ARCS V

Remedial Activities at Uncontrolled Hazardous Waste Sites in Region V

EPA United States Environmental Protection Agency

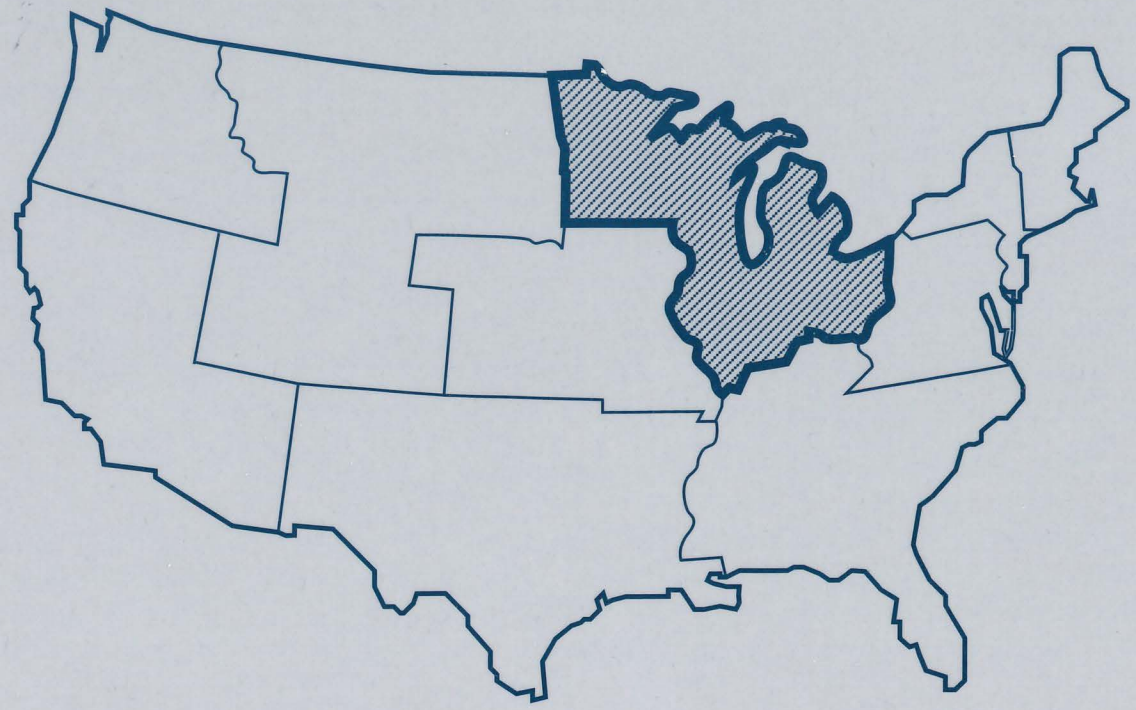
Quality Assurance Project Plan

Onalaska Municipal Landfill
Onalaska, Wisconsin

Groundwater Remedial Action

WA No. 79-5HL5/Contract No. 68-W8-0040

June 1995



CH2M HILL

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Acronyms/Abbreviations

ARARs	applicable or relevant and appropriate requirements
ASTM	American Society for Testing and Materials
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CRL	Central Regional Laboratory
DI	deionized
DMZ	Design Management Zone
DNR	Wisconsin Department of Natural Resources
DOT	Department of Transportation
DQO	data quality objective
EM	electromagnetic
ES	Enforcement Standard
EPA	U. S. Environmental Protection Agency
FAA	furnace atomic adsorption
FS	Feasibility Study
FSP	Field Sampling Plan
GC/MS	gas chromatograph/mass spectrometer
HPLC	high-pressure liquid chromatography
ICP	inductively coupled plasma
I.D.	inner diameter
LSSS	Laboratory Scientific Support Section
LEL	lower explosive limit
MCL	maximum contaminant level
MS/MSD	matrix spike/matrix spike duplicate
NEIC	National Enforcement Investigations Center
NGVD	National Geodetic Vertical Datum of 1929
NIST	National Institute of Standards and Technology
NPL	National Priorities List
O.D.	outer diameter
OVA	organic vapor analyzer
PAH	polycyclic aromatic hydrocarbon
PAL	Preventive Action Limits
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCB	polychlorinated biphenyl
PE	performance evaluation
PIC	pressurized ion chamber
%R	percent recovery
PRP	potentially responsible party
PVC	polyvinyl chloride
RA	Remedial Action
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
QA	quality assurance
QAPjP	Quality Assurance Project Plan

QAS	Quality Assurance Section
QC	quality control
RAS	Routine Analytical Services
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RPD	relative percent difference
SAS	Special Analytical Services
SOP	Standard Operating Procedure
SOW	statement of work
SVOC	semivolatile organic compound
TAL	Target Analyte List
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
USGS	U.S. Geological Survey
VOC	volatile organic compound
WA	work assignment

MKE10015F00.WP5

Section 1
Title Page

Remedial Planning Activities
(ARCS V)
Contract No. 68-W8-0040
Quality Assurance Project Plan (QAPP)

Project Title: Groundwater Remedial Action
Onalaska Municipal Landfill
Onalaska, Wisconsin

EPA No: WA 79-5HL5

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3.1 Introduction

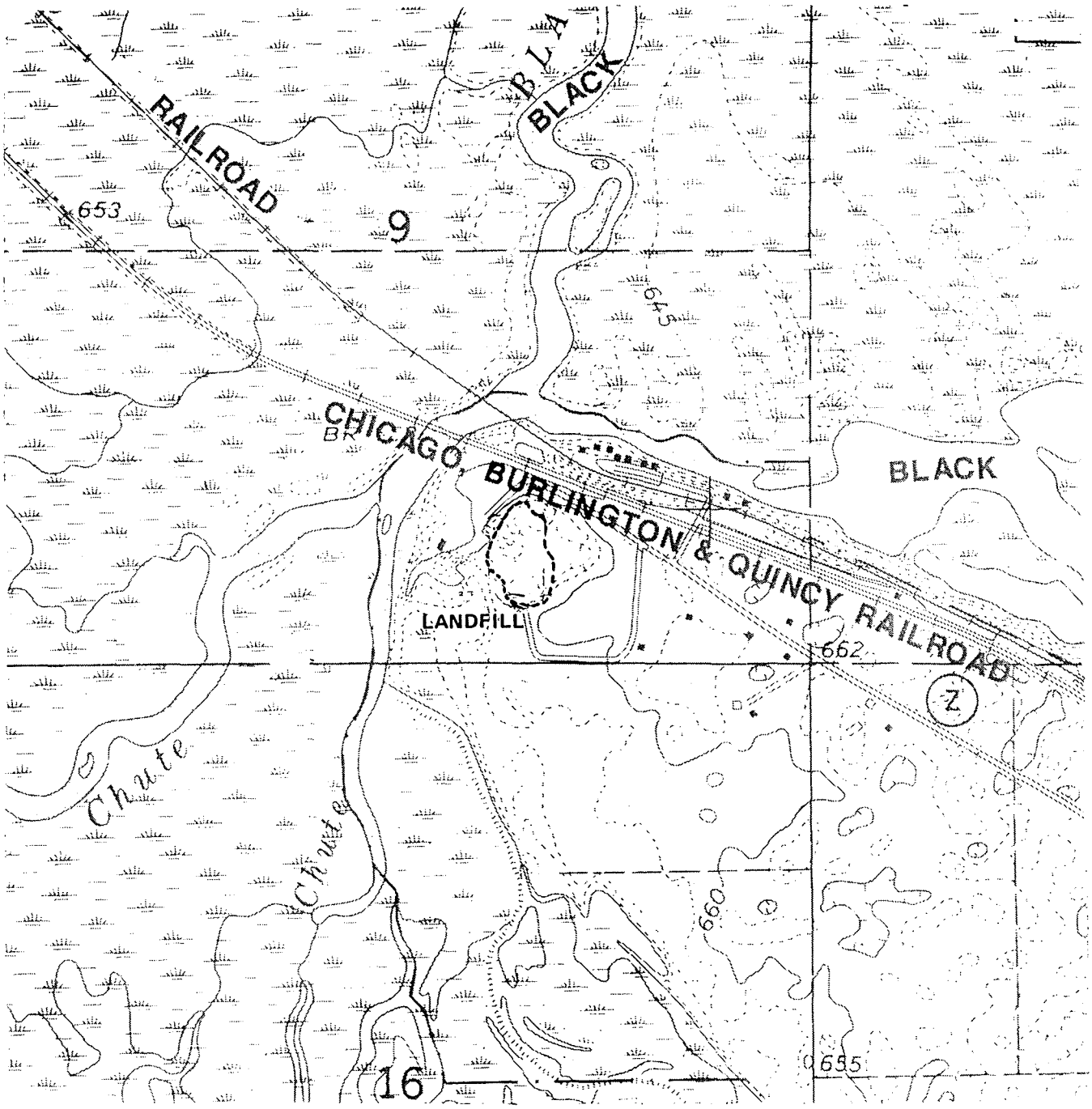
The United States Environmental Protection Agency (EPA) requires that all EPA contractors participate in a centrally managed quality assurance (QA) program. That requirement applies to all environmental monitoring and measurement efforts mandated or supported by the EPA. Each contractor generating data has the responsibility to implement minimum procedures to see that the precision, accuracy, completeness, and representativeness of its data are known and documented. To see that this responsibility is met uniformly, each EPA contractor must prepare a written Quality Assurance Project Plan (QAPjP) addressing each project it is contracted to perform.

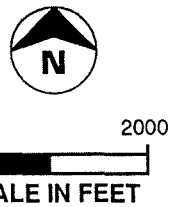
This QAPjP is prepared as part of Work Assignment No. 79-5HL5 under ARCS V (Contract No. 68-W8-0040) which authorizes CH2M HILL to complete the remedial design for the Onalaska Municipal Landfill in Onalaska, Wisconsin. This QAPjP presents the organization, objectives, functional activities, and specific QA and quality control (QC) activities associated with groundwater sampling as part of the Groundwater Monitoring Plan to implement the selected remedial action for groundwater extraction and treatment at the Onalaska Municipal Landfill site.

3.2 Site Description

The Onalaska Municipal Landfill is in La Crosse County, Wisconsin, about 10 miles north of the City of La Crosse near the confluence of the Mississippi and Black Rivers and within 400 feet of the Black River (Figure 1). Several homes are located within 500 feet of the site, and a subdivision of about 50 homes is located 1.25 miles southeast of the site. The area is generally rural. The sand and gravel aquifer is used as the water supply.

The 11-acre site was mined as a sand and gravel quarry in the early 1960s (see Figure 2). In the mid-1960s the quarry operation ceased, and the Town of Onalaska began using the quarry as a municipal landfill. Between 1969 and 1980, municipal trash and chemical wastes were disposed of in the landfill. The landfill was capped between 1980 and 1982. The site is not fenced, but two gates restrict vehicular access to it.

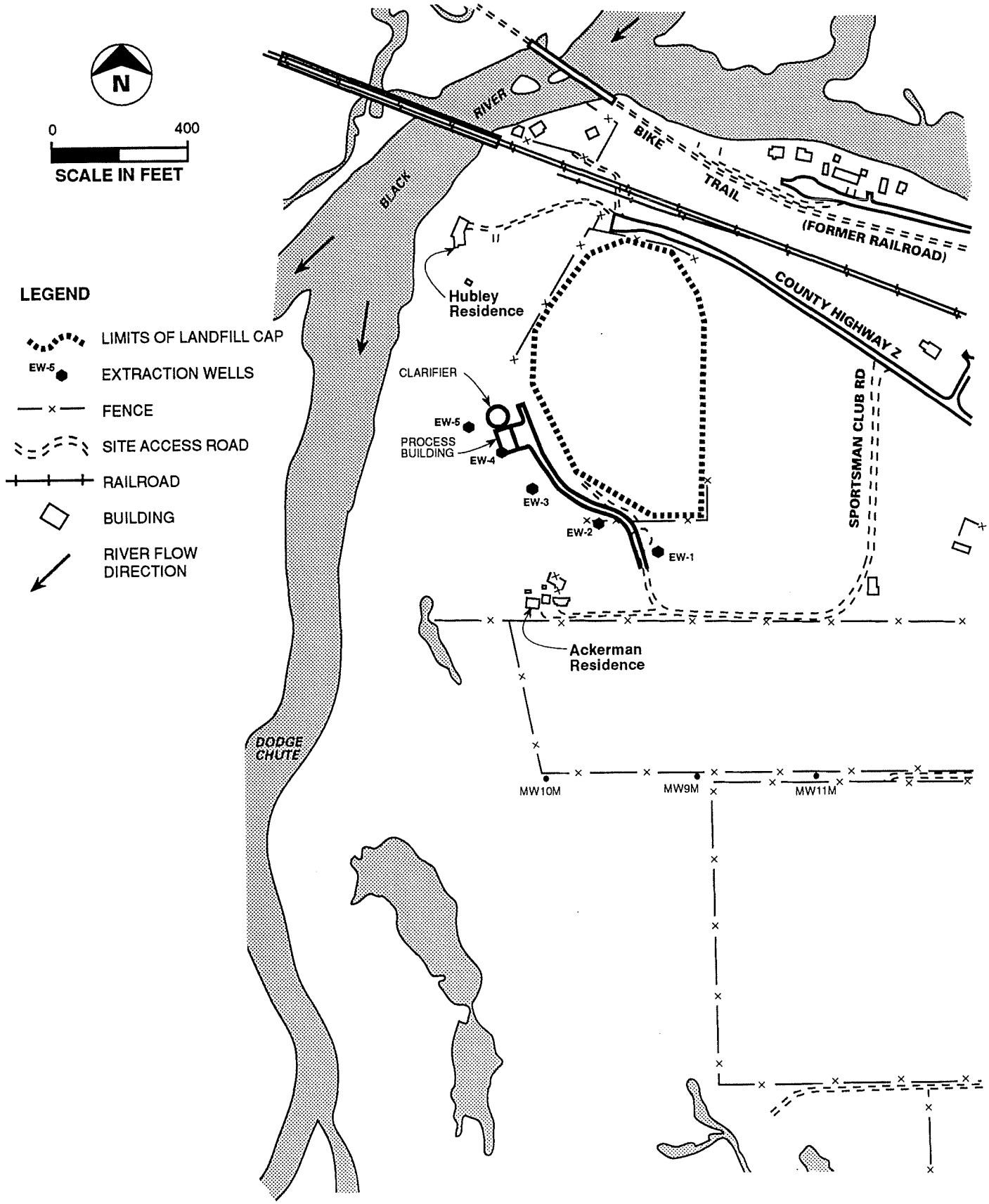




SOURCE: U.S. Geological Survey, Trempealeau, 15' Quadrangle.

FIGURE 1
SITE LOCATION MAP
ONALASKA
QAPP

GLE55672.RA.OS Site Loc Map Border 5/31/95kmw/tl



GLE65672.RA.QS Site Map 5/15/95kmw

FIGURE 2
SITE MAP
ONALASKA LANDFILL
QAPP

3.3 Site History and Background

3.3.1 Site History

The Town of Onalaska owned and was licensed to operate the Onalaska Municipal Landfill from 1969 to 1980. The Wisconsin Department of Natural Resources (DNR) ordered its closure in 1980. During 11 years of operation, the Onalaska Landfill provided waste disposal for residential, commercial, and industrial generators located within the township and nonresidents with written permits. The landfill also accepted refuse from other townships.

Landfill operations were informal. During the first 3 years of operation, there was no attendant at the landfill. Later, operating hours were posted and an operator was present to cover incoming waste and measure the nonresidential waste for billing purposes. The landfill boundaries were defined by a cable or fence partially enclosing the site. A gate was installed at the site in early 1971 to restrict site access. However, keys were readily provided to clients who wished to use the landfill outside the posted operating hours.

Seven acres of the Onalaska Landfill were reportedly reserved for using the compaction and cover method of waste disposal. The landfill was regularly inspected by the DNR. Early DNR records indicate that open burning was practiced at the site in late 1970. The DNR prohibited all open burning in January 1971 after receiving several complaints about noxious odors and sooty, black smoke from the burning of naphtha, an oily industrial solvent waste. Consequently, the DNR required that an area be designated for the disposal of industrial solvents and wastes delivered to the site. Several industrial firms are known to have used the landfill for waste disposal.

Outers Laboratories and Metallics, Inc. (two companies owned by one person), contributed significant quantities of industrial wastes to the site. Daily landfill operation reports indicate that these two companies were disposing of industrial waste oils and solvents as early as July 7, 1970. Early DNR records report that Outers delivered liquid solvent residues to the site for burning. The waste solvents consisted primarily of naphtha, toluene, and paint residues. Initially, both Outers and Metallics hauled solvent wastes in 55-gallon barrels. Once a week, 20 to 25 barrels of industrial wastes from the companies were hauled to the landfill. The barrels were emptied and the waste was burned. After burning was banned, the liquid waste was dumped in the designated area and poured into excavated holes for immediate burial. Occasionally, full barrels were left at the site if they could not be easily emptied or if they were damaged or leaking. In later years, the liquid waste was hauled in a 500-gallon truck instead of barrels. At that time, about 300 barrels were additionally mass buried at the landfill.

Reportedly, on one occasion, when a tank truck hauling the waste could not be drained because the discharge outlet was plugged with hardened paint resin and solvent, the truck was buried in the south section of the landfill. In August 1975, the DNR recommended that Outers find alternative methods to dispose of its naphtha waste. Outers investigated and eventually implemented a reclamation process to recover some of the raw materials from the waste. In April 1976, Outers informed the DNR that it was no longer disposing of liquid wastes in the landfill.

On February 9, 1978, the DNR issued an order to the township to submit an infield conditions report for the landfill because the site did not meet Wisconsin solid waste codes. Warzyn Engineering investigated the site for the township and submitted a report to the DNR on April 17, 1978. Warzyn recommended phased abandonment of the site. In June 1978, the DNR reported that the average distance between the groundwater table and the base of the refuse pile was 1 foot. Studies showed that the seasonal fluctuations in water levels sometimes allowed the groundwater to be in direct contact with a portion of the waste for extended periods of time.

On October 19, 1978, Warzyn Engineering submitted a plan of operation for phased abandonment of the landfill. On May 4, 1979, the DNR issued a plan approval and ordered the landfill closed by September 30, 1979. On May 30, 1980, the DNR modified the order to close the landfill by September 30, 1980. Closure proceeded in phases, and the final cap was placed in July 1982.

In September 1982, the DNR sampled and analyzed water from monitoring wells and private wells for compliance with drinking water standards for organic and inorganic constituents. The investigations indicated that groundwater contamination had occurred. The barium concentrations in the water from Cecil Miller's residential well south of the site exceeded the drinking water standard, and five organic compounds were detected above background levels. In January 1983, the Town of Onalaska replaced Mr. Miller's well with a deep well.

On May 2, 1983, an EPA Potential Hazardous Waste Site inspection report was submitted. In September 1984 the Onalaska Landfill was placed on the National Priorities List with a hazard ranking of 42.97.

3.3.2 Background

Except for the industrial waste solvents from Outers Laboratories and Metallics, Inc. There is little indication that the wastes within the 7 acres used for open pit disposal were segregated. Industrial, commercial, and municipal wastes are considered to be mixed throughout the fill area. Outers and Metallics used a specific area designated for liquid

industrial waste disposal according to DNR correspondence and license applications. However, the designated disposal area was not strictly limited to the industrial wastes from Outers and Metallics. Records indicate that other commercial wastes were deposited simultaneously in the area designated for liquid industrial waste disposal in October 1981 and October 1982.

For a time, open burning occurred at the site. Until early 1971 when open burning was banned, the industrial solvents from Outers and Metallics were burned regularly at apparently random locations throughout the landfill. Some refuse was also burned bimonthly. Open burning reportedly continued, even though banned, until as late as 1979.

Liquid industrial wastes consisted primarily of naphtha-based solvents used in a metal cleaning process and solvent wastes from paint spray gun cleaning and machine shop cleaning fluids. At least two kinds of naphtha were disposed of at the site—high-flash naphtha and VM&P or Stoddard naphtha. High-flash naphtha is a coal-tar derivative consisting primarily of a mixture of aromatic hydrocarbons. It was probably used as a degreasing agent or a general solvent. The VM&P or Stoddard naphthas, derived from petroleum, are slightly more volatile. They consist of a mixture of aliphatic hydrocarbons, naphthenes, and alkyl benzenes. They are used as universal solvents for general cleaning and as paint thinners. These naphthas were probably used in a paint cleaning process at one of the plants and as general solvents. Both the petroleum and coal-tar derived naphthas are less dense than water and would float on the surface of the water table if they reached the aquifer.

Some of the organic compounds detected in the groundwater during past analyses may have been derived from naphtha wastes floating on the water table. The liquid naphtha waste could generate a complex mixture of dissolved organic compounds in the groundwater over a period of time. Both types of naphtha would each produce a different suite of degradation products of varying composition. It is impossible to predict the exact composition of each mixture, but generally naphtha degradation products consist of aliphatic and aromatic carboxylic acids, toluene, and other complex mixtures of aromatic and aliphatic hydrocarbons.

3.4 Target Compounds

Contaminant concentrations in the groundwater at individual monitoring well locations within the landfill or at the landfill boundary contained contaminant concentrations that exceed one or more standards or criteria. The Safe Drinking Water Act maximum contaminant levels (MCLs) for arsenic, barium, benzene, 1,1-dichloroethene, toluene,

1,1,1-trichloroethane, trichloroethene, and xylene were exceeded at one or more monitoring well locations.

A series of shallow groundwater samples were collected during the RI and were analyzed using a close support laboratory. The primary objectives of the shallow groundwater analysis were to locate the extent of the floating non-aqueous phase and to help select groundwater monitoring well locations. The close support laboratory analyzed a total of 81 samples for the following organic compounds:

- Toluene
- Total xylenes
- 1,1,1-TCA
- TCE
- PCE

These compounds were selected on the basis of historical groundwater analysis, site history, and their chemical properties (e.g., mobility). Concentrations of toluene were observed as high as 43,000 μg/L. Of the three chlorinated compounds analyzed for, 1,1,1-TCA was the most prevalent, and was found at concentrations as high as 730 μg/L.

Two rounds of groundwater sampling for Contract Laboratory analysis were conducted. These samples were analyzed for the complete Target Compound List (TCL) and 13 Special Analytical Services (SAS) parameters.

Volatile Organic Compounds (VOCs) were generally observed to be present at concentrations much greater than semivolatile organics (sometimes more than an order of magnitude greater). The majority of the VOCs detected during the Remedial Investigation were found in shallow monitoring wells (MW-5S and MW-3S and B4S) and were BTEX compounds. The vertical extent of BTEX and chlorinated compounds contamination is mostly confined to the upper 10 to 20 feet of the aquifer. Ethylbenzene, 1,1-DCA and chloroethane were detected, however, at depths up to 50 to 60 feet below the water table. The vertical extent of semivolatile organic compounds (SVOCs) contamination is also mostly confined to the upper 10 to 20 feet of the aquifer. There were no SVOCs detected in any of the deep monitoring wells.

Highest

Monitoring wells along the southwestern edge of the landfill and southwest of the landfill have the most occurrence of inorganic chemicals above background. These are primarily shallow and medium wells that included MW-2S, MW-2M, MW-3S, MW-4S, MW-B4S, MW-5S, and MW-8S. Four chemicals: barium, iron, manganese, and sodium, were detected above background with greater frequency than the other inorganic chemicals.

The higher concentrations of these four chemical tends to occur in wells along the southwestern edge of the landfill or southwest of the landfill.

Under the remedy selected in the ROD, the following cleanup standards were adopted:

- Groundwater contaminant plume located at any point beyond the property boundary or DMZ:
  - Preventive Action Limits (PALs) from Wisconsin Administrative Code Chapter NR 140
- Groundwater contaminant plume located at landfill waste boundary:
  - Maximum Contaminant Levels (MCLs) from the Safe Drinking Water Act, 40 CFR 141.61 and 40 CFR 143
  - Maximum Contaminant Level Goals (MCLGs) above zero Safe Drinking Water Act, 40 CFR 141.50

The ROD requires that the more stringent Wisconsin standards promulgated in NR 140, WAC, be achieved "at any point beyond the property boundary or beyond the three-dimensional design management zone, whichever is closer to the waste boundary." The DMZ as defined in NR 140 is a three-dimensional boundary surrounding a regulated facility. The boundary extends from the ground surface through all saturated geological strata. The DMZ defined for the Onalaska site extends 250 feet horizontally from the waste boundary as shown in Figure 3. Because the property boundary is generally closer than the DMZ to the waste boundary, the PALs apply at the property boundary with the exception of southwest corner of the property where the PALs apply to the DMZ.

Tables 1 and 2 present a summary of monitoring well concentrations that exceeded U.S. EPA drinking water standards, criteria and guidelines, or Wisconsin groundwater protection standards.

Groundwater samples from the monitoring and extracting wells will be analyzed for the parameters stated in the Groundwater Monitoring Plan.

The Groundwater Monitoring Plan includes sampling of monitoring wells and extraction wells and collection of groundwater elevation data from the monitoring wells and piezometers. In addition, surface water and sediment samples will be collected by WDNR.

