~Trimagnesium phosphate ~Tripotassium phosphate ~Trisodium phosphate	7757-87-1 7778-53-2 7601-54-9		
1.0E-02	I				Phosphine Phosphoric Acid Phosphorus, White	7803-51-2 7664-38-2 7723-14-0		1.3E+00 4.4E+01
2.4E-06	C				Phthalates ~Bis(2-ethylhexyl)phthalate ~Butylphthalyl Butylglycolate	117-81-7 85-70-1	5.1E+00	
				V	~Dibutyl Phthalate ~Diethyl Phthalate ~Dimethylterephthalate	84-74-2 84-66-2 120-61-6		
2.0E-02	C				~Octyl Phthalate, di-N- ~Phthalic Acid, P- ~Phthalic Anhydride	117-84-0 100-21-0 85-44-9		8.8E+01
8.6E-03	C				Picloram Picramic Acid (2-Amino-4,6-dinitrophenol) Pirimiphos, Methyl	1918-02-1 96-91-3 29232-93-7		
2.0E-05	S				Polybrominated Biphenyls Polychlorinated Biphenyls (PCBs) ~Aroclor 1016	59536-65-1 12674-11-2	1.4E-03 6.1E-01	
5.7E-04	S			V	~Aroclor 1221	11104-28-2	2.1E-02	
5.7E-04	S			V	~Aroclor 1232	11141-16-5	2.1E-02	
5.7E-04	S				~Aroclor 1242	53469-21-9	2.1E-02	
5.7E-04	S				~Aroclor 1248	12672-29-6	2.1E-02	
5.7E-04	S				~Aroclor 1254	11097-69-1	2.1E-02	
5.7E-04	S				~Aroclor 1260	11096-82-5	2.1E-02	
1.1E-03	E	1.3E-03	E		~Heptachlorobiphenyl, 2,3,3',4,4',5,5'- (PCB 189)	39635-31-9	1.1E-02	5.8E+00
1.1E-03	E	1.3E-03	E		~Hexachlorobiphenyl, 2,3',4,4',5,5'- (PCB 167)	52663-72-6	1.1E-02	5.8E+00
1.1E-03	E	1.3E-03	E		~Hexachlorobiphenyl, 2,3,3',4,4',5,5'- (PCB 157)	69782-90-7	1.1E-02	5.8E+00
1.1E-03	E	1.3E-03	E		~Hexachlorobiphenyl, 2,3,3',4,4',5- (PCB 156)	38380-08-4	1.1E-02	5.8E+00
1.1E+00	E	1.3E-06	E		~Hexachlorobiphenyl, 3,3',4,4',5,5'- (PCB 169)	32774-16-6	1.1E-05	5.8E-03
1.1E-03	E	1.3E-03	E		~Pentachlorobiphenyl, 2',3,4,4',5- (PCB 123)	65510-44-3	1.1E-02	5.8E+00

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	muta- gen	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
1.1E-03	E	1.3E-03	E		~Pentachlorobiphenyl, 2,3',4,4',5- (PCB 118)	31508-00-6	1.1E-02	5.8E+00
1.1E-03	E	1.3E-03	E		~Pentachlorobiphenyl, 2,3,3',4,4'- (PCB 105)	32598-14-4	1.1E-02	5.8E+00
1.1E-03	E	1.3E-03	E		~Pentachlorobiphenyl, 2,3,4,4',5- (PCB 114)	74472-37-0	1.1E-02	5.8E+00
3.8E+00	E	4.0E-07	E		~Pentachlorobiphenyl, 3,3',4,4',5- (PCB 126)	57465-28-8	3.2E-06	1.8E-03
5.7E-04	I				~Polychlorinated Biphenyls (high risk)	1336-36-3	2.1E-02	
1.0E-04	I				~Polychlorinated Biphenyls (low risk)	1336-36-3	1.2E-01	
2.0E-05	I				~Polychlorinated Biphenyls (lowest risk)	1336-36-3	6.1E-01	
3.8E-03	E	4.0E-04	E		~Tetrachlorobiphenyl, 3,3',4,4'- (PCB 77)	32598-13-3	3.2E-03	1.8E+00
1.1E-02	E	1.3E-04	E		~Tetrachlorobiphenyl, 3,4,4',5- (PCB 81)	70362-50-4	1.1E-03	5.8E-01
6.0E-04	I				Polymeric Methylene Diphenyl Diisocyanate (PMDI)	9016-87-9		2.6E+00