Table 1
Summary of Monitoring Well Concentrations Exceeding
Wisconsin Groundwater Protection Standards
Onalaska Landfill Site

Well	Chemical	Detected Concentration (µg/L)[a]	Criteria Exceeded[b]	Criteria Level (µg/L)
MW02S-01	Benzene	5	ES	5.0
			PAL	0.5
	Arsenic	9.5	PAL	5
	Chromium	24.8	PAL	10
MW02M-01	Arsenic	19.4	PAL	5
	Barium	1390	ES	2000
			PAL	400
MW03S-01	1,1-Dichloroethene	15	ES	7.0
			PAL	0.7
	Benzene	13	ES	5
			PAL	0.5
	1,1,1-Trichloroethane	240	ES	200
			PAL	40
	Trichloroethene	11	ES	5
			PAL	0.5
	Toluene	8300	ES	343
			PAL	68.6
	Xylene	2300	ES	620
			PAL	124
	Arsenic	19.4	PAL	5
	Barium	593	ES	2000
MW03M-01	Arsenic	68.4	ES	50
			PAL	5
	Barium	2760	ES	2000
			PAL	400
MW04S-01	Toluene	530	ES	343
			PAL	68.6
	Arsenic	6.9	PAL	5
	Barium	1140	ES	2000
MW05S-01	Benzene	7	ES	5
			PAL	0.5
	Toluene	8300	ES	343
			PAL	68.6
	Xylene	1400	ES	620
			PAL	124
	Arsenic	8	PAL	5
	Barium	347	ES	2000
MW06M-01	Barium	1370	ES	2000
			PAL	400
MW08M-01	Barium	600	PAL	400
W21S-01	Barium	201	PAL	400

Note: The public welfare PAL and ES for iron was exceeded for all wells except MW06M, MW08D, MW08M, MW08S, MW10M, MW12S, and MW13S. The public welfare PAL and ES for manganese exceed in all wells.

[a]Per Remedial Investigation.

[b]Criteria abbreviation:
ES Enforcement Standard
PAL Protective Action Limit

Table 2
Summary of Monitoring Well Concentrations Exceeding
U.S. EPA Drinking Water Standards, Criteria, and Guidelines
Onalaska Site

Well	Chemical	Detected Concentration (µg/L)	Criteria[a] Exceeded	Criteria Level (µg/L)
MW02S-01	Benzene	5	MCL	5
			MCLG	0
			WQC-Risk	0.67
	Ethylbenzene	210	MCL2°	5
MWO2M-01	Barium	1,390	MCL	1,000
MW03S-01	Benzene	13	MCL	5
			MCLG	0
			WQC-Risk	0.67
	1,1-Dichloroethene	15	MCL	7
			MCLG	7
			WQC-Risk	0.7
	1,1,1-Trichloroethane	240	MCL	200
			MCLG	200
			DWLHA	200
	Trichloroethene	11	MCL	5
			MCLG	0
			WQC-Risk	2.8
	Toluene	8,300	MCL	1,000
			MCL2°	--
			MCLG	1,000
			DWLHA	1,000
	Xylene	2,300	DWLHA	--
			MCL2°	20
MW03M-01	Arsenic	68.4	MCL	50
			DWLHA	--
			WQC-Risk	0.0025
	Barium	2,760	MCL	2,000
			DWLHA	--
MW04S-01	Ethylbenzene	42	MCL2°	--
	Toluene	530	MCL2°	--
MW05S-01	Benzene	7	MCL	5
			MCLG	0
			WQC-Risk	5
	Ethylbenzene	160	MCL2°	--
	Toluene	8,300	MCL	1,000
			MCL2°	--
			MCLG	1,000
			DWLHA	1,000
	Xylene	1,400	DWLHA	--
			MCL2°	--
MW06M-01	Barium	1,370	MCL	2,000

Note: The secondary MCL for manganese exceeded in all wells except MW125 and MW135. The secondary MCL for iron exceeded in all wells except MW06M, MW08D, MW08M, MW08S, MW10M, MW12S, MW13S, MW21S

[a]Criteria abbreviations:
MCL - Maximum Contaminant Level
MCL2° - Secondary Maximum Contaminant Level
MCLG - Maximum Contaminant Level Goal
WQC-RISK - Water Quality Criteria at 10^{-6} risk level
DWLHA - Drinking Water Lifetime Healthy Advisory
Prop - Proposed

3.5 Project Objectives

The objectives of the groundwater monitoring program are to:

- Provide data to determine if groundwater contaminant concentrations in the aquifer have been reduced to below the cleanup criteria
- Provide data to verify that a hydraulic gradient is being maintained by the extraction system in order to contain and collect contaminated groundwater
- Provide data to determine if groundwater contaminant concentrations in the aquifer between the landfill and the Black River are being reduced by the extraction system
- Monitor water levels in the wetlands adjacent to the site to make sure that the extraction system is not lowering water levels to such a level as to adversely affect the wetlands

3.5.1 Intended Data Usage

These data shall be used to evaluate the effectiveness of the remedial action design and determine when groundwater extraction may cease. The data will be used to:

- Determine the change in extent or movement of the groundwater contaminant plume
- Monitor the safety of field sampling personnel and to select proper personal protective equipment by screening VOC concentrations with an HNu or organic vapor analyzer (OVA)
- Support decisions related to operation of the groundwater extraction system (such as extraction rate per well)

3.5.2 Data Quality Objectives

Data quality objectives (DQOs) define and specify the quality of data required for the intended use of the data. The degree of certainty of a data set with respect to precision, accuracy, representativeness, completeness, and comparability is an indication of the data quality.

There are five levels of Analytical Date Quality, and they are defined as follows:

1. Level I—Field Screening. The objective of this level of analysis is to generate data to be used in refining sampling plans and determining gross extent of contamination at the site. This type of data also provides real time monitoring for health and safety.

2. Level II—Field Analysis. The objective of this level of analysis is to provide real-time data for ongoing field activities. This level of analysis also provides preliminary data used to decide what additional laboratory analyses should be performed. Analyses include the use of an onsite close support laboratory.

3. Level III—Laboratory Analysis. This level of analysis is designed to provide laboratory analyses using standard EPA-approved procedures. This level provides data for site characterization, environmental monitoring, and confirmation of field data; and to support engineering studies.

4. Level IV—This level of analysis provides for the highest level of data quality with full analytical, QC, and validation procedures in accordance with EPA protocols. The data is used for risk assessment, confirmation of field analysis data, and to obtain highly documented data.

5. Level V—Nonstandard Methods, SAS. The objective of this level of analysis is to provide data not obtained through standard avenues of analytical support. This usually involves modification of existing methods or method development. The level of quality control is usually similar to that of Level IV data.

Levels I and V analytical data will be generated during groundwater monitoring at the Onalaska Municipal Landfill. DQO Level I data to be generated include field measurements of groundwater pH, temperature, and specific conductance and HNu/OVA readings. The laboratory analyses requested include the Level V chemical analyses. Level V data will be needed to provide the rigorous QA/QC required to track and monitor the groundwater contaminant plume, to determine if any remedial action is required because of risks to public health, and because nonstandard procedures are required to meet the lower detection limits of VOC and inorganic analyses.

Sample matrices and analytical parameters for each media are presented in Table 3. The number of samples in this table include QC samples. Data quality objectives for all off-site laboratory analyses are Level V.

3.6 Groundwater Monitoring Network

The groundwater monitoring network was designed to provide groundwater quality data for the site and adjacent area and is comprised of wells constructed during the RA and during the RI. The groundwater monitoring network consists of six new water table piezometers, one new monitoring well, six existing monitoring wells, and five new extraction wells. Additional monitoring wells at the landfill periphery and in the center of the landfill may be included in the groundwater network as the plume is reduced in size or as warranted. The selected monitoring wells are primarily located hydraulically downgradient to the south, southeast, and west of the landfill site. One monitoring well is located upgradient of the landfill to provide background groundwater quality. These wells will permit evaluation of the hydraulic gradient control and groundwater quality in the aquifer. Well and piezometer locations are shown in Figure 3.

3.6.1 Piezometers

Six piezometers were installed for the purposes of determining the impact of groundwater pumping on the wetlands area to the south of the site, and to ensure that the plume of contaminated groundwater is being captured by the system of extraction wells. Potential adverse impacts on the wetlands will be evaluated using pre- and post-pumping groundwater elevation data collected at the three piezometers (PZ-02 (new), PZ-03, and PZ-04) located in the wetlands area. Plume capture will be determined by the horizontal hydraulic gradients, as defined by the water table elevations in the piezometers and in the monitoring wells, such as MW-14S, which is located near the edge of the plume. Piezometer PZ-01 has been installed to measure the inward gradient along the western boundary of the plume. Piezometers PZ-05 and PZ-06 (new) will be used to measure the inward gradient along the eastern boundary of the plume. The rate of groundwater pumpage can be varied to provide the groundwater gradients necessary to capture the plume.

3.6.2 Monitoring Wells

The monitoring wells (MW-1S, MW-6S, MW-6M, MW-8S, MW-8M, MW-12S and MW-14S) shall be used to monitor:

Table 3
Sampling and Analysis Summary

Parameter	Matrix	Field Samples				Lab QC		Matrix	Field Samples				Lab QC		No. of Samples per Quarter
		FS	TB	FB	FR	MS	MSD		FS	TB	FB	FR	MS	MSD	
Benzene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
Toluene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
Xylene(s), Total	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
Ethylbenzene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
Trichloroethene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
1,1-Dichloroethane	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
1,1,1-Trichloroethane	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
1,1-Dichloroethene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
1,1,2,2-Tetrachloroethylene	Groundwater	10	1	1	1	2	2	Drinking Water	2	1	0	0	1	1	22
Arsenic	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	1	1	16
Barium	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Lead	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Iron	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Manganese	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Chloride	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Total Organic Carbon (TOC)	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Total Dissolved Solids (TDS)	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Oil and Grease	Groundwater	10	0	1	1	1	1	Drinking Water	2	0	0	0	0	0	16
Alkalinity (as $CaCO_3$)	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Hardness (as $CaCO_3$)	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Chemical Oxygen Demand (COD)	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Color	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Turbidity	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14
Odor	Groundwater	10	0	1	1	0	0	Drinking Water	2	0	0	0	0	0	14

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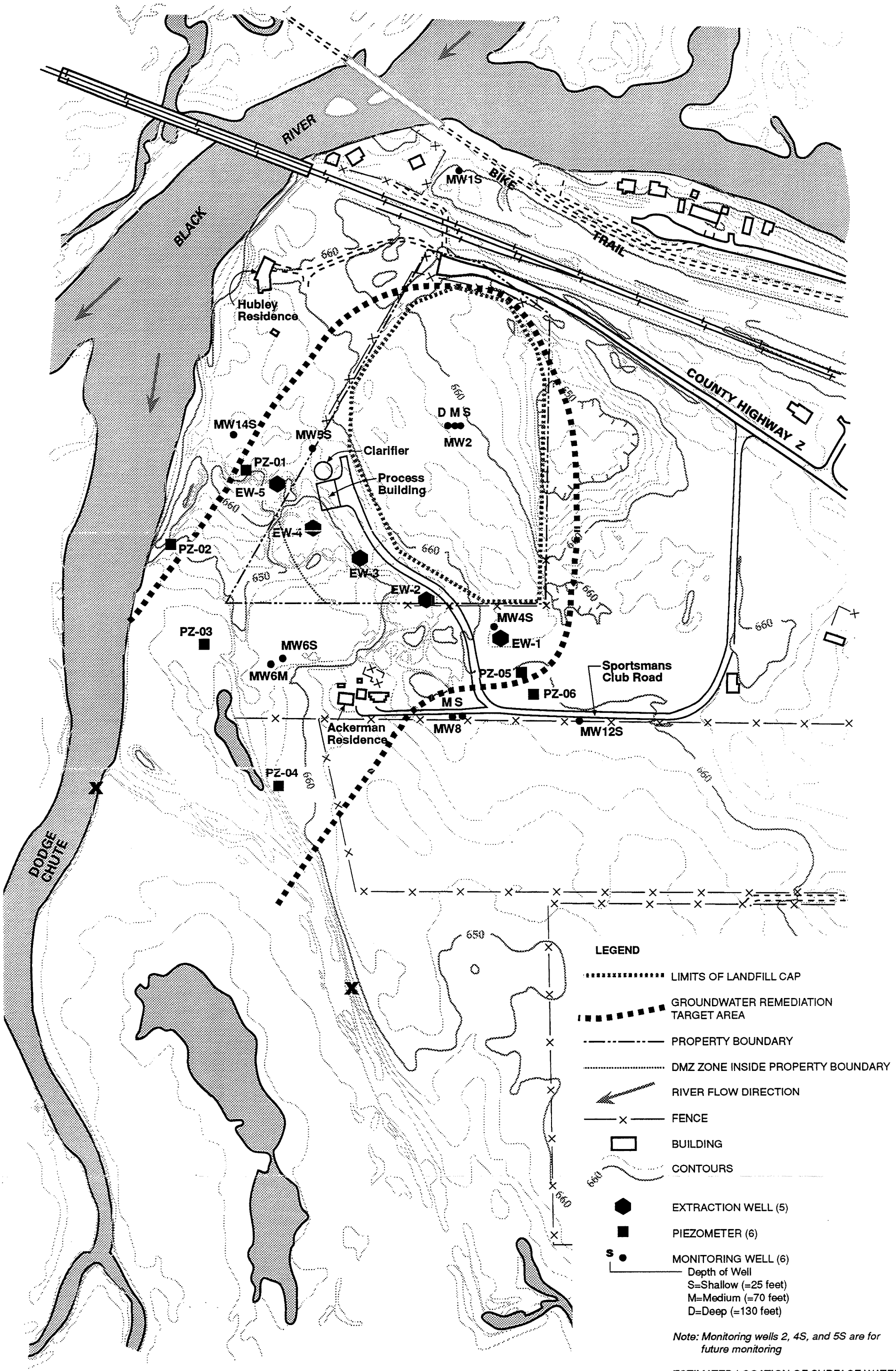

FIGURE 3
MONITORING WELL, EXTRACTION WELL, AND PIEZOMETER NETWORK
ONALASKA
QAPP

- If contaminated groundwater has been captured successfully (contaminants of concern are below action levels at point of compliance)

- Groundwater quality changes downgradient of the collection system capture zone (i.e., how quickly concentrations of contaminants of concern decrease after the extraction system is functioning)

- Hydraulic gradient control (contaminated groundwater plume is moving toward the extraction wells)

Groundwater quality downgradient of the landfill and extraction well network will be monitored in shallow wells MW-6S (new) and MW-8S and in intermediate wells MW-6M and MW-8M. These well locations were selected to place wells outside of the capture zone. MW-12S and MW-14S are located on the periphery of the capture zone and will be used to monitor groundwater quality and hydraulic gradient control east and west of the extraction well network. MW-1S will be used to monitor background groundwater quality upgradient of the landfill.

Monitoring using only shallow and intermediate wells is proposed. The majority of the VOCs detected during the Remedial Investigation were found in shallow monitoring wells (MW-5S and former wells MW-3S and B4S). The vertical extent of BTEX and chlorinated compounds contamination is mostly confined to the upper 10 to 20 feet of the aquifer. Ethylbenzene, 1,1-DCA and chloroethane were detected, however, at depths up to 50 to 60 feet below the water table. The vertical extent of semivolatile organic compounds (SVOCs) contamination is also mostly confined to the upper 10 to 20 feet of the aquifer. There were no SVOCs detected in any of the deep monitoring wells.

To verify that groundwater contaminants are not migrating vertically to lower depths, MW-2D will be sampled periodically for VOCs.

The expected reduction in contaminant concentrations within the plume capture zone will be monitored by sampling the five extraction wells. If the contaminant concentrations in these wells decline to the groundwater cleanup standards, wells along the landfill waste boundary would require monitoring. The alternative wells to be monitored are shown in Figure 3 and include MW-4S and MW-5S. These wells represent the compliance point defined in the ROD (the landfill waste boundary) for MCLs and non-zero MCLGs. The compliance point for the PALs (any point beyond the property boundary or DMZ) are represented by monitoring wells MW-4S, MW-6S, MW-6M, MW-8S, MW-8M, MW-12S, and MW-14S and extraction wells EW-1, EW-4, and EW-5. The groundwater standards and compliance points are discussed in more detail later in this document.

3.6.3 Extraction Wells

A series of five extraction wells have been installed in locations that capture the contaminant plume prior to offsite groundwater discharge. The extraction well network has been designed to extract approximately 800 gallons per minute (gpm) of contaminated groundwater for treatment. The rate of pumpage for each well can be varied during operation, based on results of monitoring wells and piezometers. Groundwater from the extraction wells will be monitored to assess the degree that contaminant cleanup is occurring.

3.6.4 Surface Water and Sediments

The groundwater beneath the site generally flows in a south-southwesterly direction toward the wetlands bordering the Black River. Although no site-derived contamination was detected in the surface water and sediment samples collected during the remedial investigation, surface water and sediments will be sampled annually during the remedial action to monitor for potential offsite contaminant migration. Surface water and sediment grab samples will be collected by Wisconsin DNR from the wetland area and Dodge Chute.

3.6.5 Background / Baseline Monitoring

The monitoring program began with the collection and analysis of four discrete samples from all 17 wells in the monitoring program to develop baseline concentrations. The samples were analyzed for the parameters listed in Table 3. The analytical results were compared to background concentrations.

3.6.6 Sampling

The Groundwater Monitoring Plan includes quarterly sampling events from monitoring wells and extraction wells, and collection of quarterly groundwater elevation data from the piezometers and monitoring wells. In addition, surface water and sediment samples will be collected by the WDNR from two or more locations.

The sampling schedule will be evaluated annually and adjusted as needed depending on the analytical results and the operation of the extraction and treatment system. The frequency of sampling will be re-evaluated annually. The sampling plan is described in detail in the Groundwater Monitoring Plan.

The primary purpose of the quarterly sampling is to continue to evaluate the groundwater extraction and treatment system for reliable operation and monitor the reduction of

contaminant concentrations in the aquifer. The quarterly sampling will also identify any seasonal fluctuations in groundwater quality. Groundwater samples from the seven monitoring wells, extraction wells number EW-1, EW-3, and EW-5, and two residential wells will be collected at the end of March, June, September, and December. The residential wells are at the Hubley and Ackerman homes. Extraction wells number EW-2 and EW-4 will be sampled biannually (during the months of June and December).

After 5 years of operation of the groundwater extraction and treatment system, the groundwater quality will be evaluated to determine if the groundwater standards have been met.

3.7 Project Schedule

Groundwater monitoring samples and groundwater elevation measurements will be taken quarterly, unless unanticipated problems indicate that monthly sampling is warranted.

The first quarterly samples were taken in March 1995. The final quarterly sampling under the work assignment is scheduled for the end of March 1997. This provides nine rounds of quarterly sampling.

The groundwater quality will be evaluated at the end of the fifth year to determine if the groundwater standards have been met. The ROD estimates that 95 percent of the contaminants will be removed from the groundwater plume within the 5-year time frame. In addition to the evaluation of results of quarterly samples collected over the 5-year period, a full priority pollutant scan will be performed to determine if additional parameters should be added to the compounds listed in Table 2. If the groundwater goals (or WACLs, if established) have not been met, sampling and remediation will continue until the cleanup goals are achieved. The frequency of sampling will be evaluated based on the trends observed in the first 5 years. If an applicable and appropriate requirement (ARAR) waiver is established, the groundwater goals and the need or frequency of further sampling will be addressed as part of the waiver process.

The need for elevation data from the other existing monitoring wells will be evaluated after the first year. Depending on the analytical results from the quarterly sampling and the absence of operational problems, the sampling schedule may be modified further.

Section 4
Project Organization and Responsibility

At the direction of the Region 5 Remedial Project Manager (RPM), with final authority by the Region 5 Regional Project Officer (RPO), CH2M HILL has overall responsibility for all phases of the Groundwater Monitoring Plan, including overall management and QA/QC for all activities within their control. CH2M HILL will perform the field sample collection and field screening measurements, and will prepare monitoring reports. The project organization chart is included as Figure 4.

4.1 Management Responsibilities

Project management will be conducted through CH2M HILL's regional office in Milwaukee. Contact will be maintained with the EPA's RPM during all phases of the project.

Monthly reports will be submitted to keep the EPA apprised of the technical, financial, and schedule status of the project. Other CH2M HILL responsibilities include controlling budgets and schedules; selecting, coordinating, and scheduling staff and subcontractors for task assignments; and maintaining project QA/QC programs.

Operational responsibilities involving execution and direct management of the technical and administrative aspects of this project have been assigned as follows:

- Remedial Project Manager (RPM)
  Kevin Adler (U.S. EPA Region 5)

- Quality Assurance Manager (QAM)
  Willie Harris (U.S. Region 5)

- State Project Manager (SPM)
  Larry Lester (WDNR)

- Site Manager (SM)
  Jim Fisher (CH2M HILL)

- Program Manager (PM)
  Alpheus Sloan (CH2M HILL)

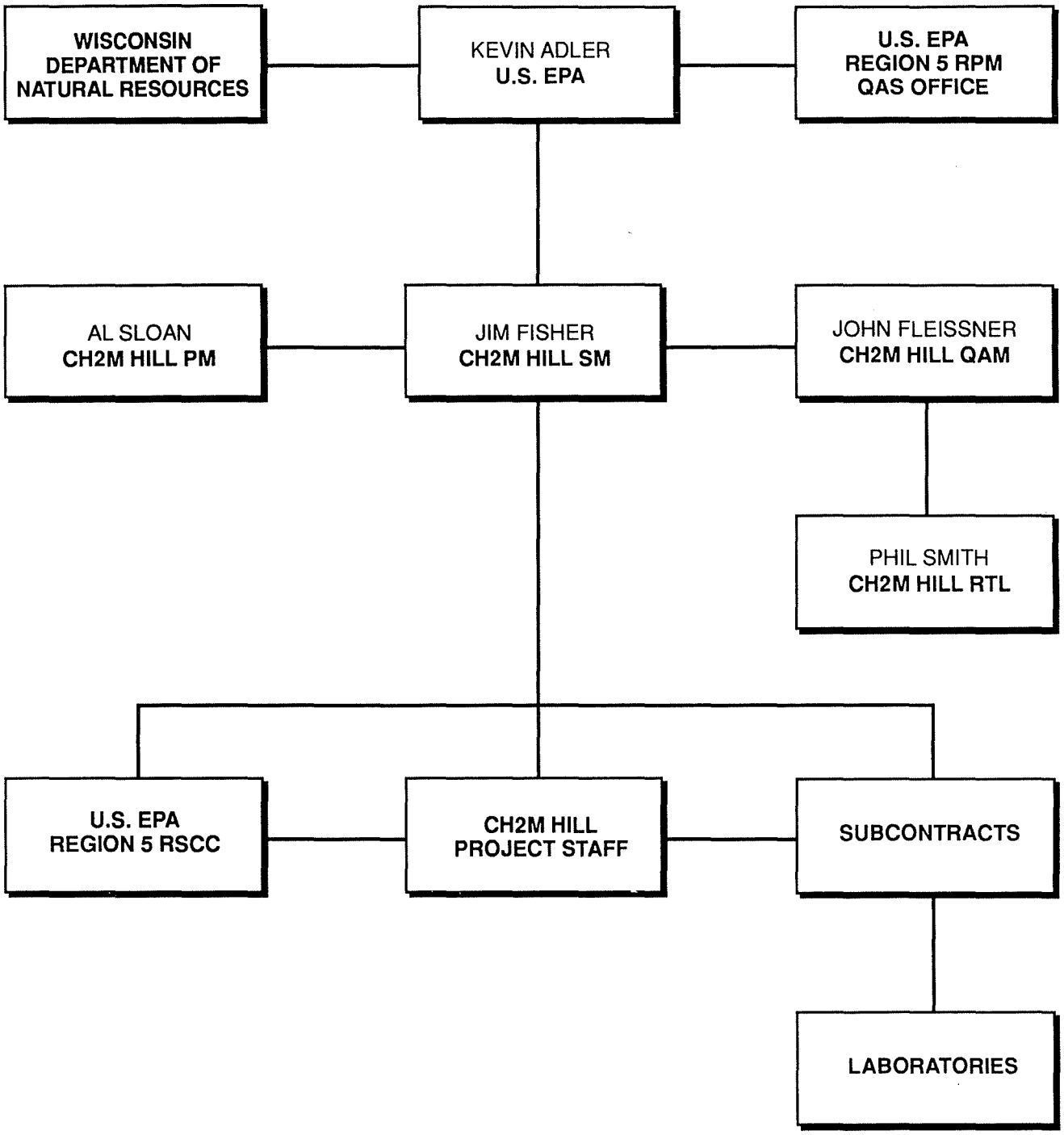

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FIGURE 4
PROJECT ORGANIZATION
ONALASKA
GWMP and QAPP

The responsibilities of the aforementioned personnel are described below.

4.1.1 U.S. EPA Region 5 Remedial Project Manager

The RPM has the responsibility for the implementation of the Remediation Plan.

4.1.2 State Project Manager

The SPM has responsibility for ensuring that the Remedial implementation meets WDNR regulations and guidelines.

4.1.3 CH2M HILL Program Manager

The PM has overall responsibility for seeing that the project meets EPA and state objectives and CH2M HILL's quality standards. In addition, he is responsible for technical quality control and project oversight, and will provide the site manager with access to corporate management.

4.1.4 CH2M HILL Site Manager

The SM is responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The SM's primary function is to see that technical, financial, and scheduling objectives are achieved. The SM will report directly to the RPM and SPM and will provide the major point of contact and control for matters concerning the project. The SM will:

- Define project objectives and develop a detailed work plan schedule
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task
- Acquire and apply technical and corporate resources as needed to maintain performance within budget and schedule constraints
- Orient all field leaders and support staff concerning the project's special considerations
- Monitor and direct the field leaders
- Develop and meet ongoing project and/or task staffing requirements, and develop mechanisms to review and evaluate each task product

- Review the work performed on each task to ensure its quality, responsiveness, and timeliness
- Review and analyze overall task performance with respect to planned requirements and authorizations
- Approve all external reports (deliverables) before their submission to EPA Region 5 and WDNR
- Be responsible for preparation and quality of interim and final reports
- Represent the project team at meetings and public hearings

4.1.5. EPA Region 5 Quality Assurance Manager

EPA Region 5 Quality Assurance officer has the responsibility to review and approve all QAPPs, and to validate data of the SAS Data and Results.

4.2 Quality Assurance Organization

Responsibilities for management and execution of QA aspects of this project are assigned as follows:

Tasks	Responsible Organization/Personnel
• Final review and approval of QAPjP	Kevin Adler, U.S. EPA Region 5 RPM Willie Harris, U.S. EPA Region 5 QA Manager (QAM)
• QA program for analytical laboratory performance and systems audits for laboratory SAS	Dan MacGregor, CH2M HILL
• QA review and approval of reports, plans and procedures, and field activities; and identifying and controlling nonconformance for corrective action while providing technical assistance to project staff. The QAD will remain independent of direct job involvement and day-to-day operations, and will have direct access to corporate executive staff as necessary to resolve any QA dispute.	John Fleissner, CH2M HILL, Quality Assurance Director (QAD)
• Evidence audits of field records	John Fleissner, CH2M HILL, QAD NEIC Evidence Audit Team (Techlaw, Inc.)

• Approval of QA programs and laboratory SAS procedures	U.S. EPA Region 5 QAM U.S. EPA Region 5 CRL

4.3 Field Operations

Responsibilities for field operations tasks including both management and execution of the field work, are assigned as follows:

Tasks	Responsible Organization/Personnel
• Sample Collections	Jim Fisher, CH2M HILL, SM Kevin Adler, U.S. EPA Region 5 RPM
• Field Measurements	Jim Fisher, CH2M HILL, SM Kevin Adler, U.S. EPA Region 5 RPM
• External Field Audits	U.S. EPA Region 5 CRL
• Internal Field Audits	Jim Fisher, CH2M HILL, SM

The responsibilities of the field team leader and field team members are described below.

4.3.1 Field Team Leaders

The field team leader is responsible for leading and coordinating the day-to-day activities of the various resource specialists under his supervision. The field team leader is a professional with extensive environmental experience who will report directly to the SM. Specific field team leader responsibilities include:

- Day-to-day coordination with the SM on field activities
- Coordination and management of field staff including sampling and drilling
- Coordination and oversight of technical efforts of subcontractors assisting the field team
- Review all field activities to ensure proper custody procedures are followed

- Implementation of QC for technical data provided by the field staff including field measurement data
- Identification of problems at the field team level, discussion of resolutions with the site manager, and communication between field team and upper management
- Adherence to work schedules provided by the SM
- Participation in the preparation of the final report

4.3.2 Field Team Members

The field team members for this project will be drawn from CH2M HILL's pool of resources. The technical team staff will gather and analyze data and prepare various task reports and support materials. All of the designated technical team members are experienced professionals who possess the degree of specialization and technical competence required to effectively and efficiently perform the required work.

4.4 Laboratories

Organizations and personnel responsible for requesting services, administration of SAS laboratories, and QA/QC tasks associated with the laboratories are assigned as follows:

Laboratory Deliverables	Responsible Organization/Personnel
• Initiation of request	Dave Shekoski, CH2M HILL*
• Preparation of SAS	Daniel MacGregor, CH2M HILL*
• Contact for laboratory deliverables	Daniel MacGregor, CH2M HILL*
• Review and approval of SAS	U.S. EPA Region 5 CRL LSSS U.S. EPA Region 5 QAM Kevin Adler, U.S. EPA, Region 5 RPM
• Data validation of laboratory deliverables	U.S. EPA Region 5 CRL LSSS

- Data assessment of laboratory deliverables — Daniel MacGregor, CH2M HILL*

* Contractor's personnel for these tasks may change, subject to staff availability. If a change is made, the EPA RPM will be notified.

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Section 5
Quality Assurance Objectives for Measurement Data

The overall QA objectives are to develop and implement procedures for field sampling, chain of custody, laboratory analysis, and reporting that will provide the quality of data required for monitoring and tracking the groundwater contaminants. Specific procedures to be used for sampling, chain-of-custody, calibration of field instruments, laboratory analysis, reporting, internal quality control, audits, preventive maintenance, and corrective actions are described in other sections of this QAPjP and the Groundwater Monitoring Plan. This section addresses the objectives of data precision, accuracy, completeness, representativeness, and comparability.

Precision measures the reproducibility of measurements under a given set of conditions. It is a measure of the variability of a group of measurements compared to an average value. Accuracy measures the bias in a measurement system. Possible sources of error are the sampling process, field contamination, preservation, handling, sample matrix, sample preparation, and analysis techniques. Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or environmental conditions. Completeness is defined as the percentage of measurements made that are judged to be valid measurements. Comparability is a qualitative parameter expressing the confidence with which one data set can be compared to another.

5.1 Level of Quality Control Effort

Field blank, trip blank, duplicate, and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling program. Field and trip blanks, consisting of distilled water, will be submitted to the analytical laboratories to provide the means to assess the quality of the data resulting from the field sampling program. Field blank samples are analyzed to check for procedural contamination at the site which may cause sample contamination. Trip blanks are used to assess the potential for contamination of samples due to contaminant migration during sample shipment and storage. Duplicate samples are analyzed to check for sampling and analytical reproducibility. Matrix spikes (MSs) provide information about the effect of the sample matrix on the extraction/digestion and measurement methodology. Whereas, inorganic analyses require one MS sample, volatile organic matrix spikes are performed in duplicate and are hereinafter referred to as MS/MSD samples.

The general level of the QC effort will be collecting one field duplicate and one field blank for every 10 or fewer investigative samples. One volatile organic analysis (VOA) trip blank consisting of distilled deionized ultra pure water will be included along with each shipment of aqueous VOA samples.

Aqueous MS/MSD samples must be collected at triple the volume for VOCs and aqueous MS samples must be collected at double the volume for metals, oil and grease, and TOC analyses. One MS and MS/MSD sample, as appropriate, will be collected/designated for every 20 or fewer investigative samples per sample matrix (i.e., groundwater, residential water). Sampling procedures are specified in the Groundwater Monitoring Plan.

The aqueous samples will be sent to a subcontracted analytical laboratory. The level of laboratory QC effort for SAS analyses is outlined individually in each SAS request form contained in Appendix A.

The QC effort for the field measurement of pH consists of pre-measurement calibration and a post-measurement verification using two standard reference solutions. This procedure will be performed daily. The QC effort for field conductivity measurements will include daily calibration of the instrument using standard solutions of known conductivity. The QC effort for temperature will consist of checking the thermometer on the conductivity meter against a certified thermometer. These procedures are described in more detail in the field equipment measurement SOPs (Appendix B).

5.1.1 Accuracy, Precision, and Sensitivity of Analysis

The fundamental QA objective with respect to accuracy, precision, and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols.

The accuracy, precision, and sensitivity requirements for SAS for the laboratory are specified in each individual SAS request form contained in Appendix A. The standard operating procedures (SOPs) for the field equipment to measure pH, conductivity, and temperature are outlined in Appendix B. QA requirements for field screening analyses are also included in SOPs found in Appendix B.

5.1.2 Completeness, Representativeness, and Comparability

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that the field measurement and laboratories will provide data meeting QC acceptance criteria for 95 percent or more for all samples tested. Following

completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{completeness (\%)} = \frac{\text{(number of valid data)}}{\text{(number of sample collected for each parameter analyzed for)}} \times 100$$

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative parameter which is dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network was designed to provide data representative of site conditions. During design and development of the sampling network, consideration was given to past waste disposal practices, existing analytical data, physical setting and processes, and constraints inherent to the Superfund program. Representativeness will be satisfied by seeing that the Groundwater Monitoring Plan is followed, proper sampling techniques are used, proper analytical procedures are followed, and holding times of the samples are not exceeded in the laboratory. Representativeness will be assessed by analyzing of field duplicated samples.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the QAPjP, are expected to provide comparable data. These new analytical data, however, may not be directly comparable to existing data because of differences in procedures and QA objectives.

5.2 Method Detection Limits

Contract-required detection limits for the Target Parameters are provided as part of the SASs in Appendix A.

Section 6
Sampling Procedures

Detailed sampling procedures are provided in the Groundwater Monitoring Plan. Table 4 of Section 3 provides a summary of sample matrices and the parameters to be sampled for.

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Section 7
Sample Custody Procedures

7.1 Introduction

It is EPA and Region 5's policy to follow the EPA Region 5 sample custody or chain-of-custody protocols as described in *NEIC Policies and Procedures*, EPA-330/9-78-001-R, revised June 1985. This custody is in three parts: field custody procedures, laboratory custody procedures, and final evidence files.

A sample or evidence file is under your custody if the documents:

- Are in your possession
- Are in your view after being in your possession
- Were in your possession and you placed them in a secured location
- Are in a designated secure area

7.2 Field Custody Procedures

The sample packaging and shipment procedures summarized below will insure that the samples will arrive at the laboratory with the chain-of-custody intact. The protocol for sample numbering is included in the Groundwater Monitoring Plan.

7.2.1 Field Procedures

(a) The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As FEW people as possible should handle the samples.

(b) Each sample bottle will have an EPA Region 5 sample tag attached which will contain the sample number, the case or SAS number, and station location.

(c) Sample tags are to be completed for each sample using waterproof ink.

7.2.2 Sample Documentation Procedures

Sample packaging and shipping procedures are based on U.S. EPA Specifications and Department of Transportation (DOT) regulations (40 CFR). The procedures vary according to sample concentration and matrix and are designed to provide optimum protection of samples and the public.

All samples will be shipped within 24 hours of collection. Shipping containers must be insulated, durable, and watertight. Sample bottles are to be cushioned in the shipping container with packing material such as vermiculite or bubble pack. To prevent contamination of samples, all containers regardless of size and type must be placed inside sealed plastic bags before being packed. Preformed poly-foam cooler liners may be used for shipment of low-concentration samples only. Following shipment, chain-of-custody records and air bills must be given to the CH2M HILL sample documentation coordinator. Field packing and shipping procedures are as follows:

1. Assemble a list of the samples to be packaged and shipped on the same day by their respective analytes and the names of the assigned laboratories.

2. Enter the SAS number, tag number, matrix, sample numbers, laboratory, date sampled, and date shipped for each sample on the sample I.D. matrix.

   Note: If portions of a given sample are to be shipped to different laboratories (e.g., for organic and inorganic analysis), two entry lines will be required for that sample number to accommodate the chain-of-custody record, airbill, and traffic report numbers corresponding to each portion of the sample.

3. Obtain the QC lot numbers of the prelabeled containers for each sample and enter them on the sample I.D. matrix.

4. Determine the number of shipping containers (coolers) required for the day's shipment. This will depend on the number of samples to be shipped, the number of containers per sample, the number of sample containers that will fit in each cooler, and the number of laboratories to be used.

   Note: A group of containers for a single sample should not be split between coolers unless the portions of the sample are to be sent to more than one laboratory for different types of analysis.

5. Complete an airbill for each laboratory address.

   Note: Several coolers may be shipped to the same address under one airbill.

   Shipment of medium and high concentration samples requires the use of a special airbill, including a shipper's certification for restricted articles.

6. Enter the airbill numbers on the sample I.D. matrix.

7. Assign a chain-of-custody record to each cooler and determine which sample containers will be shipped in each.

   Note: More than one chain-of-custody record may be needed to accommodate the number of samples to be shipped in one cooler.

8. Assign sample and tag numbers to each sample by entering these numbers on the matrix.

   Reminder: Portions of samples for organic and inorganic analysis will usually be sent to separate laboratories. Use one line on the sample I.D. matrix for the organic portion and another line for the inorganic portion.

9. Determine the number of traffic labels that will be needed for organics and inorganics.

10. Assign traffic report numbers from the labels to each sample and enter the numbers on the sample I.D. matrix.

11. Record the tag numbers on each sample container and enter the numbers on the sample I.D. matrix.

12. Complete separate traffic reports for each laboratory each day (or SAS packing lists) based on the information provided on the matrix.

13. Complete sample tags according to the information provided on the sample I.D. matrix and the parameters of analysis. Place tags in groups by sample number.

14. Complete the chain-of-custody records based on the information provided on the sample I.D. matrix.

15. Assign two EPA custody seals to each cooler. Enter the serial numbers of the seals in the "REMARKS" section of each chain-of-custody form (if the new combined chain-of-custody/traffic report forms are used, enter the serial numbers in the appropriate box) and temporarily clip seals to the form.

16. Group all the paperwork associated with each cooler in a separate clip.

17. Obtain full signatures of the Sample Team Leader (STL) and initials of significant field team members (including yourself) on the sample tags and at the top of the chain-of-custody forms.

18. Prepare samples for shipment.

All original data recorded on traffic report forms, sample identification tags, chain-of-custody records, and receipt for sample forms will be written with waterproof ink.

Step-by-step instructions for completing each form, plus example forms, are found in Appendix C.

7.2.3 Transfer of Custody Procedures

Transfer of custody procedures are as follows:

1. Samples must be accompanied by a properly completed chain-of-custody form. The sample numbers and locations will be listed on the chain-of-custody form. The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to a mobile laboratory, to the permanent laboratory, or to or from a secure storage area.

2. Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be locked and secured with strapping tape and EPA custody seals for shipment to the laboratory. The preferred procedure includes use of a custody seal attached to the front right and back left of the cooler. The custody seals

are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.

3. Whenever samples are split with a source or government agency, a separate sample receipt is prepared for those samples and marked to indicate with whom the samples are being split. The person relinquishing the samples to the facility or agency should request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, this is noted in the ''received by'' space.

4. All shipments will be accompanied by the chain-of-custody record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler for return to the sampling office.

5. If the samples are sent by common carrier, a bill of lading should be used. Receipts of bills of lading will be retained as part of the permanent documentation. If sent by mail, the package will be registered with return receipt requested. Commercial carriers are not required to sign the custody form as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

7.2.4 Field Logbook

All information pertinent to a field survey or sampling effort will be recorded in a bound logbook or equivalent standard form. Each page or form will be consecutively numbered and will be at least 4-1/2 inches by 7 inches in size. All entries will be made in indelible ink or, if weather conditions dictate, in hard lead pencil, and all corrections will consist of line-out deletions that are initialed and dated. Each logbook will be identified by the project-specific document number.

The title page of each logbook will contain the following:

- Person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- End date

At a minimum, the logbook will contain the following:

- Purpose of sampling
- Location, description, and log of photographs of the sampling point
- Weather conditions
- Identification of sampling crew members
- Type of sample (e.g., groundwater, soil, sludge, wastewater)
- Number of samples taken
- Sampling methodology, including distinction between grab and composite samples
- Modifications from Field Sampling Plan
- Sample preservation
- Date and time of collection
- Sample identification designation and tag numbers
- Signature and date by the personnel responsible for observations
- Decontamination procedures

Sampling situations vary widely. No general rules can specify the extent of information that must be entered in a logbook or standardized form. However, records will contain sufficient information so that someone can reconstruct the sampling activity without relying on the sample collector's memory. The logbook and standardized forms will be kept under strict chain of custody.

7.2.5 Corrections to Documentation

No accountable serialized documents are to be destroyed or thrown away, even if they are illegible or contain inaccuracies that require a replacement document. If an error is made on an accountable document assigned to one individual, that individual shall make corrections by making a single line through the error and entering the correct

information. The erroneous information should not be obliterated. Any subsequent error discovered on an accountable document should be corrected by the person who made the entry. All subsequent corrections must be initialed and dated.

7.2.6 Distribution of Completed Documents

Final disposition of the completed documents is as follows:

- Shipped with samples:
  - Chain-of-custody form, original (if new combined chain-of-custody traffic reports are used, two copies will be required)
  - Traffic report forms, two copies
  - Packing list, two copies
  - Sample tags
- Retained by project manager:
  - Sample identification matrix
  - Field logbooks (at completion of project)
- Sent to CH2M HILL documentation coordinator:
  - Chain-of-custody form, two copies
  - Traffic report forms, original and one copy
  - Packing list, original and one copy

7.2.7 Site Manager's Responsibility

The site manager will review all field activities to determine whether proper custody procedures were followed during the fieldwork and decide if additional samples are required. He or she should notify the U.S. EPA Remedial Project Manager of a breach or irregularity in chain-of-custody procedures.

7.3 Laboratory Custody Procedures for The Contract Laboratory

The chain-of-custody procedures for organic and inorganic compound SAS analyses are described in the Contracted Laboratories Quality Assurance Plan.

Minimum laboratory custody procedures shall consist of the following:

- Designation of a sample custodian
- Correct completion by the custodian of the chain-of-custody record, sample tag, and laboratory request sheet (including documentation of sample condition upon receipt)
- Laboratory sample tracking and documentation procedures
- Secure sample storage (of the appropriate environment—refrigerated, dry, etc.)
- Proper data logging and documentation procedures including custody of all original laboratory records

7.4 Final Evidence Files Custody Procedures

The final evidence files are maintained by CH2M HILL. This includes all analytical deliverables, data validation reports, laboratory telephone conversation records, and purge file records including laboratory chain-of-custody and sample tags. These files are maintained under document control in a secure area.

The contractor maintains the files along with all relevant records, reports, logs, field notebooks with field measurements and HNu/OVA screenings, pictures, subcontractor reports, and LSSS data reviews in a secured, limited access area and under custody of the contractor's site manager.

Section 8
Calibration Procedures and Frequency

This section describes procedures for maintaining the accuracy of all the instruments and measuring equipment which are used for conducting field tests and laboratory analyses. These instruments and equipment should be calibrated before each use or scheduled, periodic basis.

8.1 Special Analytical Services

For laboratory SAS analysis, the calibration procedures and frequency are presented in the SAS request forms in Appendix A.

8.2 Field Instruments

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications.

Equipment to be used doing the field sampling will be examined to certify that it is operating condition. This includes checking the manufacturing's operating manual and the instruction for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notation on any prior equipment problem are not overlooked, and all necessary repairs to equipment have been carried out.

Calibration procedures and frequency for field instruments including the OVA and HNu; the pH, specific conductivity, and temperature meters are found in Appendix B.

Section 9
Analytical Procedures

All samples collected during field sampling will be analyzed by a subcontract analytical laboratory.

9.1 Special Analytical Services

For laboratory SAS analyses, the analytical procedures are presented in the SAS request forms in Appendix A. Also specified in the SAS requests are calibration procedures, frequency of calibration, and the internal quality control checks required for each analysis.

9.2 Field Instruments

Analytical procedures for field instruments including the OVA and HNu, pH, specific conductivity, and temperature meters are found in Appendix B.

Section 10
Internal Quality Control Checks

10.1 Special Analytical Services

For laboratory SAS analyses, the analytical QC procedures are presented in the SAS request forms in Appendix A. Section 5 of this QAPjP provides examples of QC checks used for laboratory measurement and analysis.

10.2 Field Instruments

Field analyses will be performed onsite and will not involve samples that are collected and retained. The primary QA/QC objective is to obtain reproducible measurements to a degree of accuracy that is consistent with that capable of the analytical methodologies and sufficient to meet the intended use of the data. Field QC procedures will be limited to checking the reproducibility of measurements, by taking multiple readings and by verifying accuracy and precision through instrument calibration and calibration checks. The field measurement SOPs in Appendix B describe the QC checks for the field measurements.

Section 11
Data Reduction, Validation, and Reporting

11.1 Data Reduction

11.1.1 Laboratory Analysis

All samples collected at the Onalaska Landfill will be sent to a subcontract analytical laboratory. Data reduction, evaluation, and reporting for samples analyzed by this laboratory will be performed according to specifications outlined in the SASs.

11.1.2 Field Measurements

Raw data from field measurements and sample collection activities will be recorded in the field laboratory notebook. The method of reduction will also be documented in the laboratory notebook.

11.2 Data Validation

11.2.1 Laboratory Analysis

Validation will be accomplished by comparing the contents of the data packages and QA/QC results to the requirements described in the SAS methods. Raw data such as: GC/MS Total Ion Current (TIC) chromatograms, GC/MS mass spectra, FAA data reports, and conventional analyses data station printouts will be examined to ensure that reported results are accurate. The U.S. EPA Region 5 will be responsible for data validation. The Laboratory Data Validation Functional Guidelines (referenced below) will be used as guidelines to validate the SAS data:

- *Laboratory Data Validation Functional Guidelines for Evaluating Organic Analyses*—U.S. EPA, February 1988.

- *Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses*—U.S. EPA, July 1988.

Data validated by the U.S. EPA will be assessed by CH2M HILL to determine if project objectives and intended data usage requirements were met. If project objectives or data

usage requirements are not being met, the program will be modified in such a manner that project requirements are fulfilled.

11.2.2 Field Measurements

Data validation of field measurements will be the responsibility of the Field Team Leader. The field measurement data validation will consist of: the field notebooks being checked to verify that the QC procedures specified in the field measurement SOP in Appendix B were performed, and that the QC procedures were performed correctly and that all calculations are correct. The computer spreadsheet data and results will be proofed against the field notebooks to ensure no transcription errors occurred.

11.3 Data Reporting

11.3.1 Laboratory Analysis

The analytical laboratory will prepare and submit analytical reports to CH2M HILL in a format as described in the SAS. The Report will include the following (as a minimum):

1. Case narrative including statement of samples received, description of any deviations from SAS procedures, explanation of qualifications regarding data quality, and any other significant problems encountered during analysis.

2. Summary Reports equivalent to the CLP forms I through X, and surrogate spike results for each sample, MS/MSD results, method blank results, and initial and continuing calibration results.

3. Summary reports equivalent to the CLP forms I through XIII, and spike and duplicate results, method blank results, MS results, and initial and continuing calibration results.

4. Field and laboratory chain-of-custody documentation pertaining to each sample delivery group analyzed.

11.3.2 Field Measurements

The data will be transferred from field notebooks to a computer database and output in a spreadsheet format for use in the project reports.

11.4 Annual Evaluation

The quarterly results of the sampling and analysis program will be computed annually. The analytical results will be averaged and the data evaluated to examine spatial and temporal trends. This analysis will also include groundwater elevation readings. The types of spatial and temporal trends conducted will be evaluated after each year of sampling. Initially, the analysis will include:

- Plots of mean concentration versus time for each parameter analyzed for the individual wells
- Plots of concentration versus time of moving averages for each parameter analyzed for individual wells
- Regression analyses on plots of moving average concentration versus time to determine direction of trends

The entire monitoring program also will be reevaluated annually. Specific adjustments to the program that may be necessary include:

- Analyte List—Do analytes need to be added or deleted?
- Sampling Frequencies—Is quarterly sampling and groundwater elevation readings adequate or excessive?
- Monitoring Well Network—Is the monitoring well network adequate? Does any well need to be replaced? Should additional wells be installed? Can some of the monitoring wells be deleted from the sampling program?
- Sampling Program—Do the analytical data indicate that the overall concentrations are decreasing? Should the monitoring program continue?

At the end of the fifth year, all sampling results will be compiled. These analytical results will be averaged and evaluated for temporal trends. Compound concentrations will be compared with groundwater standards and evaluated.

Section 12
Performance and System Audits

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the Groundwater Monitoring Plan and QAPjP. The audits of field and laboratory activities include two separate independent parts: Internal and External audits.

12.1 External Audits

12.1.1 Laboratories

The system audits, when necessary will include examination laboratory documentation on sample receiving, sample log-in, sample storage chain of custody procedure, sample preparation and analysis, instrument operating records, etc. The performance audits will consist of sending performance evaluation (PE) samples to the laboratories for on-going assessment of laboratory precision and accuracy. The analytical results of the analysis of PE samples are evaluated by EPA to ensure the laboratory maintain a good performance.

12.1.2 Field Audits

All field activities conducted by CH2M HILL may be subject to onsite audit by the U.S. EPA Region 5 Central District office and/or CRL. Audits will be arranged with the U.S. EPA Remedial Project Manager.

12.2 Internal Audits

12.2.1 Field Audits

Field performance audits are conducted to evaluate the execution of sample identification and control, chain of custody procedures, field documentation, training, and sampling operation. Audits evaluate compliance with the procedures outlined in the QAPjP and Groundwater Monitoring Plan. Field audits will be initiated by the site manager.

The site manager will perform the audit during a sampling event and will keep a written record of the evaluation.

The site manager will evaluate the following items:

- Responsibilities and Organization—To determine if the planned organization is operational and if necessary details of site activities are being communicated to project participants.
- Sample Collection—To ensure that written procedures outlined in the FSP are being implemented.
- Documentation—To ensure that all forms, identification tags, and field notebooks are being prepared and maintained.
- Quality Assurance Checks—To determine that quality control and assurance checks are being performed as specified in the QAPjP and Groundwater Monitoring Plan.
- Field Equipment—To ensure that calibration and maintenance are being done and recorded.
- Training—To ensure that the sampling team members are adequately trained in field sampling and documentation procedures.
- Chain-of-Custody Procedures—To determine if custody documentation is being completed and maintained and samples are kept in custody at all times.

Following the audit, the auditor will review the preliminary results of his evaluation with the field team leader. The auditor will prepare an audit report containing the results of the evaluation and recommendations for any corrective action. The audit report will be reviewed by the project manager. The site manager shall implement any agreed upon corrective action. The site manager will also be responsible for verifying the implementation of the corrective action. Any noncompliance with standard procedures shall be identified and corrected.

Section 13
Preventive Maintenance

13.1 Laboratory Instruments

The laboratories participating in the SAS program will follow SOPs for preventive maintenance for each measurement system and required support activity. All instrument maintenance activities will be documented in instrument logbooks to provide a history of maintenance records. If the CRL is used, laboratory instruments will be maintained according to CRL SOP.

13.2 Field Instruments

Preventative maintenance for field instruments is found with the field testing procedures in Appendix B.