				V	Polynuclear Aromatic Hydrocarbons (PAHs)			
				V	~Acenaphthene	83-32-9		
1.1E-04	C			M	~Anthracene	120-12-7		
1.1E-04	C			M	~Benz[a]anthracene	56-55-3	1.1E-01	
1.1E-04	C			M	~Benzo[j]fluoranthene	205-82-3	1.1E-01	
1.1E-03	C			M	~Benzo[a]pyrene	50-32-8	1.1E-02	
1.1E-04	C			M	~Benzo[b]fluoranthene	205-99-2	1.1E-01	
1.1E-04	C			M	~Benzo[k]fluoranthene	207-08-9	1.1E-01	
1.1E-05	C			M	~Chloronaphthalene, Beta-	91-58-7		
1.2E-03	C			M	~Chrysene	218-01-9	1.1E+00	
1.1E-03	C			M	~Dibenz[a,h]anthracene	53-70-3	1.0E-02	
1.1E-03	C			M	~Dibenzo[a,e]pyrene	192-65-4	1.1E-02	
7.1E-02	C			M	~Dimethylbenz(a)anthracene, 7,12-	57-97-6	1.7E-04	
				M	~Fluoranthene	206-44-0		
1.1E-04	C			M	~Fluorene	86-73-7		
				M	~Indeno[1,2,3-cd]pyrene	193-39-5	1.1E-01	
				M	~Methylnaphthalene, 1-	90-12-0		
3.4E-05	C	3.0E-03	I	V	~Methylnaphthalene, 2-	91-57-6		
1.1E-04	C			V	~Naphthalene	91-20-3	3.6E-01	1.3E+01
				V	~Nitropyrene, 4-	57835-92-4	1.1E-01	
				V	~Pyrene	129-00-0		
				V	Prochloraz	67747-09-5		
				V	Profluralin	26399-36-0		
				V	Prometon	1610-18-0		
				V	Prometryn	7287-19-6		
				V	Propachlor	1918-16-7		
				V	Propanil	709-98-8		
				V	Propargite	2312-35-8		
				V	Propargyl Alcohol	107-19-7		
				V	Propazine	139-40-2		
				V	Propham	122-42-9		
				V	Propiconazole	60207-90-1		
8.0E-03	I		V		Propionaldehyde	123-38-6		3.5E+01
1.0E+00	X		V		Propyl benzene	103-65-1		4.4E+03
3.0E+00	C		V		Propylene	115-07-1		1.3E+04
2.7E-04	A				Propylene Glycol	57-55-6		
					Propylene Glycol Dinitrate	6423-43-4		1.2E+00
					Propylene Glycol Monoethyl Ether	1569-02-4		
2.0E+00	I				Propylene Glycol Monomethyl Ether	107-98-2		8.8E+03
3.7E-06	I	3.0E-02	I	V	Propylene Oxide	75-56-9	3.3E+00	1.3E+02
				V	Pursuit	81335-77-5		
				V	Pydrin	51630-58-1		
				V	Pyridine	110-86-1		
				V	Quinalphos	13593-03-8		
3.0E-02	A				Quinoline	91-22-5		
					Refractory Ceramic Fibers	NA		1.3E+02
					Resmethrin	10453-86-8		
6.3E-05	C			M	Ronnel	799-84-3		
				M	Rotenone	83-79-4		
				M	Safrole	94-59-7	1.9E-01	
					Savey	78587-05-0		
2.0E-02	C				Selenious Acid	7783-00-8		
					Selenium	7782-49-2		8.8E+01
2.0E-02	C				Selenium Sulfide	7446-34-6		8.8E+01
3.0E-03	C				Sethoxydim	74051-80-2		
					Silica (crystalline, respirable)	7631-86-9		1.3E+01
					Silver	7440-22-4		
					Simazine	122-34-9		
					Sodium Acifluorfen	62476-59-9		
1.3E-02	C				Sodium Azide	26628-22-8		
					Sodium Diethyldithiocarbamate	148-18-5		
					Sodium Fluoride	7681-49-4		5.7E+01
					Sodium Fluoroacetate	62-74-8		
					Sodium Metavanadate	13718-26-8		