Section 14
Specific Routine Procedures to Assess Data Precision, Accuracy, and Completeness

14.1 Field Measurements

Field data will be assessed by the field leader. The field leader will review the field results for compliance with the established QC criteria that are specified in the QAPjP and Groundwater Monitoring Plan. Accuracy of the field measurements will be assessed using daily instrument calibration, calibration check, and analysis of blanks. Precision will be assessed on the basis of reproducibility by multiple reading of a single sample. Upon completion of the field measurements the field data precision will be calculated using Equation 14-2. Data completeness will be calculated using Equation 14-1.

$$\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100 \qquad \text{Eq. 14-1}$$

14.2 Laboratory Data

Laboratory results will be assessed for compliance with required precision, accuracy, and completeness as follows:

14.2.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results between matrix spike/matrix spike duplicate (MS/MSD) and field and laboratory duplicate analyses. The relative percent difference (%RPD) will be calculated for each pair of duplicate analysis using the Equation 14-2.

$$\%\ \text{RPD} = \frac{S - D}{(S + D)/2} \times 100 \qquad \text{Eq. 14-2}$$

Where: S = First sample value (original or MS value)
D = Second sample value (duplicate or MSD value)

14.2.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Section III of the QAPjP using the analytical results of method blanks, reagent/preparation blanks, MS and MS/MSD samples, field blanks, and trip blanks. The percent recovery (%R) of spike samples will be calculated using Equation 14-3.

$$\%\ R = \frac{A - B}{C} \times 100 \qquad \text{Eq. 14-3}$$

Where:

A = The analyte concentration determined experimentally from the spiked sample

B = The background level determined by a separate analysis of the unspiked sample

C = The amount of the spike added

14.2.3 Completeness

The data completeness of laboratory analyses results will be assessed for compliance with the amount of data required for decision making. The completeness is calculated using Equation 14-1.

14.3 Project Assessment

Overall data assessment and data completeness assessment will be determined by CH2M HILL.

Section 15
Corrective Actions

Corrective actions may be required for two classes of problems: analytical and equipment problems, and noncompliance problems. Analytical and equipment problems may occur during sampling and sample handling, sample preparation, laboratory instrumental analysis, and data review.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the appropriate personnel. If the problem is field related, the field team leader is promptly notified. If the problem is analytical in nature, information on the problem will be promptly communicated to CH2M HILL. The field team leader or their designer will then determine the corrective action. Implementation of corrective action will be confirmed in writing.

15.1 Sample Collection / Field Measurements

Field personnel will be responsible for reporting all suspected technical or QA nonconformances or suspected deficiencies of any activity or issued document by reporting the situation to the SM or his designee. The SM will be responsible for assessing the suspected problems in consultation with the Project QAD. A decision will be made based on the potential for the situation to impact the quality of the data. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, then a nonconformance report will be initiated by the manager.

The SM will be responsible for ensuring that corrective action for nonconformances are initiated by:

- Evaluating all reported nonconformances.
- Controlling additional work on nonconforming items.
- Determining disposition or action to be taken.
- Maintaining a written log of nonconformances in a field record book.
- Reviewing nonconformance reports and corrective actions taken.

- Ensuring nonconformance reports are included in the final site documentation in project files.

If appropriate, the SM will see that no additional work that is dependent on the nonconforming activity is performed until the corrective actions are completed.

Corrective action for field measurements may include:

- Repeat the measurement to check the error
- Check for all proper adjustments for ambient conditions such as temperature
- Check the batteries
- Re-Calibration
- Check the calibration
- Replace the instrument or measurement devices
- Stop work (if necessary)

The SM or his designee is responsible for all site activities. In this role, the SM, at times, is required to adjust the site programs to accommodate site specific needs. When it becomes necessary to modify a program, the responsible person notifies the RPM of the anticipated change and implements the necessary changes after obtaining their approval. The change in the program will be documented on the field record book. The entry will be signed by the initiators and the SM.

The SM for the Onalaska Landfill site is responsible for the controlling, tracking, and implementation of the identified changes. Reports on all changes will be distributed to all affected parties which include the U.S. EPA RPM.

15.2 Laboratory Analyses—Laboratory Corrective Actions

For the laboratory's Special Analytical Services (SASs), corrective action is implemented at several different levels. The laboratories are required to have a written SOP specifying corrective action to be taken when an analytical error is discovered or the analytical system is determined to be out of control. The SOP requires documentation of the

corrective action and notification by the analyst about the errors and corrective procedures. Corrective actions by a laboratory will be implemented according to their Standard Operating Procedures (SOPs).

CH2M HILL may request corrective action for any contractual nonconformance identified by audits or data validation. Corrective action may include:

- Re-analyzing the samples, if holding time criteria permits.
- Resampling and analyzing.
- Evaluating and amending sampling procedures and/or evaluating and amending analytical procedures.
- Accepting the data and acknowledging the level of uncertainty.

If resampling is deemed necessary due to laboratory problems, RPM and the SM must identify the necessary approach including cost recovery from the laboratory for the additional sampling effort.

Section 16
Quality Assurance Reports to Management

The preparation of a separate QA report for this project is not anticipated. The annual reports for the Groundwater Monitoring Plan will contain separate QA sections that summarize data quality information collected during the previous year. Changes in the Field Sampling Plan or QAPjP will be documented in the annual report. The quarterly reports will contain qualified data (if available) summarized in tables.

The contents of the QA section of the annual report will include but not be limited to the following elements:

- Project status
- Indication of whether the QA objectives are being met
- Performance and system audits conducted during the previous monitoring period
- Data validation narrative summary and data quality assessment
- QA problems and corrective actions
- Changes to the QAPjP or Groundwater Monitoring Plan
- Qualified Data summarized in tables

APPENDIX A
SAS REQUEST FORMS

U.S. Environmental Protection Agency-Region 5
Central Regional Laboratory
536 S. Clark - 10th Floor
Chicago, IL 60605
PHONE: (312) 353-2720 or FAX 886-2591

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :_____
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of volatile organic compounds at part per billion (ppb) levels in groundwater samples using purge and trap capillary column gas chromatography-mass spectrometry (GC/MS). Attachment 1 lists target compounds and detection limits.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round analyze 17 low concentration groundwater samples. This number is inclusive of investigation and field QC samples (MS/MSD, field and trip blanks).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund Remedial

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipments by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required within 28 days of sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Analysis: EPA SW-846 Method 8260 (November 1990) with special technical instructions as noted in sect

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS number detection limits, etc.):**

See attachment 2.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

The data deliverables as described in the current CLP RAS Organic SOW OLM01.8 shall be used.

The laboratory shall report its own verified detection limits on the Form Is for all field and analytical samples.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airb may be submitted with a record of the location of the originals, to the Region within the time frame listed in secti 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits	Precision Desired (+/- % or Conc.)
See attachment 1	See attachment 1	+/- 20% of target detection limits listed in attachment 1

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits (+/- % or conc.)
Internal Standards	Each Sample, calibration standard, blank, and matrix spike	See attachment 2 (item 2A)
Surrogate Standards	Each sample, calibration standard, blank, and matrix spike	See attachment 2 (item 2B)
Matrix spike/matrix spike duplicate	1 set per group of 20 samples or less	As per CLP RAS Organic SOW
Method blank	As per attachment 2 and CLP RAS organic SOW	As per attachment 2 and CLP RAS organic SOW

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

See attachment 2 and CLP RAS organic SOW OLM01.8 for corrective actions.
Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytica services. Should you have any questions or need any assistance, please call the Region.

8260SAS.WP

ATTACHMENT 1

Organic Target Analytes	Aqueous Detection Limits (µg/L)
Benzene	1.0
Toluene	1.0
Xylene(s)	1.0
Ethylbenzene	1.0
Trichloroethene	1.0
1,1-Dichloroethane	1.0
1,1,1-Trichloroethane	1.0
1,1-Dichloroethene	1.0
1,1,2,1-Tetrachloroethylene	1.0

8260A1.WP

ATTACHMENT 2
SPECIAL TECHNICAL INSTRUCTIONS

1. Method Detection Limit (MDL) Study

The MDL study shall be performed prior award of contract. The MDL study shall consist of a statistically determined MDL using the procedure described in the Federal Register (V.49 #209, Appendix B to Part 136, 10-26) and verified through a spike at the computed MDL.

2. Sample Analysis

Analysis of all samples shall follow EPA SW-846 Method 8260 (attached) with modifications/specifications outlined below. **Corrective actions and QC limits shall follow the CLP RAS Organic SOW OLM01.8 unless otherwise noted below.**

A. A 25 mL purge will be necessary to achieve required detection limits.

B. Internal Standards

The internal standard compounds shall be pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Spiked at a concentration level of 1.0 µg/L.

C. Surrogate Standards

Surrogate standards shall additionally be spiked into all samples, blanks, calibration standards, matrix spike/matrix spike duplicate samples, etc. The surrogate standard compound shall be toluene-d_5, 4-bromofluoro-benzene, and dibromofluoromethane. The concentration of each surrogate shall be equivalent to the internal standards (1.0 µg/L) in each investigative and QC sample. Prepare according to EPA SW-846 Method 8260, Section 5.7 and 5.9 and spike when internal standards are introduced (Section 7.5.1). Recovery limits are: toluene-d_5 (88 to 110 percent), 4-bromofluorobenzene (86 to 115 percent), and dibromofluoromethane (86-118 percent).

D. Tuning Criteria

Bromofluorobenzene (BFB) tuning criteria (EPA SW-846 Method 8260) Table 4 and Section 7.4.1 must be every 12 hours and prior to analysis of any calibration standard, sample blank, etc.

E. Calibration

(1) Initial Calibration

Initial Calibration shall consist of five points as discussed in EPA SW-846 Method 8260, Section 5.12. These calibration points shall be prepared as described in Section 5.12 of the method. RFs of all other compounds must be ≥ 0.05. The percent relative standard deviation (percent RSD) for the RFs of all compounds must be ≤ 30 percent.

(2) Continuing Calibration

A continuing calibration standard shall be analyzed every 12 hours containing all compounds at a concentration near the mid point concentration for the working range of GC/MS. The continuing calibration response factors shall be used to quantitate all samples analyzed. Spiked at concentrations as described in the method. The RFs of the compounds must be ≥ 0.05. The percent difference (percent D) for the RFs of all compounds must be ≤ 25 percent.

F. Matrix Spike/Matrix Spike Duplicate

A matrix spike/matrix spike duplicate sample shall be selected by field samplers and shall be additionally analyzed as 1 set per group of 20 samples. The spike compounds will consist of all target compounds (benzene, toluene, xylenes, ethylbenzene, trichloroethene, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1-dichlorothene, and 1,1,2,1-tetrachloroethylene) at concentrations representative of what is expected to be found in the samples. Calculate spike recovery (percent R) and relative percent difference (RFD) as per the CLP RAS organic SOW OLM01.8.

G. Qualitative/Quantitative Analysis

EPA SW-246 Method 8260, Table 5, defines the primary and secondary characteristic masses used for the SAS target compounds (Attachment 5).

H. Method blanks

Method blanks shall be analyzed every 12 hours after initial and continuing calibration standards. An acceptable method blank must contain less than five times the verified MDL for methylene chloride, acetone, toluene, and 2-butanone and less than the MDL for the other target compounds.

I. Dilutions

If samples require dilutions in order to bring some compounds within the calibration range, the lab shall report both the undiluted and diluted result (including all CLP SOW deliverables) where compounds are quantitated. Results from samples requiring dilution will be qualified as diluted and flagged with a "D".

J. Preservation/Container Requirements

Samples will arrive preserved with HCl to a pH <2. Three VOA vials (40 mL each) will be sent per sample.

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VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No.[b]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	a	a
Bromobenzene	108-86-1	a	a
Bromochloromethane	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
n-Butylbenzene	104-51-8	a	a
sec-Butylbenzene	135-98-8	a	a
tert-Butylbenzene	98-06-6	a	a
Carbon tetrachloride	56-23-5	a	a
Chlorobenzene	108-90-7	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
2-Chlorotoluene	95-49-8	a	a
4-Chlorotoluene	106-43-4	a	a
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,2-Dichlorobenzene	95-50-1	a	a
1,3-Dichlorobenzene	541-73-1	a	a
1,4-Dichlorobenzene	106-46-7	a	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
cis-1,2-Dichloroethene	156-59-2	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloropropane	142-28-9	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
2,2-Dichloropropane	594-20-7	a	a
1,1-Dichloropropene	563-58-6	a	a
Ethylbenzene	100-41-4	a	a
Hexachlorobutadiene	87-68-3	a	a
Isopropylbenzene	98-82-8	a	a
p-Isopropyltoluene	99-87-6	a	a
Methylene chloride	75-09-2	a	a
Naphthalene	91-20-3	a	a
n-Propylbenzene	103-65-1	a	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
1,2,3-Trichlorobenzene	87-61-6	a	a
1,2,4-Trichlorobenzene	120-82-1	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
1,2,4-Trimethylbenzene	95-63-6	a	a
1,3,5-Trimethylbenzene	108-67-8	a	a
Vinyl chloride	75-01-4	a	a
o-Xylene	95-47-6	a	a
m-Xylene	108-38-3	a	a
p-Xylene	106-42-3	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.

1.2 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for lists of analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25 mL sample volumes are presented.

1.3 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8260 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with organic-free reagent water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantitated by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning. Screening of the samples prior to purge and trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.1.1 The recommended purging chamber is designed to accept 5 mL (and 25 mL if the lowest detection limit is required) samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices (i.e. needle spargers), may be utilized, provided equivalent performance is demonstrated.

4.1.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must

contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Traps normally last 2-3 months when used daily. Some signs of a deteriorating trap are: uncharacteristic recoveries of surrogates, especially toluene-d_8; a loss of the response of the internal standards during a 12 hour shift; and/or a rise in the baseline in the early portion of the scan.

4.1.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The trap bake-out temperature should not exceed 220°C. The desorber design illustrated in Figure 2 meets these criteria.

4.1.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.1.5 Trap Packing Materials

4.1.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.1.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.1.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.1.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through a 26 mesh screen (or equivalent).

4.2 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.3 Gas chromatography/mass spectrometer/data system

4.3.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. For some column configuration, the column oven must be cooled to < 30°C, therefore, a

subambient oven controller may be required. The capillary column should be directly coupled to the source.

4.3.1.1 Capillary precolumn interface when using cryogenic cooling - This device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary precolumn. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.3.1.1.1 During the cryofocussing step, the temperature of the fused silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.3.2 Gas chromatographic columns (Recommended)

4.3.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5 μm film thickness, or equivalent.

4.3.2.2 Column 2 - 30 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific) or VOCOL (Supelco), 3 μm film thickness, or equivalent.

4.3.2.3 Column 3 - 30 m x 0.32 mm ID capillary column coated with DB-5 (J&W Scientific) or SE-54 (Supelco), 1 μm film thickness, or equivalent.

4.3.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 50 ng of the GC/MS tuning standard (BFB) is injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

4.3.4 GC/MS interface - The GC is interfaced to the MS with an all glass enrichment device and an all glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in Section 8.2 can be achieved. Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 4) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. This interface is only needed for the wide bore columns ($\geq$ 0.53 mm ID).

4.3.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be

interfaced to the mass spectrometer. 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 an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000 µL.

4.6 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.7 Syringes - 5, 10, or 25 mL, gas-tight with shutoff valve.

4.8 Balance - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.9 Glass scintillation vials - 20 mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.10 Vials - 2 mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

4.12 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.13 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

5.4.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17,

240-5 or equivalent), $C_8H_{18}O_5$ - Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

5.4.1.1 Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is not contaminated by solvent vapors.

5.4.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10 mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.7.5 Prepare fresh standards for gases every two months or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.8 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace for one week only.

5.9 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.7, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 μg/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 μL of the surrogate spiking solution prior to analysis.

5.10 Internal standards - The recommended internal standards are chlorobenzene-d_5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d_4, and pentafluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 μg/L.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/μL of BFB in methanol should be prepared.

5.12 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.7 and 5.8). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above,

the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Calibration standards must be prepared daily.

5.13 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. It is desirable to perform a matrix spike using compounds found in samples. Some permits may require spiking specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C to -20°C in amber bottles with Teflon lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Direct injection - In very limited applications (e.g. aqueous process wastes) direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L). Therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected, or for water-soluble compounds that do not purge. The system must be calibrated by direct injection using the same solvent (e.g. water) for standards as the sample matrix (bypassing the purge-and-trap device).

7.2 Chromatographic conditions (Recommended)

7.2.1 General:

Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.2 Column 1 (A sample chromatogram is presented in Figure 5)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.3 Column 2, Cryogenic cooling (A sample chromatogram is presented in Figure 6)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 160°C
Final temperature:	160°C, hold until all expected compounds have eluted.

7.2.4 Column 2, Non-cryogenic cooling (A sample chromatogram is presented in Figure 7)

Carrier gas flow rate:	It is recommended that carrier gas flow and split and make-up gases be set using performance of standards as guidance. Set the carrier gas head pressure to ≈ 10 psi and the split to ≈ 30 mL/min. Optimize the make-up gas flow for the separator (approximately 30 mL/min) by injecting BFB, and determining the optimum response when varying the make-up gas. This will require several injections of BFB. Next, make several injections of the volatile working standard with all analytes of interest. Adjust the carrier and split to provide optimum chromatography and response. This is an especially critical adjustment for the volatile gas analytes. The head pressure should optimize between 8-12 psi and the split between 20-60 mL/min. The use of the splitter is important to minimize the effect of water on analyte response, to allow the use of a larger volume of helium during trap desorption, and to slow column flow.
Initial temperature:	45°C, hold for 2 minutes
Temperature program:	8°C/min to 200°C
Final temperature:	200°C, hold for 6 minutes.

A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

7.2.5 Column 3 (A sample chromatogram is presented in Figure 8)

Carrier gas (He) flow rate:	4 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.3 Initial calibration for purge-and-trap procedure

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50 ng injection or purging of 4-bromofluorobenzene (2 μL

injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.2 Assemble a purge-and-trap device that meets the specification in Section 4.1. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 minutes while backflushing at 180°C with the column at 220°C.

7.3.3 Connect the purge-and-trap device to a gas chromatograph.

7.3.4 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method. The purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed. To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to a purging device.

7.3.5 Carry out the purge-and-trap analysis procedure as described in Section 7.5.1.

7.3.6 Tabulate the area response of the characteristic ions (see Table 5) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.6.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

7.3.7 The average RF must be calculated and recorded for each compound. A system performance check should be made before this

calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.3.7.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.3.7.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.7.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.8 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs). Record the %RSDs for all compounds. The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = Relative standard deviation.
$\bar{x}$ = Mean of 5 initial RFs for a compound.
SD = Standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC must be less than 30 percent. This criterion must be met for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.4 Daily GC/MS calibration

7.4.1 Prior to the analysis of samples, inject or purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.4.2 The initial calibration curve (Section 7.3) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Section 7.4.3) and CCC (Section 7.4.4).

7.4.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.4.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Section 7.3.8 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{\overline{RF_I} - RF_c}{\overline{RF_I}} \times 100$$

where:

$\overline{RF_I}$ = Average response factor from initial calibration (Section 7.3).

RF_c = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (> 25% difference), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 25% difference criterion.

7.4.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during

data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last daily calibration (Section 7.4), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.5 GC/MS analysis

7.5.1 Water samples

7.5.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (HECD), and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.5.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.5.1.3 Set up the GC/MS system as outlined in Sections 4.3 and 7.2.

7.5.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.4) before analyzing samples.

7.5.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 7.3.7).

7.5.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second

analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.5.1.7.1 Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.5.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.1.7.3 Inject the proper aliquot of sample from the syringe prepared in Section 7.5.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.1.7.4 Fill a 5 mL syringe with the diluted sample as in Section 7.5.1.6.

7.5.1.8 Compositing samples prior to GC/MS analysis

7.5.1.8.1 Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25 mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

7.5.1.8.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.5.1.8.3 Mix well and draw out a 5 mL aliquot for analysis.

7.5.1.8.4 Follow sample introduction, purging, and desorption steps described in the method.

7.5.1.8.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25 mL sample is to be purged.

7.5.1.9 Add 10.0 µL of surrogate spiking solution (Section 5.9) and 10 µL of internal standard spiking solution (Section 5.10) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration

of 50 μg/L of each surrogate standard.

7.5.1.10 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.5.1.11 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature. Be sure the trap is cooler than 25°C.

7.5.1.12 Sample desorption - The mode of sample desorption is determined by the type of capillary column employed for the analysis. When using a wide bore capillary column, follow the desorption conditions of Section 7.5.1.13. The conditions for using narrow bore columns are described in Section 7.5.1.14.

7.5.1.13 Sample desorption for wide bore capillary column. Under most conditions, this type of column must be interfaced to the MS through an all glass jet separator.

7.5.1.13.1 After the 11 minute purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4) and initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for 4 minutes. If the non-cryogenic cooling technique is followed, the trap must be preheated to 150°C just prior to trap desorption at 180°C. While the purged analytes are being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5 mL or 25 mL portions of organic-free reagent water depending on the size of the purge device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

7.5.1.13.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 160°C and hold until all analytes elute.

7.5.1.13.3 After desorbing the sample for 4 minutes, condition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

7.5.1.14 Sample desorption for narrow bore capillary column. Under normal operating conditions, most narrow bore capillary columns can be interfaced directly to the MS without a jet separator.

7.5.1.14.1 After the 11 minute purge, attach the trap to the cryogenically cooled interface at -150°C and adjust the purge-and-trap system to the desorb mode (Figure 4). Introduce the trapped materials to the interface by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 4 mL/min for 5 minutes. While the extracted sample is being introduced into the interface, empty the purging device using the sample syringe and rinse the chamber with two 5 mL or 25 mL portions of organic-free reagent water depending on the size of the purging device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle. After desorbing for 5 minutes, flash heat the interface to 250°C and quickly introduce the sample on the chromatographic column. Start the temperature program sequence, and initiate data acquisition.

7.5.1.14.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 70°C and then at 15°C/min to 145°C. After desorbing the sample for 5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 15 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

7.5.1.15 If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.5.1.16 For matrix spike analysis, add 10 μL of the matrix spike solution (Section 5.13) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 μg/L of each matrix spike standard.

7.5.1.17 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.6.1 and 7.6.2 for qualitative and quantitative analysis.

7.5.2 Water-miscible liquids

7.5.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.5.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100 mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas-tight syringe.

7.5.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 µL, but not more than 100 µL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.5.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (> 1 mg/kg).

7.5.3.1 Low-concentration method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples. See Figure 9 for an illustration of a low soils impinger.

7.5.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.5.3.1.2 The GC/MS system should be set up as in Sections 7.5.1.3-7.5.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.5.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution (Section 5.9) and internal standard solution (Section 5.10) to the syringe through the valve (surrogate spiking solution and internal standard solution may be mixed together). The addition of 10 µL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 µg/kg of each surrogate standard.

7.5.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 7.5.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.5.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.5.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.5.3.1.6 Add the spiked organic-free reagent water to the purging device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Sections 7.5.3.1.4 and 7.5.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.5.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minutes. Be sure the trap is cooler than 25°C.

7.5.3.1.8 Proceed with the analysis as outlined in Sections 7.5.1.12-7.5.1.17. Use 5 mL of the same organic-free reagent water as in the blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.5.3.1.9 For matrix spike analysis of low-concentration sediment/soils, add 10 µL of the matrix spike

solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.5.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

7.5.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.5.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Section 7.5.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.5.3.2.2 For sediment/soil or solid waste, quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. For a solvent miscible sample, dilute the sample to 10 mL with the appropriate solvent after adding 1.0 mL of the surrogate spiking solution. Cap and shake for 2 minutes.

NOTE: Sections 7.5.3.2.1 and 7.5.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.5.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 µL aliquot of each of these extracts in Section 7.5.3.2.6 will give a concentration equivalent to 6,200 µg/kg of each surrogate standard.

7.5.3.2.4 The GC/MS system should be set up as in Sections 7.5.1.3-7.5.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.5.3.2.5 The information in Table 10 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Section 7.5.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (excluding solvent in standards).

7.5.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/solvent sample into the purging chamber.

7.5.3.2.8 Proceed with the analysis as outlined in Sections 7.5.1.12-7.5.1.17. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 µL of the dilution solvent to simulate the sample conditions.

7.5.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Section 5.9), and 1.0 mL of matrix spike solution (Section 5.13) as in Section 7.5.3.2.2. This results in a 6,200 µg/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 µL aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Section 7.5.3.2.6).

7.6 Data interpretation

7.6.1 Qualitative analysis

7.6.1.1 An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference

spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within ± 20% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.6.2 Quantitative analysis

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 6).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Response factor for compound being measured (Section 7.3.6).
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste:

High-concentration:

$$\text{concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-concentration:

$$\text{concentration } (\mu g/kg) = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.

V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).

V_i = Volume of extract added (μL) for purging.

W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.6.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The percent dry weight of the sample (as calculated in Section 7.5.3.1.5) should be reported along with the data in either instance.

7.6.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory should maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check sample should be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a calibration blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous

8.6.2.2.3 If the checks in 8.6.2.2.1 reveal no errors, the recovery problem encountered with the dosed sample is judged to be matrix-related, non system-related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

8.7 As part of the QC program for the laboratory, method accuracy for each matrix studied should be assessed and records should be maintained. After the analysis of five spiked samples (of the same matrix) as in Step 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.8 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.8.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.8.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery ($\bar{p}$) and standard deviation of the percent recovery (s_p) for each of the surrogates.

8.8.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

$$\text{Upper Control Limit (UCL)} = \bar{p} + 3s_p$$
$$\text{Lower Control Limit (LCL)} = \bar{p} - 3s_p$$

8.8.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 9. The limits given in Table 9 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Section 8.8.3 should fall within those given in Table 9 for these matrices.

8.8.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.8.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer should be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.10 In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of the measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.4.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 μg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 7. Calculated MDLs are presented in Table 1.

9.3 The method was tested using water spiked at 0.1 to 0.5 μg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 8. MDL values were also calculated from these data and are presented in Table 2.