					Stirofos (Tetrachlorovinphos)	961-11-5		

TR=1E-06
 HQ=1.0

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k v o l u t e g e n	muta- g e n	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
					Strontium, Stable	7440-24-6		
					Strychnine	57-24-9		
1.0E+00	I		V		Styrene	100-42-5		4.4E+03
2.0E-03	P				Sulfolane	126-33-0		8.8E+00
1.0E-03	C				Sulfonylbis(4-chlorobenzene), 1,1'-	80-07-9		
					Sulfuric Acid	7664-93-9		4.4E+00
					Systhane	88671-89-0		
					TCMTB	21564-17-0		
					Tebuthiuron	34014-18-1		
					Temephos	3383-96-8		
					Terbacil	5902-51-2		
					Terbufos	13071-79-9		
					Terbutryn	886-50-0		
					Tetrabromodiphenyl ether, 2,2',4,4'-(BDE-47)	5436-43-1		
					Tetrachlorobenzene, 1,2,4,5-	95-94-3		
7.4E-06	I		V		Tetrachloroethane, 1,1,1,2-	630-20-6	1.7E+00	
5.8E-05	C		V		Tetrachloroethane, 1,1,2,2-	79-34-5	2.1E-01	
2.6E-07	I	4.0E-02	I	V	Tetrachloroethylene	127-18-4	4.7E+01	1.8E+02
					Tetrachlorophenol, 2,3,4,6-	58-90-2		
					Tetrachlorotoluene, p- alpha, alpha, alpha-	5216-25-1		
					Tetraethyl Dithiopyrophosphate	3689-24-5		
8.0E+01	I		V		Tetrafluoroethane, 1,1,1,2-	811-97-2		3.5E+05
					Tetryl (Trinitrophenylmethylnitramine)	479-45-8		
					Thallium (I) Nitrate	10102-45-1		
					Thallium (Soluble Salts)	7440-28-0		
					Thallium Acetate	563-68-8		
					Thallium Carbonate	6533-73-9		
					Thallium Chloride	7791-12-0		
					Thallium Sulfate	7446-18-6		
					Thiobencarb	28249-77-6		
					Thiodiglycol	111-48-8		
					Thiofanox	39196-18-4		
					Thiophanate, Methyl	23564-05-8		
1.0E-04	A				Thiram	137-26-8		
					Tin	7440-31-5		
5.0E+00	I		V		Titanium Tetrachloride	7550-45-0		4.4E-01
					Toluene	108-88-3		2.2E+04
					Toluene-2,5-diamine	95-70-5		
					Toluidine, p-	106-49-0		
1.9E-07	P	6.0E-01	P	V	Total Petroleum Hydrocarbons (Aliphatic High)	NA		
4.5E-06	P	1.0E-01	P	V	Total Petroleum Hydrocarbons (Aliphatic Low)	NA	6.5E+01	2.6E+03
					Total Petroleum Hydrocarbons (Aliphatic Medium)	NA	2.7E+00	4.4E+02
7.8E-06	P	3.0E-02	P	V	Total Petroleum Hydrocarbons (Aromatic High)	NA		
		3.0E-03	P	V	Total Petroleum Hydrocarbons (Aromatic Low)	NA	1.6E+00	1.3E+02
					Total Petroleum Hydrocarbons (Aromatic Medium)	NA		1.3E+01
3.2E-04	I				Toxaphene	8001-35-2	3.8E-02	
					Tralometrin	66841-25-6		
					Tri-n-butyltin	688-73-3		
					Triacetin	102-76-1		
					Triallate	2303-17-5		
					Trialsulfuron	82097-50-5		
					Tribromobenzene, 1,2,4-	615-54-3		
					Tributyl Phosphate	126-73-8		
					Tributyltin Compounds	NA		
3.0E+01	H		V		Tributyltin Oxide	56-35-9		
					Trichloro-1,2,2-trifluoroethane, 1,1,2-	76-13-1		1.3E+05