10.0 REFERENCES

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TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
Dichlorodifluoromethane	1.55	0.70	3.13	0.10
Chloromethane	1.63	0.73	3.40	0.13
Vinyl Chloride	1.71	0.79	3.93	0.17
Bromomethane	2.01	0.96	4.80	0.11
Chloroethane	2.09	1.02	--	0.10
Trichlorofluoromethane	2.27	1.19	6.20	0.08
1,1-Dichloroethene	2.89	1.57	7.83	0.12
Methylene chloride	3.60	2.06	9.27	0.03
trans-1,2-Dichloroethene	3.98	2.36	9.90	0.06
1,1-Dichloroethane	4.85	2.93	10.80	0.04
2,2-Dichloropropane	6.01	3.80	11.87	0.35
cis-1,2-Dichloroethene	6.19	3.90	11.93	0.12
Chloroform	6.40	4.80	12.60	0.03
Bromochloromethane	6.74	4.38	12.37	0.04
1,1,1-Trichloroethane	7.27	4.84	12.83	0.08
Carbon tetrachloride	7.61	5.26	13.17	0.21
1,1-Dichloropropene	7.68	5.29	13.10	0.10
Benzene	8.23	5.67	13.50	0.04
1,2-Dichloroethane	8.40	5.83	13.63	0.06
Trichloroethene	9.59	7.27	14.80	0.19
1,2-Dichloropropane	10.09	7.66	15.20	0.04
Bromodichloromethane	10.59	8.49	15.80	0.08
Dibromomethane	10.65	7.93	15.43	0.24
trans-1,3-Dichloropropene	--	--	16.70	--
Toluene	12.43	10.00	17.40	0.11
cis-1,3-Dichloropropene	--	--	17.90	--
1,1,2-Trichloroethane	13.41	11.05	18.30	0.10
Tetrachloroethene	13.74	11.15	18.60	0.14
1,3-Dichloropropane	14.04	11.31	18.70	0.04
Dibromochloromethane	14.39	11.85	19.20	0.05
1,2-Dibromoethane	14.73	11.83	19.40	0.06
1-Chlorohexane	15.46	13.29	--	0.05
Chlorobenzene	15.76	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	15.94	13.33	20.87	0.05
Ethylbenzene	15.99	13.39	21.00	0.06
p-Xylene	16.12	13.69	21.30	0.13
m-Xylene	16.17	13.68	21.37	0.05
o-Xylene	17.11	14.52	22.27	0.11
Styrene	17.31	14.60	22.40	0.04
Bromoform	17.93	14.88	22.77	0.12
Isopropylbenzene	18.06	15.46	23.30	0.15
1,1,2,2-Tetrachloroethane	18.72	16.35	24.07	0.04

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes)			MDL[d] (µg/L)
	Column 1[a]	Column 2[b]	Column 2'[c]	
Bromobenzene	18.95	15.86	24.00	0.03
1,2,3-Trichloropropane	19.02	16.23	24.13	0.32
n-Propylbenzene	19.06	16.41	24.33	0.04
2-Chlorotoluene	19.34	16.42	24.53	0.04
1,3,5-Trimethylbenzene	19.47	16.90	24.83	0.05
4-Chlorotoluene	19.50	16.72	24.77	0.06
tert-Butylbenzene	20.28	17.57	26.60	0.14
1,2,4-Trimethylbenzene	20.34	17.70	31.50	0.13
sec-Butylbenzene	20.79	18.09	26.13	0.13
p-Isopropyltoluene	21.20	18.52	26.50	0.12
1,3-Dichlorobenzene	21.22	18.14	26.37	0.12
1,4-Dichlorobenzene	21.55	18.39	26.60	0.03
n-Butylbenzene	22.22	19.49	27.32	0.11
1,2-Dichlorobenzene	22.52	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	24.53	21.08	--	0.26
1,2,4-Trichlorobenzene	26.55	23.08	31.50	0.04
Hexachlorobutadiene	26.99	23.68	32.07	0.11
Naphthalene	27.17	23.52	32.20	0.04
1,2,3-Trichlorobenzene	27.78	24.18	32.97	0.03
INTERNAL STANDARDS/SURROGATES				
4-Bromofluorobenzene	18.63	15.71	23.63	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[c] Column 2' - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10°/min, program to 120°C at 5°/min, then program to 180°C at 8°/min.

[d] MDL based on a 25 mL sample volume.

TABLE 2.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

TABLE 2.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (µg/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25 mL sample volume.

TABLE 3.
ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

	Estimated Quantitation Limits		
	Ground water µg/L		Low Soil/Sediment[b] µg/kg
Volume of water purged	5 mL	25 mL	
All analytes in Table 1	5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following information for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[c]EQL = [EQL for low soil sediment (Table 3)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4.
BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 5.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Benzene	78	-
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223, 227
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Methylene chloride	84	86, 49
Naphthalene	128	-
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 119

TABLE 5.
(Continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	168, 129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	130, 132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
4-Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	
Toluene-d_8	98	
Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	

TABLE 6.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

Pentafluorobenzene	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromofluorobenzene (surrogate)
Bromochloromethane	Carbon tetrachloride
Bromomethane	2-Chloroethyl vinyl ether
2-Butanone	1,2-Dibromoethane
Carbon disulfide	Dibromomethane
Chloroethane	1,2-Dichloroethane
Chloroform	1,2-Dichloroethane-d_4 (surrogate)
Chloromethane	1,2-Dichloropropane
Dichlorodifluoromethane	1,1-Dichloropropene
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,1-Dichloroethene	trans-1,3-Dichloropropene
cis-1,2-Dichloroethene	4-Methyl-2-pentanone
trans-1,2-Dichloroethene	Toluene
2,2-Dichloropropane	Toluene-d_8 (surrogate)
Iodomethane	1,1,2-Trichloroethane
Methylene chloride	Trichloroethene
1,1,1-Trichloroethane	
Trichlorofluoromethane	1,4-Dichlorobenzene-d_4
Vinyl acetate	
Vinyl chloride	Bromobenzene
	n-Butylbenzene
Chlorobenzene-d_5	sec-Butylbenzene
	tert-Butylbenzene
Bromoform	2-Chlorotoluene
Chlorodibromomethane	4-Chlorotoluene
Chlorobenzene	1,2-Dibromo-3-chloropropane
1,3-Dichloropropane	1,2-Dichlorobenzene
Ethylbenzene	1,3-Dichlorobenzene
2-Hexanone	1,4-Dichlorobenzene
Styrene	Hexachlorobutadiene
1,1,1,2-Tetrachloroethane	Isopropyl benzene
Tetrachloroethene	p-Isopropyltoluene
Xylene	Naphthalene
	n-Propylbenzene
	1,1,2,2-Tetrachloroethane
	1,2,3-Trichlorobenzene
	1,2,4-Trichlorobenzene
	1,2,3-Trichloropropane
	1,2,4-Trimethylbenzene
	1,3,5-Trimethylbenzene

TABLE 7.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE BORE CAPILLARY COLUMN

Analyte	Conc. Range, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8

TABLE 7.
(Continued)

Analyte	Conc. Range, µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data form three concentrations.

TABLE 8.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED
WITH A NARROW BORE CAPILLARY COLUMN

Analyte	Conc. µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery	Percent Rel. Std. Dev.
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7

TABLE 8.
(Continued)

Analyte	Conc. µg/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery	Percent Rel. Std. Dev.
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 9.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117

[a] Single laboratory data for guidance only.

TABLE 10.

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SAMPLES

Approximate Concentration Range	Volume of Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

FIGURE 1.
PURGING DEVICE

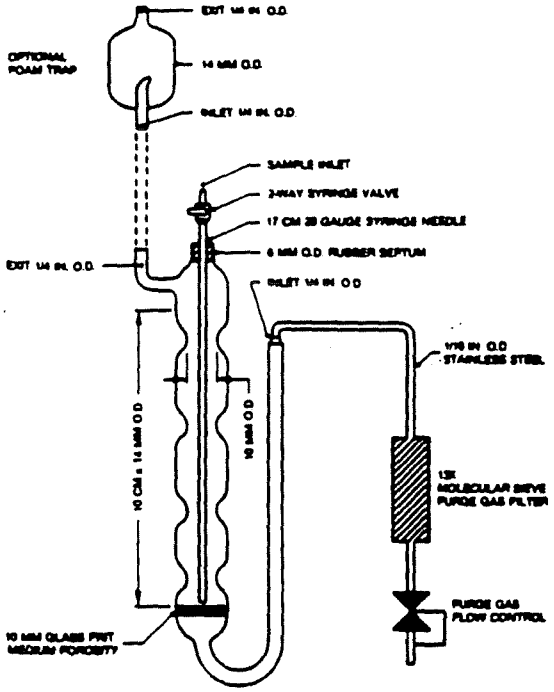


FIGURE 2.
TRAP PACKING AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

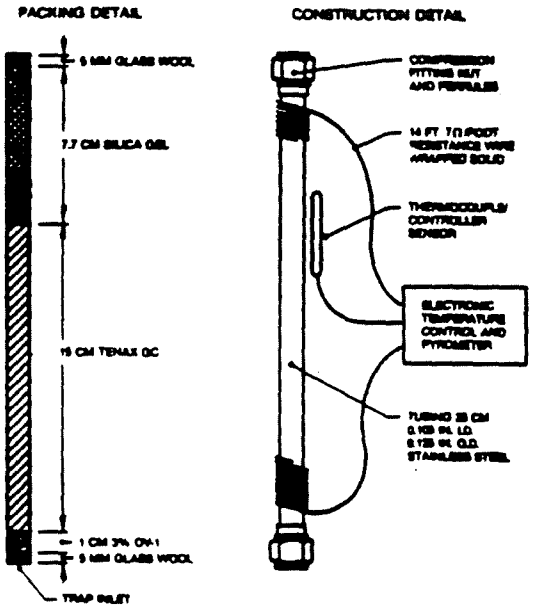


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE

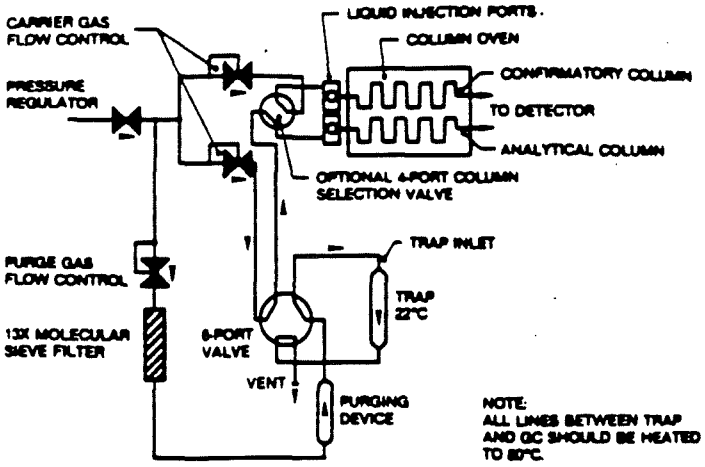


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

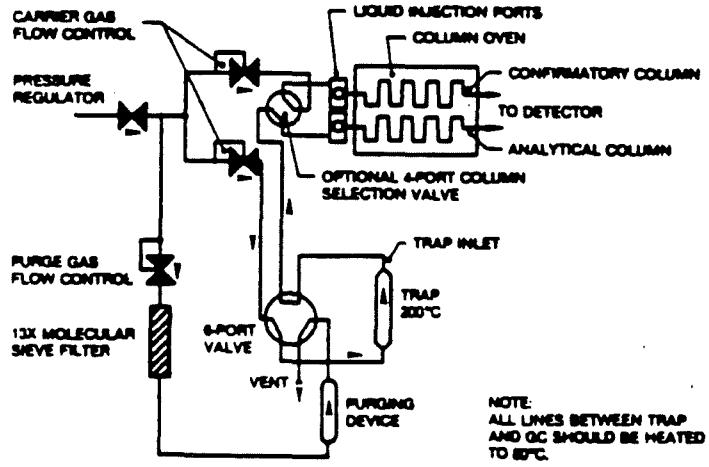


FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

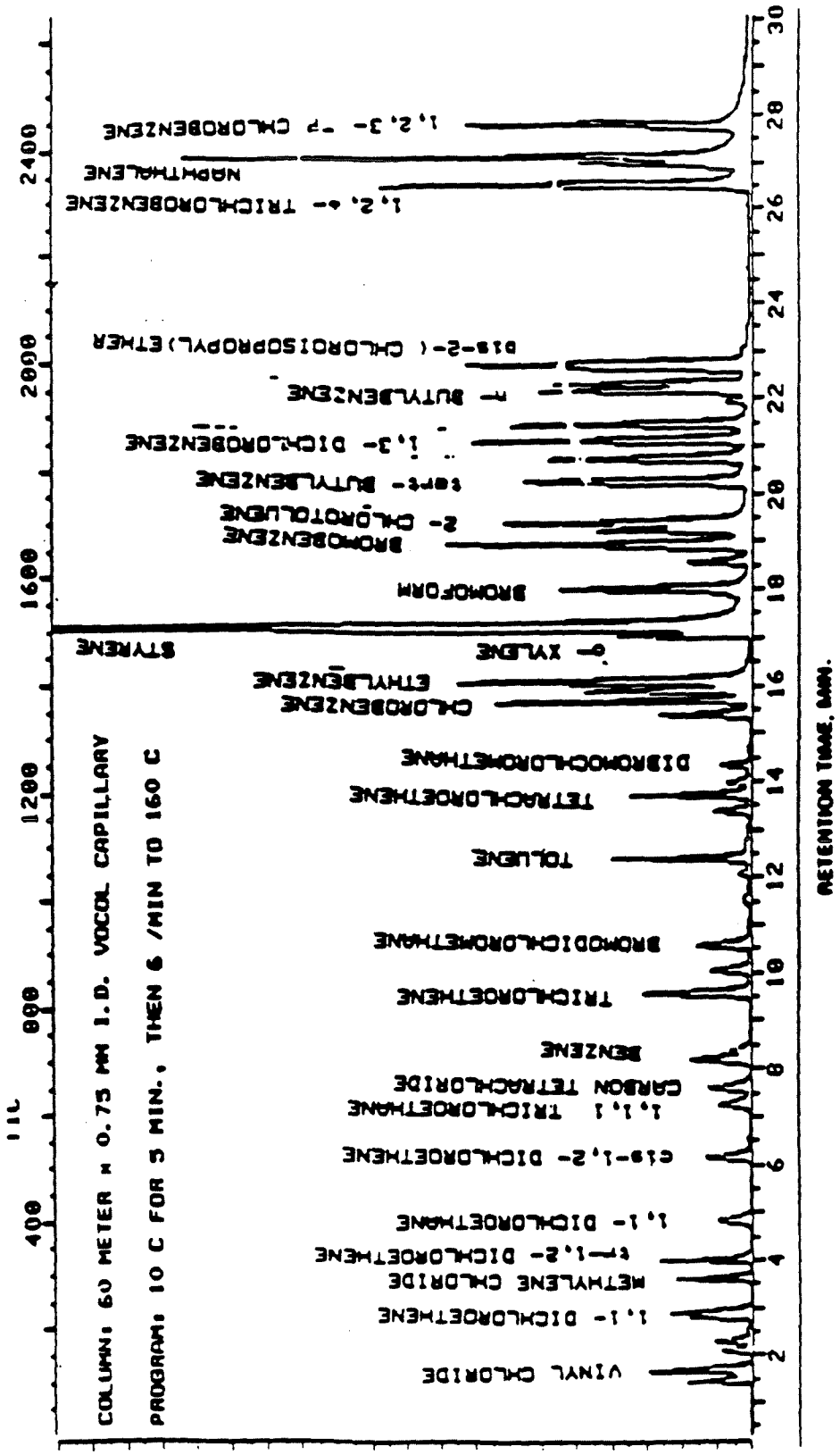


FIGURE 6.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

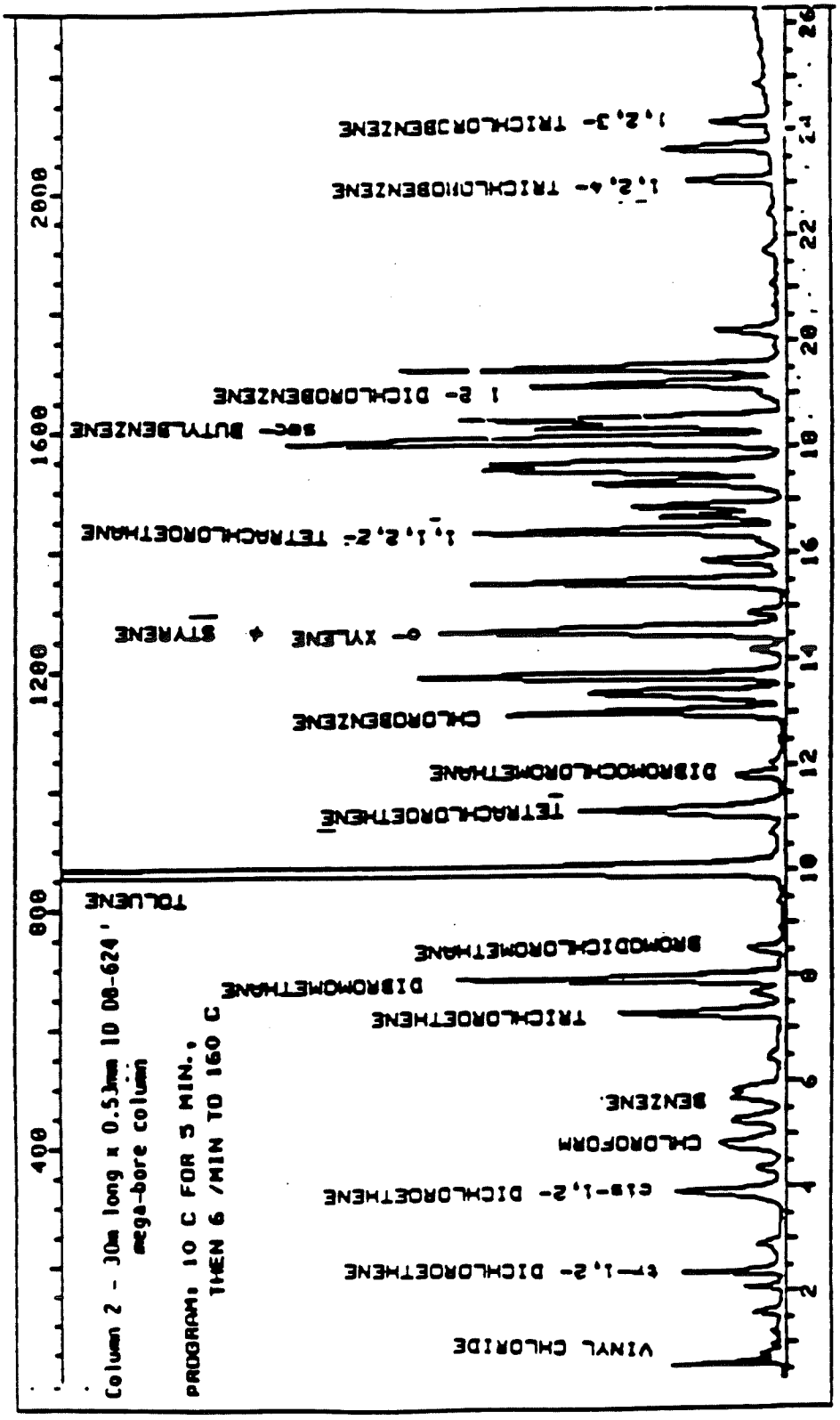


FIGURE 7.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

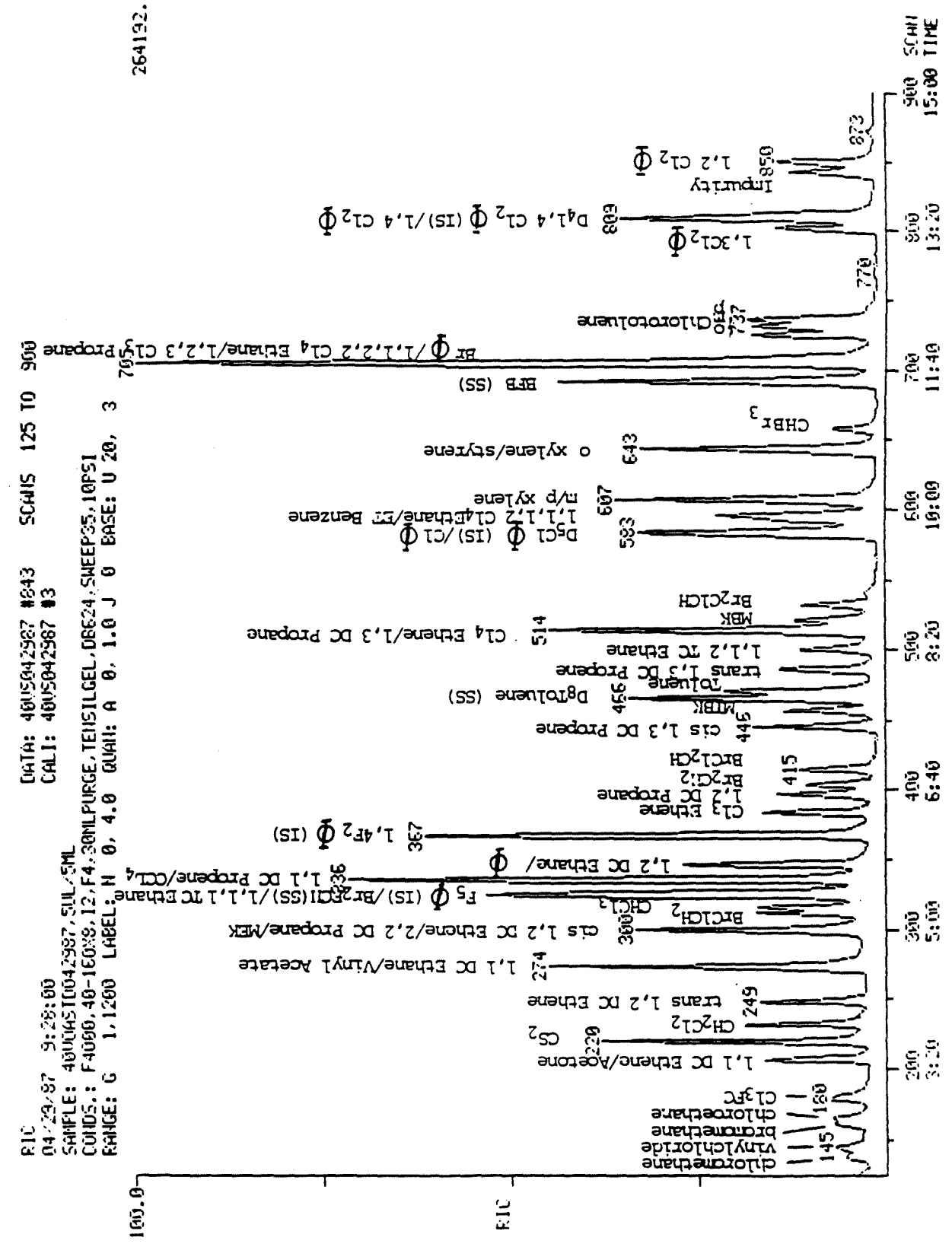


FIGURE 8.
GAS CHROMATOGRAM OF TEST MIXTURE

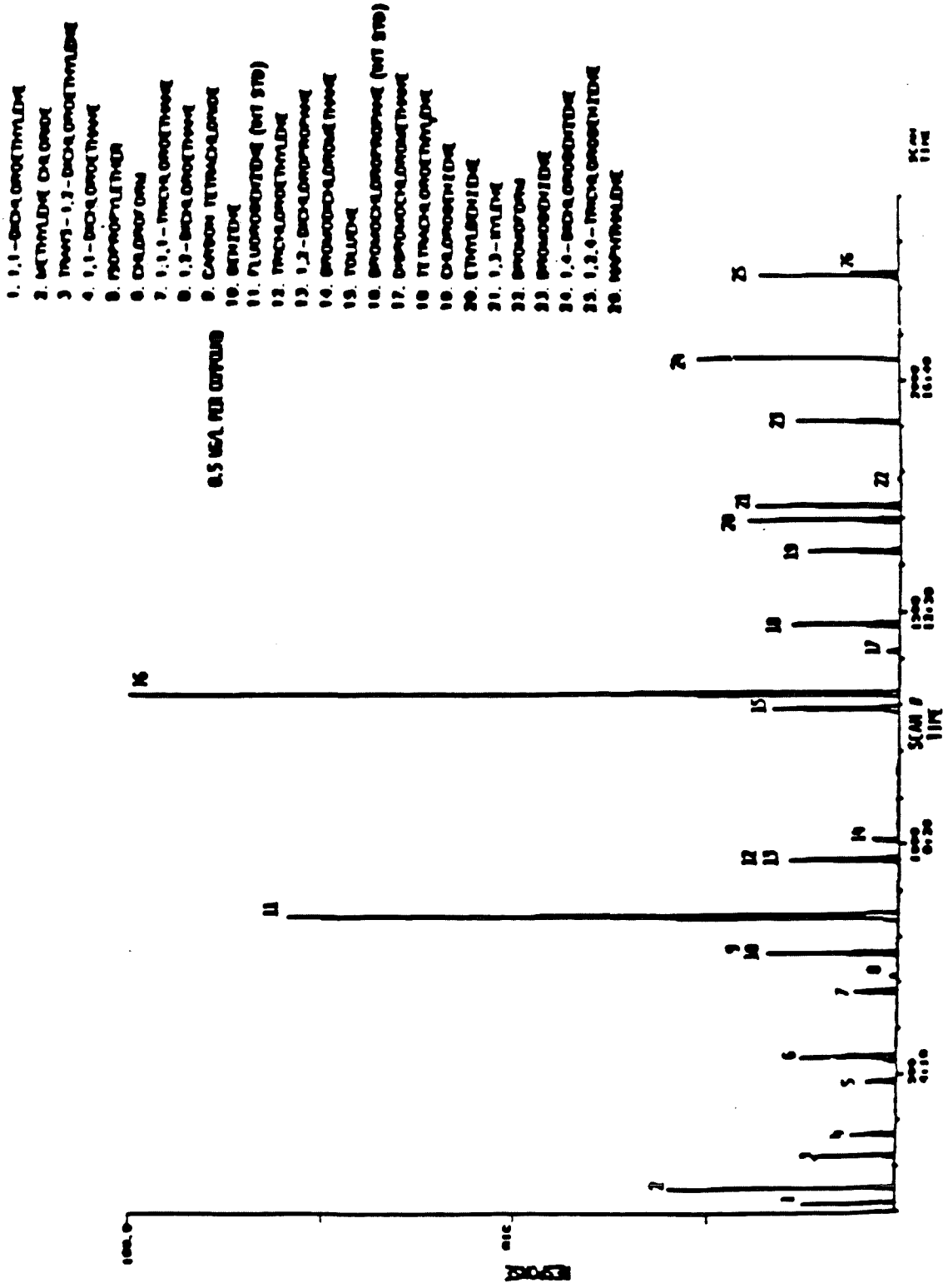
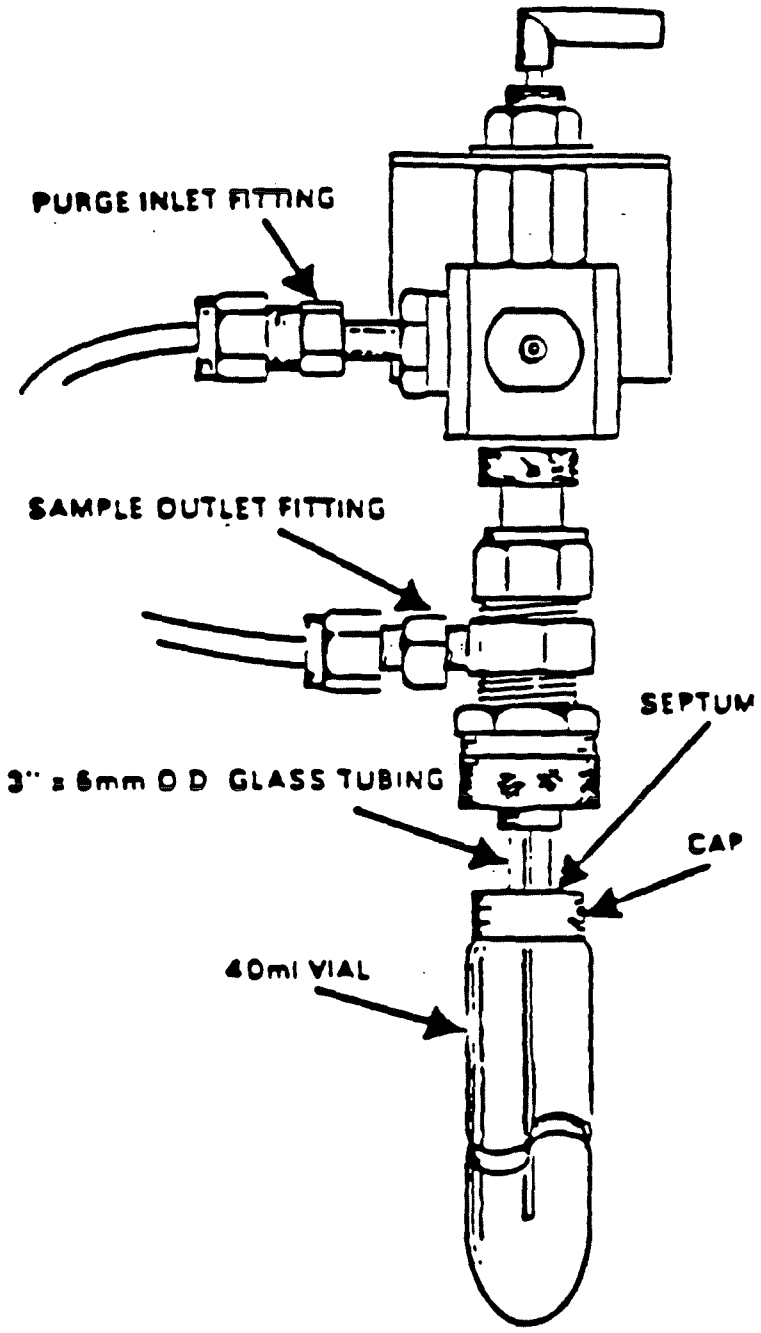
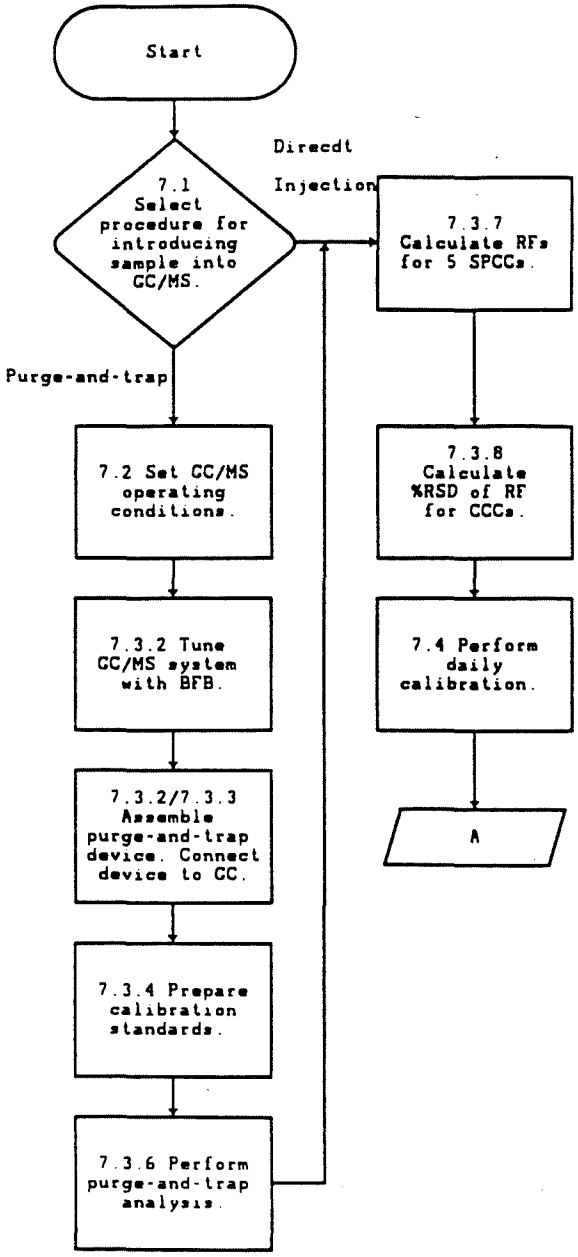
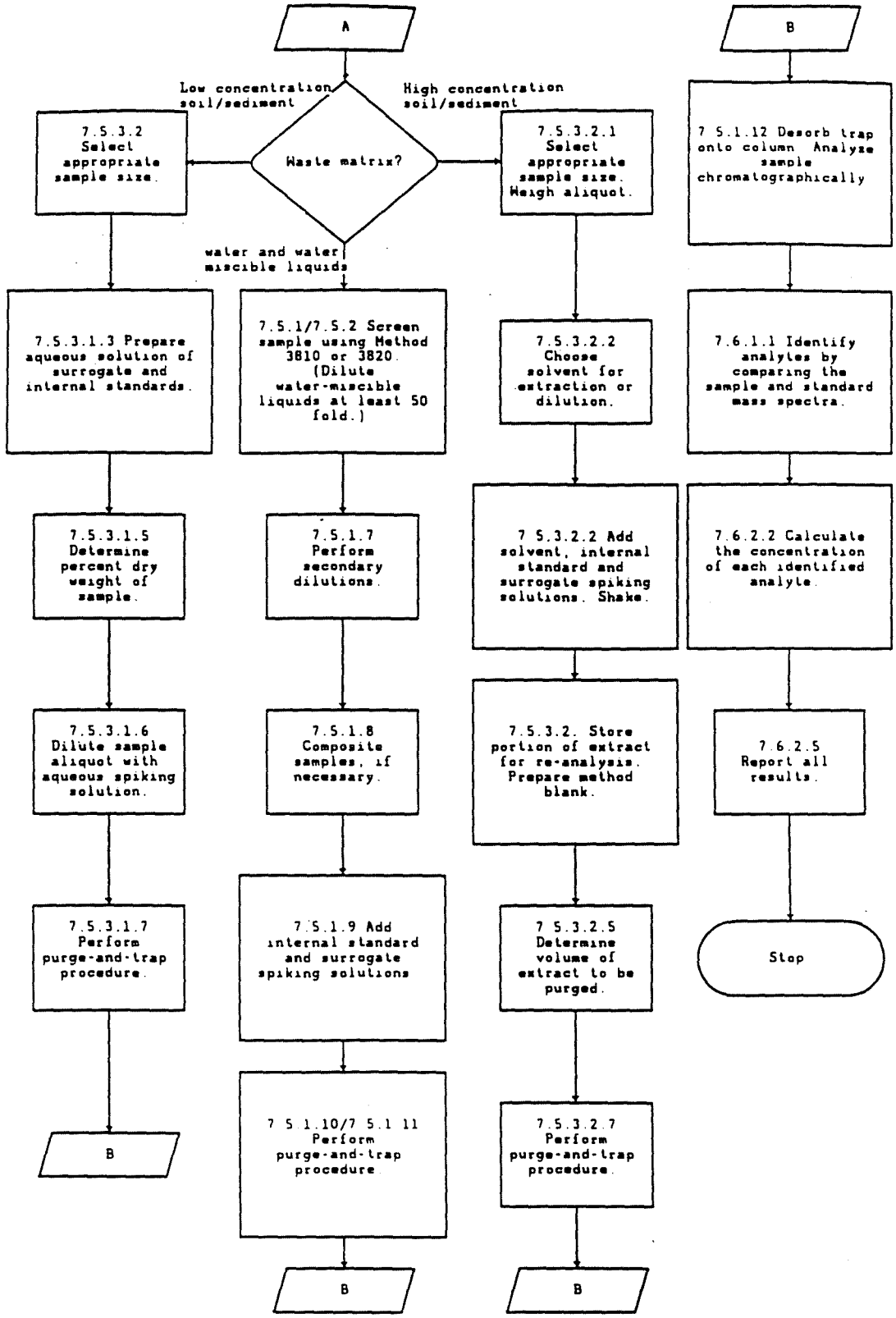


FIGURE 9.
LOW SOILS IMPINGER




Start
7.1 Select procedure for introducing sample into GC/MS.
Direcdt Injection
Purge-and-trap
7.3.7 Calculate RFs for 5 SPCCs.
7.2 Set GC/MS operating conditions.
7.3.8 Calculate %RSD of RF for CCCs.
7.3.2 Tune GC/MS system with BFB.
7.4 Perform daily calibration.
7.3.2/7.3.3 Assemble purge-and-trap device. Connect device to GC.
A
7.3.4 Prepare calibration standards.
7.3.6 Perform purge-and-trap analysis.


A
B
Low concentration soil/sediment
High concentration soil/sediment
Waste matrix?
water and water miscible liquids
7.5.3.2 Select appropriate sample size.
7.5.3.2.1 Select appropriate sample size. Weigh aliquot.
7 5.1.12 Desorb trap onto column Analyze sample chromatographically
7.5.3.1.3 Prepare aqueous solution of surrogate and internal standards.
7.5.1/7.5.2 Screen sample using Method 3810 or 3820. (Dilute water-miscible liquids at least 50 fold.)
7.5.3.2.2 Choose solvent for extraction or dilution.
7.6.1.1 Identify analytes by comparing the sample and standard mass spectra.
7.5.3.1.5 Determine percent dry weight of sample.
7.5.1.7 Perform secondary dilutions.
7 5.3.2.2 Add solvent, internal standard and surrogate spiking solutions. Shake.
7.6.2.2 Calculate the concentration of each identified analyte.
7.5.3.1.6 Dilute sample aliquot with aqueous spiking solution.
7.5.1.8 Composite samples, if necessary.
7.5.3.2. Store portion of extract for re-analysis. Prepare method blank.
7.6.2.5 Report all results.
7.5.3.1.7 Perform purge-and-trap procedure.
7.5.1.9 Add internal standard and surrogate spiking solutions
7 5.3.2.5 Determine volume of extract to be purged.
Stop
B
7 5 1.10/7 5.1 11 Perform purge-and-trap procedure.
7.5.3.2.7 Perform purge-and-trap procedure.
B
B
B

METHOD 5030

PURGE-AND-TRAP

1.0 SCOPE AND APPLICATION

1.1 This method describes sample preparation and extraction for the analysis of volatile organics by a purge-and-trap procedure. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8020, and 8030. Although applicable to Method 8240, the purge-and-trap procedure is already incorporated into Method 8240.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C (vapor pressure is approximately equal to mm Hg @ 25°C) and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system.

1.4 This method also describes the preparation of water-miscible liquids, solids, wastes, and soil/sediments for analysis by the purge-and-trap procedure.

2.0 SUMMARY OF METHOD

2.1 The purge-and-trap process: An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC following the normal water method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap 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 laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A field reagent blank prepared from reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL: These syringes should be equipped with a 20-gauge (0.006-in I.D.) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe: 5-mL, gas-tight with shutoff valve.

4.4 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials: 20-mL, with screw-caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner.

4.6 Volumetric flasks: 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials: 2-mL, for GC autosampler.

4.8 Spatula: Stainless steel.

4.9 Disposable pipets: Pasteur.

4.10 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.10.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

4.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.10.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.10.5 **Trap Packing Materials**

4.10.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.10.5.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

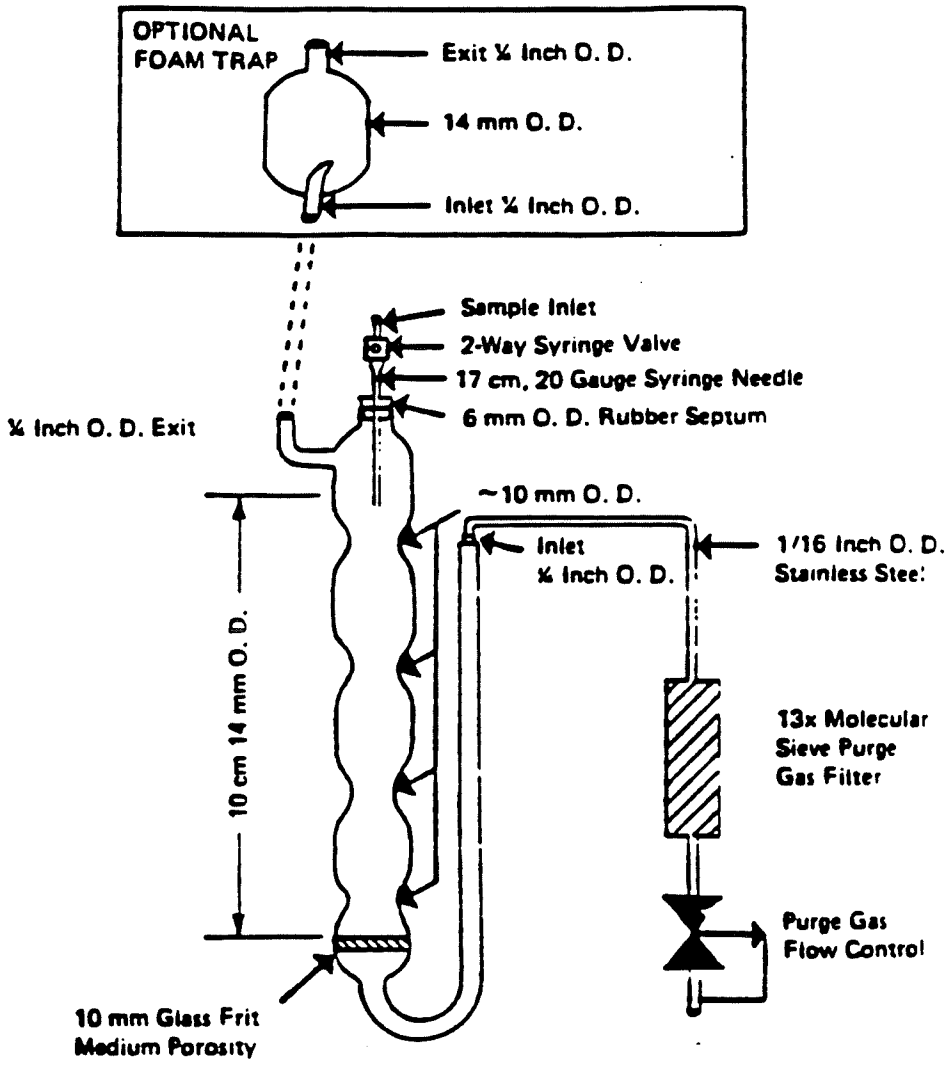


Figure 1. Purging chamber.

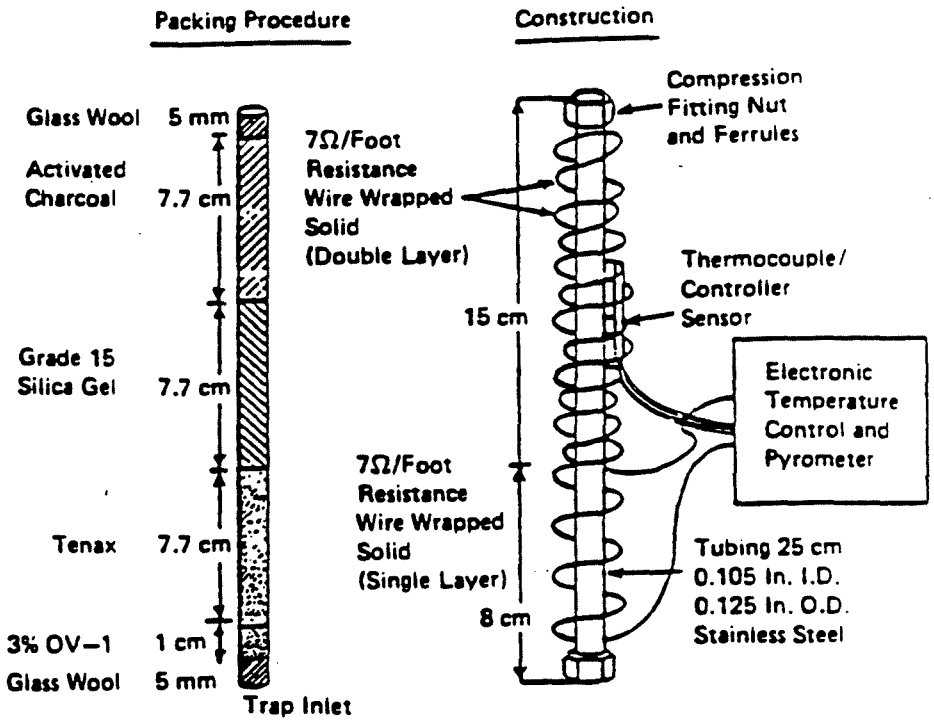


Figure 2. Trap packings and construction for Method 8010.

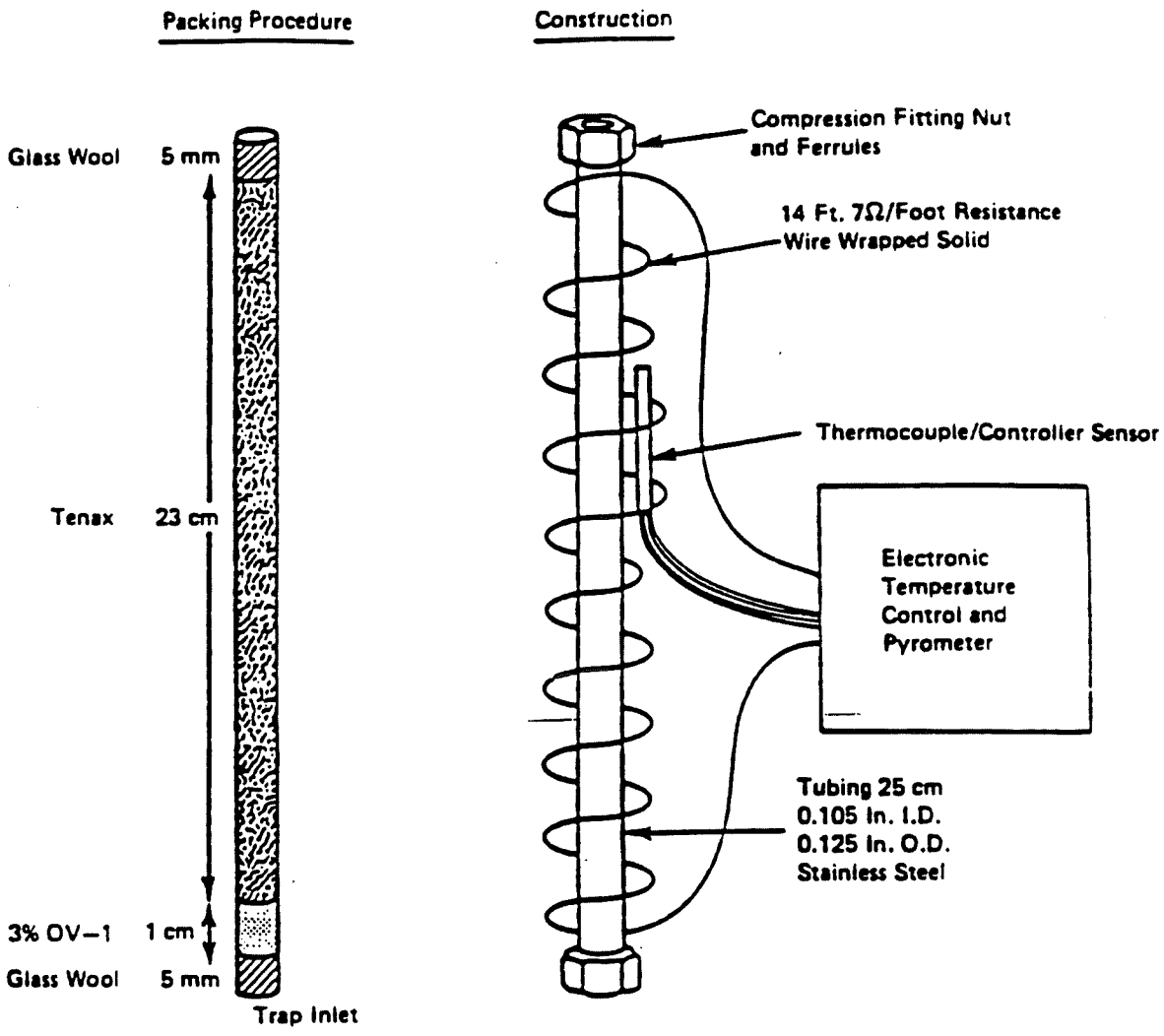


Figure 3. Trap packing and construction for Methods 8020 and 8030.

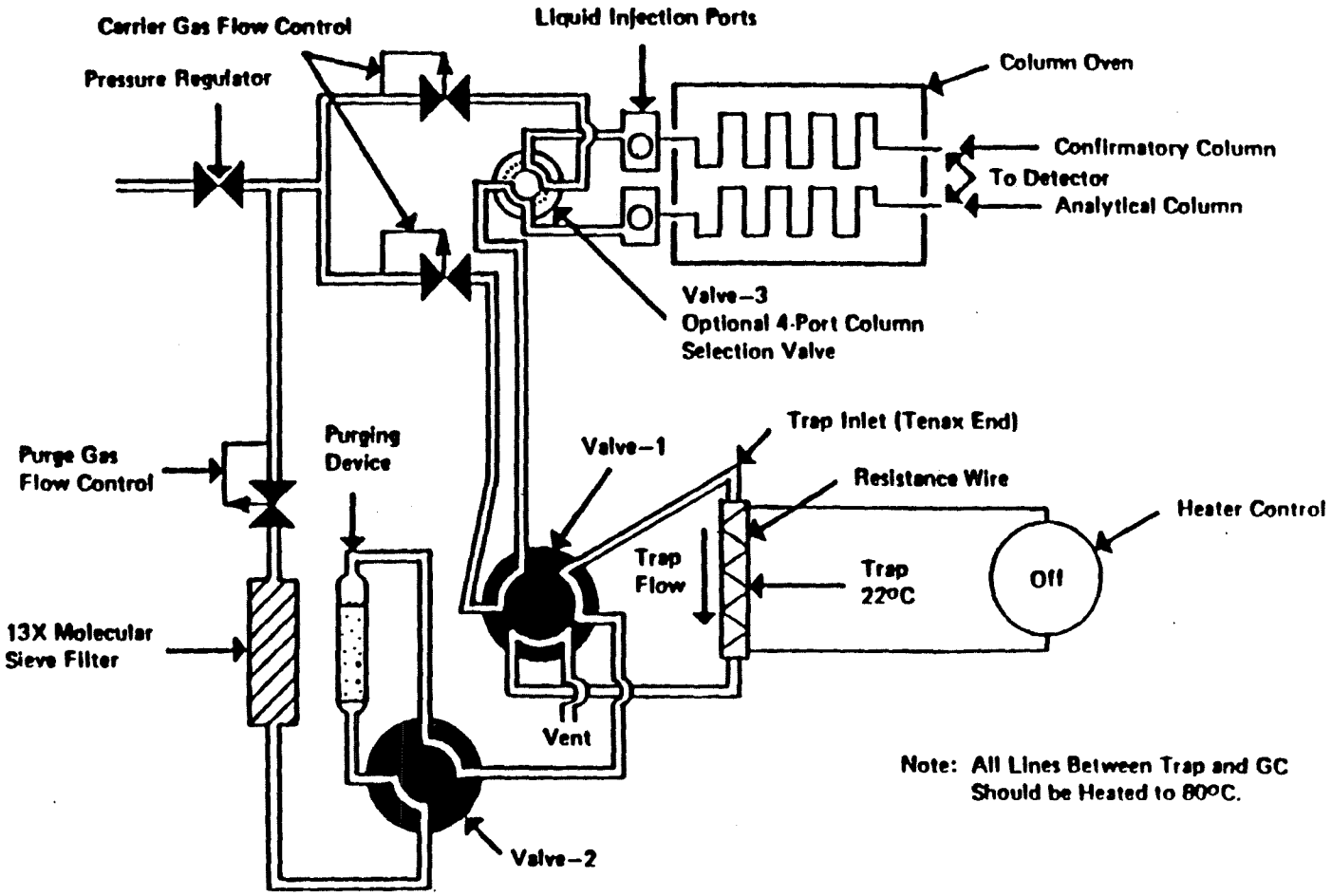


Figure 4. Purge-and-trap system, purge-sorb mode, for Methods 8010, 8020, and 8030.