					Trichloroacetic Acid	76-03-9		
					Trichloroaniline HCl, 2,4,6-	33663-50-2		
					Trichloroaniline, 2,4,6-	634-93-5		
					Trichlorobenzene, 1,2,3-	87-61-6		
2.0E-03	P		V		Trichlorobenzene, 1,2,4-	120-82-1		8.8E+00
5.0E+00	I		V		Trichloroethane, 1,1,1-	71-55-6		2.2E+04
1.6E-05	I	2.0E-04	X	V	Trichloroethane, 1,1,2-	79-00-5	7.7E-01	8.8E-01
4.1E-06	I	2.0E-03	I	V	Trichloroethylene	79-01-6	3.0E+00	8.8E+00
		7.0E-01	H	V	Trichlorofluoromethane	75-69-4		3.1E+03
					Trichlorophenol, 2,4,5-	95-95-4		
3.1E-06	I				Trichlorophenol, 2,4,6-	88-06-2	4.0E+00	
					Trichlorophenoxyacetic Acid, 2,4,5-	93-76-5		
					Trichlorophenoxypropionic acid, -2,4,5	93-72-1		
					Trichloropropane, 1,1,2-	598-77-6		
3.0E-04	I		V	M	Trichloropropane, 1,2,3-	96-18-4		1.3E+00
3.0E-04	P		V		Trichloropropene, 1,2,3-	96-19-5		1.3E+00
					Tricresyl Phosphate (TCP)	1330-78-5		
					Tridiphane	58138-08-2		
7.0E-03	I		V		Triethylamine	121-44-8		3.1E+01

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Toxicity and Chemical-specific					Contaminant	Carcinogenic Target Risk (TR) = 1E-06	Noncancer Hazard Index (HI) = 1	
IUR (ug/m ³) ⁻¹	k e y	RfC _i (mg/m ³)	k e y	v o l u t i l e n c e	Analyte	CAS No.	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL HI=1 (ug/m ³)
					Trifluralin	1582-09-8		
					Trimethyl Phosphate	512-56-1		
5.0E-03			P	V	Trimethylbenzene, 1,2,3-	526-73-8		2.2E+01
					Trimethylbenzene, 1,2,4-	95-63-6		
7.0E-03			P	V	Trimethylbenzene, 1,3,5-	108-67-8		3.1E+01
				V	Trinitrobenzene, 1,3,5-	99-35-4		
					Trinitrotoluene, 2,4,6-	118-96-7		
					Triphenylphosphine Oxide	791-28-6		
					Tris(1,3-Dichloro-2-propyl) Phosphate	13674-87-8		
					Tris(1-chloro-2-propyl)phosphate	13674-84-5		
					Tris(2-chloroethyl)phosphate	115-96-8		
					Tris(2-ethylhexyl)phosphate	78-42-2		
4.0E-05			A		Uranium (Soluble Salts)	NA		1.8E-01
2.9E-04	C				Urethane	51-79-6	4.2E-02	
8.3E-03	P	7.0E-06	P		Vanadium Pentoxide	1314-62-1	1.5E-03	3.1E-02
				A	Vanadium and Compounds	7440-62-2		4.4E-01
					Vernolate	1929-77-7		
					Vinclozolin	50471-44-8		
					Vinyl Acetate	108-05-4		8.8E+02
2.0E-01	I		V		Vinyl Bromide	593-60-2	3.8E-01	1.3E+01
3.2E-05	H	3.0E-03	I	V	Vinyl Chloride	75-01-4	2.8E+00	4.4E+02
4.4E-06	I	1.0E-01	I	V	Warfarin	81-81-2		
					Xylene, p-	106-42-3		4.4E+02
1.0E-01	S		V		Xylene, m-	108-38-3		4.4E+02
					Xylene, o-	95-47-6		4.4E+02
1.0E-01	S		V		Xylenes	1330-20-7		4.4E+02
					Zinc Phosphide	1314-84-7		
					Zinc and Compounds	7440-66-6		
					Zincb	12122-67-7		
					Zirconium	7440-67-7		

TR=1E-06
HQ=1.0