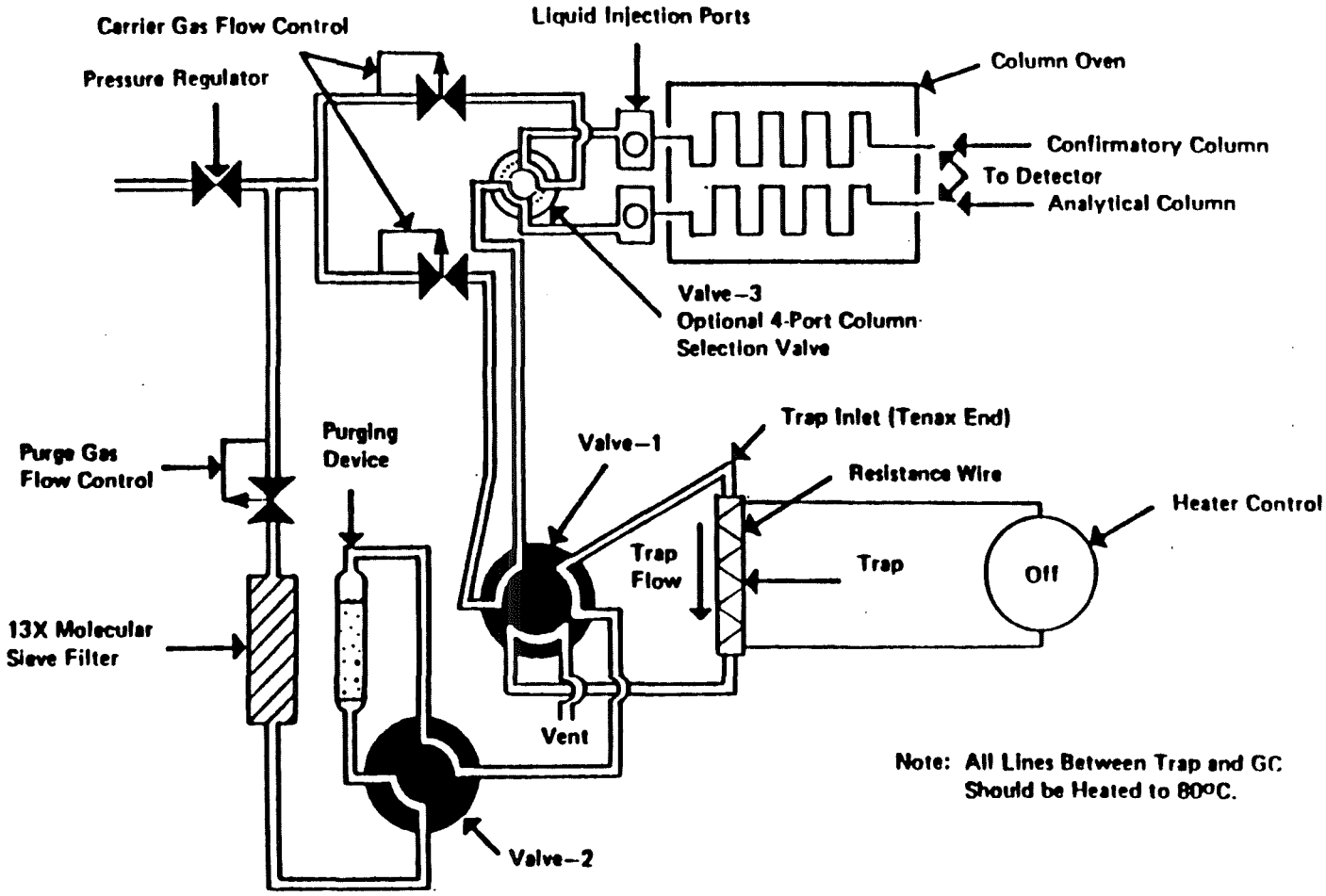


Figure 5. Purge-and-trap system, desorb mode, for Methods 8010, 8020, and 8030.

4.10.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

4.10.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, by crushing through 26 mesh screen.

4.11 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over a temperature range from ambient to 100°C.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing trap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the water temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.2 Methanol: Pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Initial calibration: Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, Section 7.4, while the specific determinative methods and Method 3500 give details on preparation of standards.

7.1.1 Assemble a purge-and-trap device that meets the specification in Section 4.10. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.1.2 Connect the purge-and-trap device to a gas chromatograph.

7.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of reagent water to the purging device. The reagent water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-uL or 25-uL microsyringe equipped with a long needle (Paragraph 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL of the internal standard solution. Close the 2-way syringe valve at the sample inlet.

7.1.4 Carry out the purge-and-trap analysis procedure using the specific conditions given in Table 1.

7.1.5 Calculate response factors or calibration factors for each analyte of interest using the procedure described in Method 8000, Section 7.4.

7.1.6 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. If the purge-and-trap procedure is used with Method 8010, the following five compounds are checked for a minimum average response factor: chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.1.6.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2 On-going calibration: Refer to Method 8000, Sections 7.4.2.3 and 7.4.3.4 for details on continuing calibration.

TABLE 1. PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method			
	8010	8015	8020	8030
Purge gas	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium
Purge gas flow rate (mL/min)	40	20	40	20
Purge time (min)	11.0 ± 0.1	15.0 ± 0.1	12.0 ± 0.1	15.0 ± 0.1
Purge temperature (°C)	Ambient	85 ± 2	Ambient	85 ± 2
Desorb temperature (°C)	180	180	180	180
Backflush inert gas flow (mL/min)	20-60	20-60	20-60	20-60
Desorb time (min)	4	1.5	4	1.5

7.3 Sample preparation:

7.3.1 Water samples:

7.3.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be utilized are: the use of an automated headspace sampler (modified Method 3810), interfaced to a gas chromatograph (GC), equipped with a photo ionization detector (PID), in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC with a FID and/or an ECD.

7.3.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.3.1.3 Assemble the purge-and-trap device. The operating conditions for the GC are given in Section 7.0 of the specific determinative method to be employed.

7.3.1.4 Daily GC calibration criteria must be met (Method 8000, Section 7.4) before analyzing samples.

7.3.1.5 Adjust the purge gas flow rate (nitrogen or helium) to that shown in Table 1, on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.3.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

7.3.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.3.1.7.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.3.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.3.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 7.3.1.5 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.3.1.7.4 Fill a 5-mL syringe with the diluted sample as in Paragraph 7.3.1.5.

7.3.1.8 Add 10.0 uL of surrogate spiking solution (found in each determinative method, Section 5.0) and, if applicable, 10 uL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.3.1.10 Close both valves and purge the sample for the time and at the temperature specified in Table 1.

7.3.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for the time specified in Table 1.

7.3.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.3.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow

through the trap. The trap temperature should be maintained at 180°C for Methods 8010 and 8020, and 210°C for Methods 8015 and 8030. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.3.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.3.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.3.2 **Water-miscible liquids:**

7.3.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

7.3.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.3.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3.3 **Sediment/soil and waste samples:** It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. See Paragraph 7.3.1.1 for recommended screening techniques. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (>1 mg/kg).

7.3.3.1 Low-level method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on

purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

7.3.3.1.1 Use a 5-g sample if the expected concentration is <0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

7.3.3.1.2 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature for Methods 8010 and 8020.

7.3.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution and internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Paragraph 7.3.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.3.3.1.5 In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination. Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3.3.1.6 Add the spiked reagent water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, steps 7.3.3.1.4 and 7.3.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.3.3.1.7 Heat the sample to 40°C ± 1°C (Methods 8010 and 8020) or to 85°C ± 2°C (Methods 8015 and 8030) and purge the sample for the time shown in Table 1.

7.3.3.1.8 Proceed with the analysis as outlined in Paragraphs 7.3.1.11-7.3.1.15. Use 5 mL of the same reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the high-level method must be followed.

7.3.3.2 High-level method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the extract is added to reagent water containing surrogate and, if applicable, internal and matrix spiking standards. This is purged at the temperatures indicated in Table 1. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.3.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Paragraph 7.3.3.1.5. For waste that is soluble in methanol, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.3.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

NOTE: Steps 7.3.3.2.1 and 7.3.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of reagent methanol to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis.

7.3.3.2.4 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the addition of the methanol extract to reagent water.

7.3.3.2.5 Table 2 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a high-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.3.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.3.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.3.2.8 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 uL of methanol to simulate the sample conditions.

7.3.3.2.9 For a matrix spike in the high-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution and 1.0 mL of matrix spike solution. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Paragraph 7.3.3.2.6).

TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 ug/kg	100 uL
1,000-20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a]The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.4 Sample analysis:

7.4.1 The samples prepared by this method may be analyzed by Methods 8010, 8015, 8020, 8030, and 8240. Refer to these methods for appropriate analysis conditions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for sample preparation procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

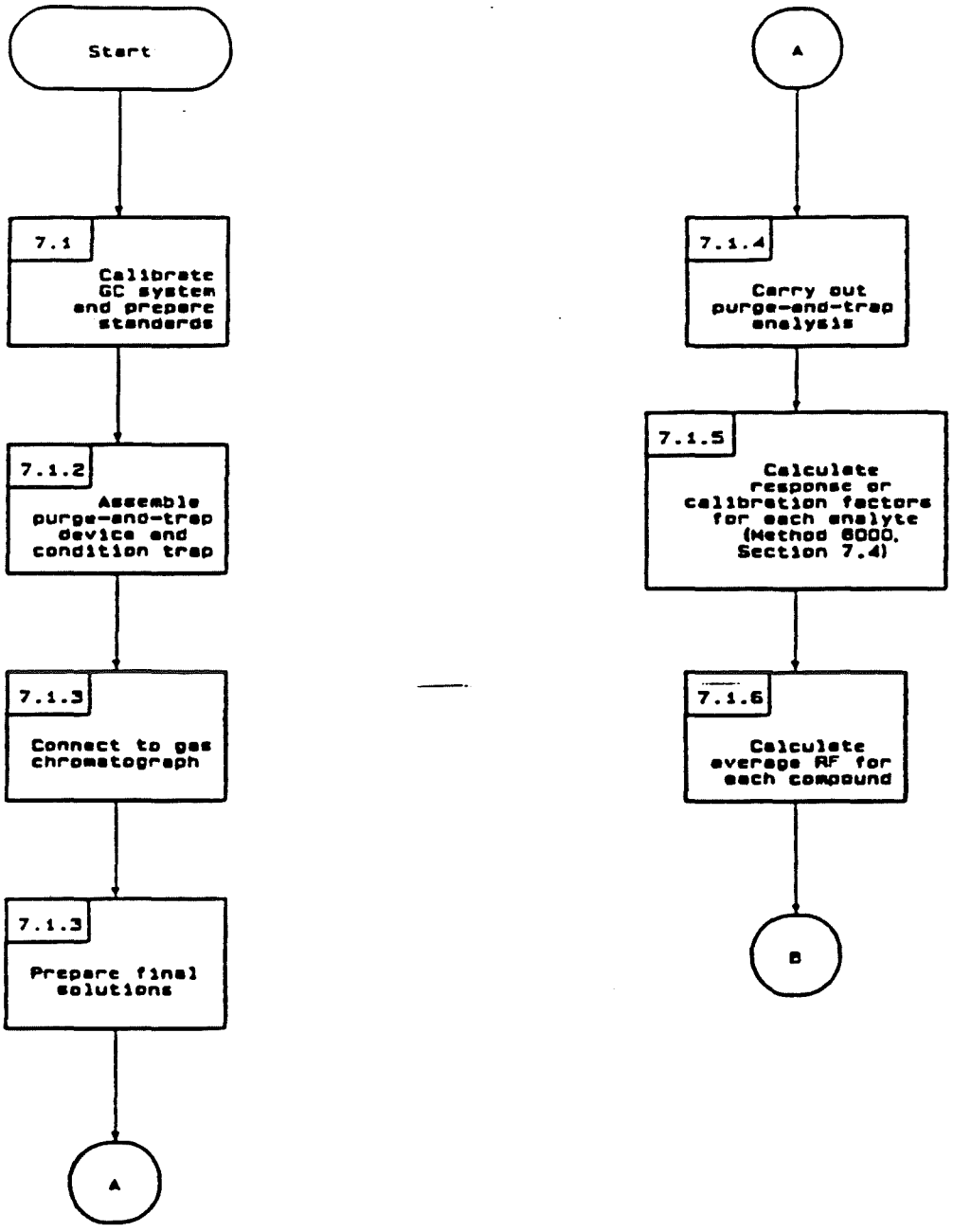
8.3 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect <1 ug/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or the sample should be subjected to additional cleanup.

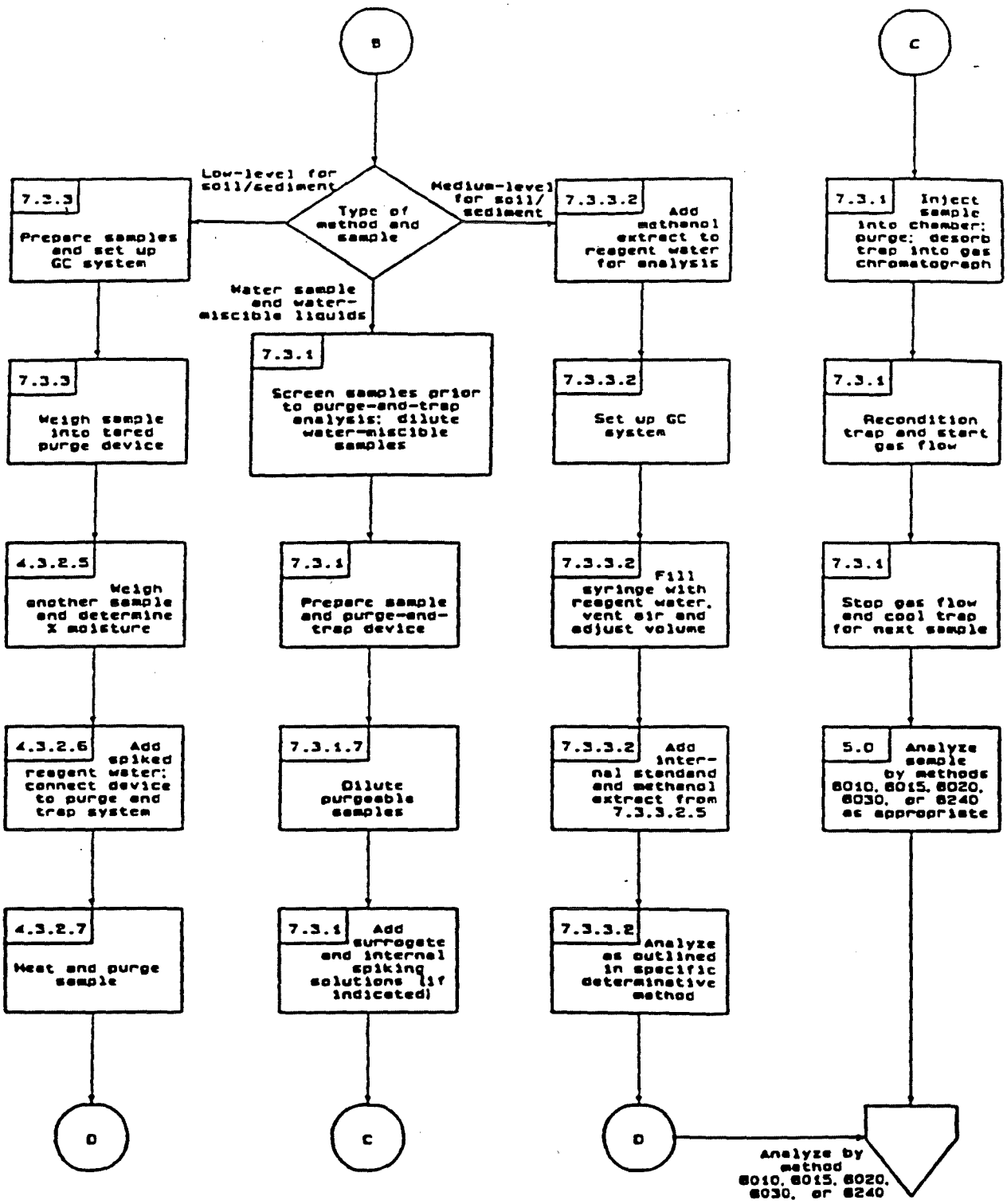
9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.


Start
7.1
Calibrate GC system and prepare standards
7.1.2
Assemble purge-and-trap device and condition trap
7.1.3
Connect to gas chromatograph
7.1.3
Prepare final solutions
A
A
7.1.4
Carry out purge-and-trap analysis
7.1.5
Calculate response or calibration factors for each analyte (Method 8000, Section 7.4)
7.1.6
Calculate average RF for each compound
B


B
C
Type of method and sample
Low-level for soil/sediment
Medium-level for soil/sediment
Water sample and water-miscible liquids
7.3.3
Prepare samples and set up GC system
7.3.3.2
Add methanol extract to reagent water for analysis
7.3.1
Inject sample into chamber; purge; desorb trap into gas chromatograph
7.3.3
Weigh sample into tared purge device
7.3.1
Screen samples prior to purge-and-trap analysis; dilute water-miscible samples
7.3.3.2
Set up GC system
7.3.1
Recondition trap and start gas flow
4.3.2.5
Weigh another sample and determine % moisture
7.3.1
Prepare sample and purge-and-trap device
7.3.3.2
Fill syringe with reagent water, vent air and adjust volume
7.3.1
Stop gas flow and cool trap for next sample
4.3.2.6
Add spiked reagent water; connect device to purge and trap system
7.3.1.7
Dilute purgeable samples
7.3.3.2
Add internal standard and methanol extract from 7.3.3.2.5
5.0
Analyze sample by methods 8010, 8015, 8020, 8030, or 8240 as appropriate
4.3.2.7
Heat and purge sample
7.3.1
Add surrogate and internal spiking solutions (if indicated)
7.3.3.2
Analyze as outlined in specific determinative method
D
C
D
Analyze by method 8010, 8015, 8020, 8030, or 8240

U.S. Environmental Protection Agency-Region 5
Central Regional Laboratory
536 S. Clark - 10th Floor
Chicago, IL 60605
PHONE: (312) 353-2720 or FAX 886-2591

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :_____
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of volatile organic compounds at part per billion (ppb) levels in residential wells using purge and trap capillary column gas chromatography-mass spectrometry (GC/MS). Attachment 1 lists target compounds and detection limits.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round analyze 5 low concentration residential well samples. This number is inclusive of investigation and field QC samples (MS/MSD, field and trip blanks).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund Remedial

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipments by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required within 28 days of sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Analysis: EPA SDWA 500 Method 524.2 (December 1988) with special technical instructions as noted in se 8.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS number detection limits, etc.):**

See attachment 2.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

The data deliverables as described in the current CLP RAS Organic SOW OLM01.8 shall be used.

The laboratory shall report its own verified detection limits on the Form I's for all field and analytical samples.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitted to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airb may be submitted with a record of the location of the originals, to the Region within the time frame listed in secti 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits	Precision Desired (+/- % or Conc.)
See attachment 1	See attachment 1	+/- 20% of target detection limits listed in attachment 1

QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits (+/- % or conc.)
Internal Standards	Each Sample, calibration standard, blank, and matrix spike	See attachment 2 (item 2A)
Surrogate Standards	Each sample, calibration standard, blank, and matrix spike	See attachment 2 (item 2B)
Matrix spike/matrix spike duplicate *	1 set per group of 20 samples or less	As per CLP RAS Organic SOW
Method blank	As per attachment 2 and CLP RAS organic SOW	As per attachment 2 and CLP RAS organic SOW

* Matrix spike/matrix spike duplicate will be run during first round of sampling, future rounds of sampling will sho precision and accuracy through lab control sample/lab control duplicate.

III. **ACTION REQUIRED IF LIMITS ARE EXCEEDED:**

See attachment 2 and CLP RAS organic SOW OLM01.8 for corrective actions. Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

524SAS.WP

ATTACHMENT 1

Organic Target Analytes	Aqueous Detection Limits (µg/L)
Benzene	1.0
Toluene	1.0
Xylene(s)	1.0
Ethylbenzene	1.0
Trichloroethene	1.0
1,1-Dichloroethane	1.0
1,1,1-Trichloroethane	1.0
1,1-Dichloroethene	1.0
1,1,2,1-Tetrachloroethylene	1.0

524A1.WP

ATTACHMENT 2
SPECIAL TECHNICAL INSTRUCTIONS

1. Method Detection Limit (MDL) Study

The MDL study shall be performed prior to award of contract. The MDL study shall consist of a statistically determined MDL using the procedure described in the Federal Register (V.49 #209, Appendix B to Part 136, 10-26) and verified through a spike at the computed MDL.

2. Sample Analysis

Analysis of all samples shall follow EPA SDWA 500 Method 524.2 (attached) with modifications/specifications outlined below. **Corrective actions and QC limits shall follow the CLP RAS Organic SOW OLM01.8 unless otherwise noted below.**

A. Internal Standards

The internal standard compounds shall be pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Spiked at a concentration level of 1.0 µg/L.

B. Surrogate Standards

Surrogate standards shall additionally be spiked into all samples, blanks, calibration standards, matrix spike/matrix spike duplicate samples, etc. The surrogate standard compound shall be toluene-d_5, 4-bromofluoro-benzene, and dibromofluoromethane. The concentration of each surrogate shall be equivalent to the internal standards (1.0 µg/L) in each investigative and QC sample. Prepare according to EPA SDWA 500 Method 524.2 and spike when internal standards are introduced (Section 7.5.1). Recovery limits are: toluene-d_5 (88 to 110 percent), 4-bromofluorobenzene (86 to 115 percent), and dibromofluoromethane (86-118 percent).

C. Tuning Criteria

Bromofluorobenzene (BFB) tuning criteria (EPA SDWA 500 Method 524.2) Table 3 and Section 9.2.2 must be every 12 hours and prior to analysis of any calibration standard, sample blank, etc.

D. Calibration

(1) Initial Calibration

Initial Calibration shall consist of five points as discussed in EPA SDWA 500 Method 524.2, Section 7.8.1. These calibration points shall be prepared as described in Section 7.8.2 of the method. RFs of all other compounds must be ≥ 0.05. The percent relative standard deviation (percent RSD) for the RFs of all compounds must be ≤ 30 percent.

(2) Continuing Calibration

A continuing calibration standard shall be analyzed every 12 hours containing all compounds at a concentration near the mid point concentration for the working range of GC/MS. The continuing calibration response factors shall be used to quantitate all samples analyzed. Spiked at concentrations as described in the method. The RFs of the compounds must be ≥ 0.05. The percent difference (percent D) for the RFs of all compounds must be ≤ 25 percent.

E. Matrix Spike/Matrix Spike Duplicate

A matrix spike/matrix spike duplicate sample shall be selected by field samplers and shall be additionally analyzed as 1 set per group of 20 samples. The spike compounds will consist of all target compounds (benzene, toluene, xylenes, ethylbenzene, trichloroethene, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1-dichlorothene, and 1,1,2,1-tetrachloroethylene) at concentrations representative of what is expected to be found in the samples. Calculate spike recovery (percent R) and relative percent difference (RFD) as per the CLP RAS organic SOW OLM01.8.

F. Qualitative/Quantitative Analysis

EPA SDWA 500 Method 524.2, Table 1, defines the primary and secondary characteristic masses used for the SAS target compounds (Attachment 5).

G. Method blanks

Method blanks shall be analyzed every 12 hours after initial and continuing calibration standards. An acceptable method blank must contain less than five times the verified MDL for methylene chloride, acetone, toluene, and 2-butanone and less than the MDL for the other target compounds.

H. Dilutions

If samples require dilutions in order to bring some compounds within the calibration range, the lab shall report both the undiluted and diluted result (including all CLP SOW deliverables) where compounds are quantitated. Results from samples requiring dilution will be qualified as diluted and flagged with a "D".

I. Preservation/Container Requirements

Samples will arrive preserved with HCl to a pH <2. Three VOA vials (40 mL each) will be sent per sample.

524A2.WP

METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 3.0

A. Alford-Stevens, J. W. Eichelberger, W. L. Budde - Method 524, Revision 1.0 (1983)

R. W. Slater, Jr. - Method 524.2, Revision 2.0 (1986)

J. W. Eichelberger, W. L. Budde - Method 524.2, Revision 3.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1-2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

Compound	Chemical Abstract Service Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9

2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 Method detection limits (MDLs) (3) are compound and instrument dependent and vary from approximately 0.02-0.35 µg/L. The applicable concentration range of this method is primarily column dependent and is approximately 0.02 to 200 µg/L for the wide-bore thick-film columns. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Analytes that are not separated chromatographically, but which have different mass spectra and non-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample (Sect 11.6.2). Analytes which have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different retention times (Sect.11.6.3). Coeluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

2. SUMMARY OF METHOD

2.1 Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The column is temperature programmed to separate the method analytes which are then detected with the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method

analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of one or more compounds (analytes, surrogates, internal standard, or other test compounds) used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- a solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- a sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used

to check laboratory performance with externally prepared test materials.

4. INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (4-6) for the information of the analyst.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloro-

form, 1,2-dibromoethane,tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLE CONTAINERS -- 60-mL to 120-mL screw cap vials (Pierce #19832 or equivalent) each equipped with a PTFE-faced silicone septum (Pierce #12718 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for 1 hr, then remove and allow to cool in an area known to be free of organics.

6.2 PURGE AND TRAP SYSTEM -- The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

6.2.1 The all glass purging device (Figure 1) should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) purging device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, however, the purge gas must be introduced at a point about 5 mm from the base of the water column.

6.2.2 The trap (Figure 2) must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. If it is not necessary to determine dichlorodifluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.2.3 The use of the methyl silicone coated packing is recommended, but not mandatory. The packing serves a dual purpose of protecting the Tenax adsorbant from aerosols, and also of

insuring that the Tenax is fully enclosed within the heated zone of the trap thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.2.4 The desorber (Figure 2) must be capable of rapidly heating the trap to 180°C either prior to or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop in excess of 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities. The desorber design illustrated in Fig. 2 meets these criteria.

6.3 GAS CHROMATOGRAPHY/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.3.1 The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. The column oven must be cooled to 10°C; therefore, a subambient oven controller is required. If syringe injections of BFB will be used, a split/splitless injection port is required.

6.3.2 Capillary Gas Chromatography Columns. Any gas chromatography column that meets the performance specifications of this method may be used. Separations of the calibration mixture must be equivalent or better than those described in this method. Three useful columns have been identified.

6.3.2.1 Column 1 -- 60 m x 0.75 mm ID VOCOL (Supelco, Inc.) glass wide-bore capillary with a 1.5 μm film thickness.

Column 2 -- 30 m x 0.53 mm ID DB-624 (J&W Scientific, Inc.) fused silica capillary with a 3 μm film thickness.

Column 3 -- 30 m x 0.32 mm ID DB-5 (J&W Scientific, Inc.) fused silica capillary with a 1 μm film thickness.

6.3.3 Interfaces between the GC and MS. The interface used depends on the column selected and the gas flow rate.

6.3.3.1 The wide-bore columns 1 and 2 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface (7), an all-glass jet separator, or a cryogenic (Sect. 6.3.3.2) device

are acceptable interfaces. Any interface can be used if the performance specifications described in this method can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few mm of the MS ion source.

6.3.3.2 The narrow bore column 3 cannot accept the thermal desorption gas flow, and a cryogenic interface is required. This interface (Tekmar Model 1000 or equivalent) condenses the desorbed sample components at liquid nitrogen temperature, and allows the helium gas to pass through to an exit. The condensed components are frozen in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed from the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed with a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.3.4 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 260 amu with a complete scan cycle time (including scan overhead) of 2 sec or less. (Scan cycle time = Total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC. An average spectrum across the BFB GC peak may be used to test instrument performance.

6.3.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software should also allow calculation of response factors as defined in Sect. 9.2.6 (or construction of a second or third order regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Sect. 12.

6.4 SYRINGE AND SYRINGE VALVES

6.4.1 Two 5-mL or 25-mL glass hypodermic syringes with Luer-Lok tip (depending on sample volume used).

6.4.2 Three 2-way syringe valves with Luer ends.

6.4.3 One 25-μL micro syringe with a 2 in x 0.006 in ID, 22° bevel needle (Hamilton #702N or equivalent).

6.4.4 Micro syringes - 10, 100 μL.

6.4.5 Syringes - 0.5, 1.0, and 5-mL, gas tight with shut-off valve.

6.5 MISCELLANEOUS

6.5.1 Standard solution storage containers -- 15-mL bottles with PTFE-lined screw caps.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 TRAP PACKING MATERIALS

7.1.1 2,6-Diphenylene oxide polymer, 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

7.1.2 Methyl silicone packing (optional) -- OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

7.1.3 Silica gel -- 35/60 mesh, Davison, grade 15 or equivalent.

7.1.4 Coconut charcoal -- Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

7.2 REAGENTS

7.2.1 Methanol -- Demonstrated to be free of analytes.

7.2.2 Reagent water -- Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 min followed by a 1-h purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1) -- Carefully add measured volume of conc. HCl to equal volume of reagent water.

7.2.4 Vinyl chloride -- Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are available from several

sources (for example, Matheson, Ideal Gas Products, and Scott Gases).

7.2.5 Ascorbic acid -- ACS reagent grade, granular.

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures. One of these solutions is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1-5 mg/mL.

7.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

7.3.2 If the analyte is a liquid at room temperature, use a 100-μL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The gas will rapidly dissolve in the methanol.

7.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

7.3.4 Store stock standard solutions in 15-mL bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at 4°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at <0°C; at room temperature, they must be discarded after 1 day.

7.4 PRIMARY DILUTION STANDARDS -- Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern and the surrogates (but not the internal standard!) in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions in Sect. 7.4.4 also apply to primary dilution standard solutions.

7.5 FORTIFICATION SOLUTIONS FOR INTERNAL STANDARD AND SURROGATES

7.5.1 A solution containing the internal standard and the surrogates is required to prepare laboratory reagent blanks (also used as a laboratory performance check solution), and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2- dichlorobenzene-d_4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 µg/mL of each. A 5-µL aliquot of this solution added to a 25-mL water sample volume gives concentrations of 1 µg/L of each. A 5-µL aliquot of this solution added to a 5-mL water sample volume gives a concentration of 5 µg/L of each). Additional internal standrds and surrogate analytes are optional.

7.5.2 A solution of the internal standard alone is required to prepare calibration standards and laboratory fortified blanks. The internal standard should be in methanol at a concentration of 5 µg/mL.

7.6 PREPARATION OF LABORATORY REAGENT BLANK -- Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject 10 µL of the fortification solution containing the internal standard and surrogates through the Luer Lok valve into the reagent water. Transfer the LRB to the purging device. See Sect. 11.1.2.

7.7 PREPARATION OF LABORATORY FORTIFIED BLANK -- Prepare this exactly like a calibration standard (Sect. 7.8). This is a calibration standard that is treated as a sample.

7.8 PREPARATION OF CALIBRATION STANDARDS

7.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. A minimum of three CAL solutions is required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards, and for a factor of 100 at least five standards. One calibration standard should contain each analyte of concern and each surrogate at a concentration of 2-10 times the method detection limit (Tables 4-6) for that compound. The other CAL standards should contain each analyte of concern and each surrogate at concentrations that define the range of the method. Every CAL solution contains the internal standard at the same concentration (5 µg/L suggested for a 5-mL sample; 1 µg/L for a 25-mL sample).

7.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard (containing analytes and surrogates) to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the

flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hr unless transferred to a sample bottle and sealed immediately.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION, DECHLORINATION, AND PRESERVATION

8.1.1 Collect all samples in duplicate. If samples contain residual chlorine, and measurements of the concentrations of disinfection by-products (trihalomethanes, etc.) at the time of sample collection are desired, add about 25 mg of ascorbic acid to the sample bottle before filling. Fill sample bottles to overflowing, but take care not to flush out the rapidly dissolving ascorbic acid. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Adjust the pH of the duplicate samples to <2 by carefully adding one drop of 1:1 HCl for each 20 mL of sample volume. Seal the sample bottles, PFTE-face down, and shake vigorously for 1 min.

8.1.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

8.1.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill duplicate sample bottles from the 1-quart container.

8.1.4 The samples must be chilled to 4°C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4°C on arrival at the laboratory.

8.2 SAMPLE STORAGE

8.2.1 Store samples at 4°C until analysis. The sample storage area must be free of organic solvent vapors.

8.2.2 Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

8.3 FIELD REAGENT BLANKS

8.3.1 Duplicate field reagent blanks must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent

water, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks.

8.3.2 Use the same procedures used for samples to add ascorbic acid and HCl to blanks (Sect. 8.1.1).

9. CALIBRATION

9.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8 hr. period during which analyses are performed. Additional periodic calibration checks are good laboratory practice.

9.2 Initial calibration

9.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Sect. 9.2.2.

9.2.2 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng of BFB and acquire mass spectra for m/z 35-260 at 70 eV (nominal). Use the purging procedure and/or GC conditions given in Sect. 11. If the spectrum does not meet all criteria in Table 2, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

9.2.3 Purge a medium CAL solution, for example 10-20 μg/L, using the procedure given in Sect. 11.

9.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software. Figure 3 shows an acceptable total ion chromatogram.

9.2.4.1 GC performance. Good column performance will produce symmetrical peaks with minimum tailing for most compounds. If peaks are broad, or sensitivity poor, see Sect. 9.3.6 for some possible remedial actions.

9.2.4.2 MS sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in calibration solution, and make correct tentative identifications. If fewer than 99% of the

compounds are recognized, system maintenance is required. See Sect. 9.3.6.

9.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

9.2.6 Calculate a response factor (RF) for each analyte, surrogate, and isomer pair for each CAL solution using the internal standard fluorobenzene. Table 1 contains suggested quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Sect. 6.3.4), and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte.
A_{is} = integrated abundance of the quantitation ion of the internal standard.
Q_x = quantity of analyte purged in ng or concentration units.
Q_{is} = quantity of internal standard purged in ng or concentration units.

9.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Sect. 9.2.7.

9.2.7 As an alternative to calculating mean response factors and applying the RSD test, use the GC/MS data system software or other available software to generate a second or third order regression calibration curve.

9.3 Continuing calibration check. Verify the MS tune and initial calibration at the beginning of each 8-hr work shift during which analyses are performed using the following procedure.

9.3.1 Introduce into the GC (either by purging a laboratory reagent blank or making a syringe injection) 25 ng of BFB and acquire a mass spectrum that includes data for m/z 35-260. If the spectrum does not meet all criteria (Table 2), the MS must be

retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

9.3.2 Purge a medium concentration CAL solution and analyze with the same conditions used during the initial calibration.

9.3.3 Demonstrate acceptable performance for the criteria shown in Sect. 9.2.4.

9.3.4 Determine that the absolute areas of the quantitation ions of the internal standard and surrogates have not decreased by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Sect. 9.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

9.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a second or third order regression is used, the point from the continuing calibration check for each analyte and surrogate must fall, within the analyst's judgement, on the curve from the initial calibration. If these conditions do not exist, remedial action must be taken which may require re-initial calibration.

9.3.6 Some possible remedial actions. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, etc. require returning to the initial calibration step.

9.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

9.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

9.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

9.3.6.4 Break off a short portion (about 1 meter) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

9.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

9.3.6.6 Clean the MS ion source and rods (if a quadrupole).

9.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

9.3.6.8 Replace the MS electron multiplier, or any other faulty components.

9.4 Optional calibration for vinyl chloride using a certified gaseous mixture of vinyl chloride in nitrogen can be accomplished by the following steps.

9.4.1 Fill the purging device with 25.0 mL (or 5-mL) of reagent water or aqueous calibration standard.

9.4.2 Start to purge the aqueous mixture. Inject a known volume (between 100 and 2000 µL) of the calibration gas (at room temperature) directly into the purging device with a gas tight syringe. Slowly inject the gaseous sample through a septum seal at the top of the purging device at 2000 µL/min. If the injection of the standard is made through the aqueous sample inlet port, flush the dead volume with several mL of room air or carrier gas. Inject the gaseous standard before 5 min of the 11-min purge time have elapsed.

9.4.3 Determine the aqueous equivalent concentration of vinyl chloride standard, in µg/L, injected with the equation:

$$S = 0.102\ (C)(V)$$

where S = Aqueous equivalent concentration of vinyl chloride standard in µg/L;
C = Concentration of gaseous standard in ppm (v/v);
V = Volume of standard injected in milliliters.

10. QUALITY CONTROL

10.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

10.2 Initial demonstration of low system background. Before any samples are analyzed, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. Sources of background contamination are glassware, purge gas, sorbants, and equipment. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limit.

10.3 Initial demonstration of laboratory accuracy and precision. Analyze five to seven replicates of a laboratory fortified blank containing each analyte of concern at a concentration in the range of 0.2-5 µg/L (see regulations and maximum contaminant levels for guidance on appropriate concentrations).

10.3.1 Prepare each replicate by adding an appropriate aliquot of a quality control sample to reagent water. If a quality control sample containing the method analytes is not available, a primary dilution standard made from a source of reagents different than those used to prepare the calibration standards may be used. Also add the appropriate amounts of internal standard and surrogates if they are being used. Analyze each replicate according to the procedures described in Section 11, and on a schedule that results in the analyses of all replicates over a period of several days.

10.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte. Calculate the MDL of each analyte using the procedures described in Sect. 13.2 (2).

10.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 80-120% and the RSD should be <20%. Some analytes, particularly the early eluting gases and late eluting higher molecular weight compounds, are measured with less accuracy and precision than other analytes. The method detection limits must be sufficient to detect analytes at the required levels. If these criteria are not met for an analyte, take remedial action and repeat the measurements for that analyte to demonstrate acceptable performance before samples are analyzed.

10.3.4 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

10.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks. These should remain reasonably constant over time. A drift of more than 50% in any area is indicative of a loss in sensitivity, and the problem must be found and corrected. These integrated areas should also be reasonably constant in laboratory fortified blanks and samples.

11.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY -- Acquire and store data over the mass range 35-260 with a total cycle time (including scan overhead time) of 2 sec or less. Cycle time must be adjusted to measure five or more spectra during the elution of each GC peak. Several alternative temperature programs can be used.

11.3.1 Single ramp linear temperature program for wide bore columns 1 and 2 with a jet separator. Adjust the helium carrier gas flow rate to about 15 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of desorption, then programmed to 160°C at 6°C/min, and held until all components have eluted.

11.3.2 Multi-ramp linear temperature program for wide bore column 2 with the open split interface. Adjust the helium carrier gas flow rate to about 4.6 mL/min. The column temperature is reduced 10°C and held for 6 min from the beginning of desorption, then heated to 70°C at 10°/min, heated to 120°C at 5°/min, heated to 180° at 8°/min, and held at 180° until all compounds have eluted.

11.3.3 Single ramp linear temperature program for narrow bore column 3 with a cryogenic interface. Adjust the helium carrier gas flow rate to about 4 mL/min. The column temperature is reduced 10°C and held for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°C/min for 10 min, then 15°C/min for 5 min to 145°C, and held until all components have eluted.

11.4 TRAP RECONDITIONING -- After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 sec, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.5 TERMINATION OF DATA ACQUISITION -- When all the sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as a function of time. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

11.6 IDENTIFICATION OF ANALYTES -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

11.6.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 Identification requires expert judgement when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.6.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not acceptable because the concentration of the background in the blank is highly variable.

12. CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation.

12.1.1 Calculate analyte and surrogate concentrations.

$$C_x = \frac{(A_x)(Q_{is})\ 1000}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample.
A_x = integrated abundance of the quantitation ion of the analyte in the sample.
A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample.
Q_{is} = total quantity (in micrograms) of internal standard added to the water sample.
V = original water sample volume in mL.
RF = mean response factor of analyte from the initial calibration.

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the second or third order regression curves.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1- 99 µg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations in µg/L.

13. ACCURACY AND PRECISION

13.1 Single laboratory accuracy and precision data were obtained for the method analytes using laboratory fortified blanks with analytes at concentrations between 1 and 5 µg/L. Four sets of results were obtained using the three columns specified (Sect. 6.3.2) and the open split, cryogenic, and jet separator interfaces (Sect. 6.3.3). These data are shown in Tables 4-6.

13.2 With these data, method detection limits were calculated using the formula (2):

$$MDL = S\ t_{(n-1,1\text{-alpha} = 0.99)}$$

where:

$t_{(n-1,1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates

S = the standard deviation of the replicate analyses.

14. REFERENCES

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TABLE 1. MOLECULAR WEIGHTS AND QUANTITATION IONS FOR METHOD ANALYTES

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
Internal standard			
Fluorobenzene	96	96	77
Surrogates			
4-Bromofluorobenzene	174	95	174,176
1,2-Dichlorobenzene-d4	150	152	115,150
Target Analytes			
Benzene	78	78	77
Bromobenzene	156	156	77,158
Bromochloromethane	128	128	49,130
Bromodichloromethane	162	83	85,127
Bromoform	250	173	175,252
Bromomethane	94	94	96
n-Butylbenzene	134	91	134
sec-Butylbenzene	134	105	134
tert-Butylbenzene	134	119	91
Carbon tetrachloride	152	117	119
Chlorobenzene	112	112	77,114
Chloroethane	64	64	66
Chloroform	118	83	85
Chloromethane	50	50	52
2-Chlorotoluene	126	91	126
4-Chlorotoluene	126	91	126
Dibromochloromethane	206	129	127
1,2-Dibromo-3-Chloropropane	234	75	155,157
1,2-Dibromoethane	186	107	109,188
Dibromomethane	172	93	95,174
1,2-Dichlorobenzene	146	146	111,148
1,3-Dichlorobenzene	146	146	111,148
1,4-Dichlorobenzene	146	146	111,148
Dichlorodifluoromethane	120	85	87
1,1-Dichloroethane	98	63	65,83
1,2-Dichloroethane	98	62	98
1,1-Dichloroethene	96	96	61,63
cis-1,2-Dichloroethene	96	96	61,98
trans-1,2-Dichloroethene	96	96	61,98
1,2-Dichloropropane	112	63	112
1,3-Dichloropropane	112	76	78
2,2-Dichloropropane	112	77	97
1,1-Dichloropropene	110	75	110,77

TABLE 1. (continued)

Compound	MW[a]	Primary Quantitation Ion	Secondary Quantitation Ions
cis-1,3-dichloropropene	110	75	110
trans-1,3-dichloropropene	110	75	110
Ethylbenzene	106	91	106
Hexachlorobutadiene	258	225	260
Isopropylbenzene	120	105	120
4-Isopropyltoluene	134	119	134,91
Methylene chloride	84	84	86,49
Naphthalene	128	128	
n-Propylbenzene	120	91	120
Styrene	104	104	78
1,1,1,2-Tetrachloroethane	166	131	133,119
1,1,2,2-Tetrachloroethane	166	83	131,85
Tetrachloroethene	164	166	168,129
Toluene	92	92	91
1,2,3-Trichlorobenzene	180	180	182
1,2,4-Trichlorobenzene	180	180	182
1,1,1-Trichloroethane	132	97	99,61
1,1,2-Trichloroethane	132	83	97,85
Trichloroethene	130	95	130,132
Trichlorofluoromethane	136	101	103
1,2,3-Trichloropropane	146	75	77
1,2,4-Trimethylbenzene	120	105	120
1,3,5-Trimethylbenzene	120	105	120
Vinyl Chloride	62	62	64
o-Xylene	106	106	91
m-Xylene	106	106	91
p-Xylene	106	106	91

[a]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.

TABLE 2. CHROMATOGRAPHIC RETENTION TIMES FOR METHOD ANALYTES ON THREE COLUMNS WITH FOUR SETS OF CONDITIONS[a]

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]
Internal standard				
Fluorobenzene	8:49	6:27	14:06	8:03
Surrogates				
4-Bromofluorobenzene	18:38	15:43	23:38	
1,2-Dichlorobenzene-d4	22:16	19:08	27:25	
Target Analytes				
Benzene	8:14	5:40	13:30	7:25
Bromobenzene	18:57	15:52	24:00	16:25
Bromochloromethane	6:44	4:23	12:22	5:38
Bromodichloromethane	10:35	8:29	15:48	9:20
Bromoform	17:56	14:53	22:46	15:42
Bromomethane	2:01	0:58	4:48	1:17
n-Butylbenzene	22:13	19:29	27:32	17:57
sec-Butylbenzene	20:47	18:05	26:08	17:28
tert-Butylbenzene	20:17	17:34	25:36	17:19
Carbon Tetrachloride	7:37	5:16	13:10	7:25
Chlorobenzene	15:46	13:01	20:40	14:20
Chloroethane	2:05	1:01		1:27
Chloroform	6:24	4:48	12:36	5:33
Chloromethane	1:38	0:44	3:24	0:58
2-Chlorotoluene	19:20	16:25	24:32	16:44
4-Chlorotoluene	19:30	16:43	24:46	16:49
Cyanogen chloride				1:03
Dibromochloromethane	14:23	11:51	19:12	12:48
1,2-Dibromo-3-Chloropropane	24:32	21:05		18:02
1,2-Dibromoethane	14:44	11:50	19:24	13:36
Dibromomethane	10:39	7:56	15:26	9:05
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38
Dichlorodifluoromethane	1:33	0:42	3:08	0:53
1,1-Dichloroethane	4:51	2:56	10:48	4:02
1,2-Dichloroethane	8:24	5:50	13:38	7:00
1,1-Dichloroethene	2:53	1:34	7:50	2:20
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32
1,2-Dichloropropane	10:05	7:40	15:12	8:56
1,3-Dichloropropane	14:02	11:19	18:42	12:29
2,2-Dichloropropane	6:01	3:48	11:52	5:19
1,1-Dichloropropene	7:49	5:17	13:06	7:10

TABLE 2. (continued)

Compound	Retention Time (min:sec) Column 1[b]	Column 2[b]	Column 2[c]	Column 3[d]
cis-1,3-dichloropropene			17:54	
trans-1,3-dichloropropene			16:42	
Ethylbenzene	15:59	13:23	21:00	14:44
Hexachlorobutadiene	26:59	23:41	32:04	19:14
Isopropylbenzene	18:04	15:28	23:18	16:25
4-Isopropyltoluene	21:12	18:31	26:30	17:38
Methylene Chloride	3:36	2:04	9:16	2:40
Naphthalene	27:10	23:31	32:12	19:04
n-Propylbenzene	19:04	16:25	24:20	16:49
Styrene	17:19	14:36	22:24	15:47
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47
Tetrachloroethene	13:44	11:09	18:36	13:12
Toluene	12:26	10:00	17:24	11:31
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59
Trichloroethene	9:35	7:16	14:48	9:01
Trichlorofluoromethane	2:16	1:11	6:12	1:46
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59
Vinyl chloride	1:43	0:47	3:56	1:02
o-Xylene	17:07	14:31	22:16	15:47
m-Xylene	16:10	13:41	21:22	15:18
p-Xylene	16:07	13:41	21:18	15:18

[a]Columns 1-3 are those given in Sect. 6.3.2.1; retention times were measured from the beginning of thermal desorption from the trap (columns 1-2) or from the beginning of thermal release from the cryogenic interface (column 3).
[b]GC conditions given in Sect. 11.3.1.
[c]GC conditions given in Sect. 11.3.2.
[d]GC conditions given in Sect. 11.3.3.

TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE (BFB)

Mass (M/Z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

TABLE 4. ACCURACY AND PRECISION DATA FROM 16-31 DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 1[a]

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
Benzene	0.1-10	97	5.7	0.04
Bromobenzene	0.1-10	100	5.5	0.03
Bromochloromethane	0.5-10	90	6.4	0.04
Bromodichloromethane	0.1-10	95	6.1	0.08
Bromoform	0.5-10	101	6.3	0.12
Bromomethane	0.5-10	95	8.2	0.11
n-Butylbenzene	0.5-10	100	7.6	0.11
sec-Butylbenzene	0.5-10	100	7.6	0.13
tert-Butylbenzene	0.5-10	102	7.3	0.14
Carbon tetrachloride	0.5-10	84	8.8	0.21
Chlorobenzene	0.1-10	98	5.9	0.04
Chloroethane	0.5-10	89	9.0	0.10
Chloroform	0.5-10	90	6.1	0.03
Chloromethane	0.5-10	93	8.9	0.13
2-Chlorotoluene	0.1-10	90	6.2	0.04
4-Chlorotoluene	0.1-10	99	8.3	0.06
Dibromochloromethane	0.1-10	92	7.0	0.05
1,2-Dibromo-3-chloropropane	0.5-10	83	19.9	0.26
1,2-Dibromoethane	0.5-10	102	3.9	0.06
Dibromomethane	0.5-10	100	5.6	0.24
1,2-Dichlorobenzene	0.1-10	93	6.2	0.03
1,3-Dichlorobenzene	0.5-10	99	6.9	0.12
1,4-Dichlorobenzene	0.2-20	103	6.4	0.03
Dichlorodifluoromethane	0.5-10	90	7.7	0.10
1,1-Dichloroethane	0.5-10	96	5.3	0.04
1,2-Dichloroethane	0.1-10	95	5.4	0.06
1,1-Dichloroethene	0.1-10	94	6.7	0.12
cis-1,2 Dichloroethene	0.5-10	101	6.7	0.12
trans-1,2-Dichloroethene	0.1-10	93	5.6	0.06
1,2-Dichloropropane	0.1-10	97	6.1	0.04
1,3-Dichloropropane	0.1-10	96	6.0	0.04
2,2-Dichloropropane	0.5-10	86	16.9	0.35
1,1-Dichloropropene	0.5-10	98	8.9	0.10
cis-1,2-Dichloropropene				
trans-1,2-Dichloropropene				
Ethylbenzene	0.1-10	99	8.6	0.06
Hexachlorobutadiene	0.5-10	100	6.8	0.11
Isopropylbenzene	0.5-10	101	7.6	0.15
4-Isopropyltoluene	0.1-10	99	6.7	0.12
Methylene chloride	0.1-10	95	5.3	0.03
Naphthalene	0.1-100	104	8.2	0.04
n-Propylbenzene	0.1-10	100	5.8	0.04
Styrene	0.1-100	102	7.2	0.04

TABLE 4. (Continued)

Compound	True Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Det. Limit (µg/L)
1,1,1,2-Tetrachloroethane	0.5-10	90	6.8	0.05
1,1,2,2-Tetrachloroethane	0.1-10	91	6.3	0.04
Tetrachloroethene	0.5-10	89	6.8	0.14
Toluene	0.5-10	102	8.0	0.11
1,2,3-Trichlorobenzene	0.5-10	109	8.6	0.03
1,2,4-Trichlorobenzene	0.5-10	108	8.3	0.04
1,1,1-Trichloroethane	0.5-10	98	8.1	0.08
1,1,2-Trichloroethane	0.5-10	104	7.3	0.10
Trichloroethene	0.5-10	90	7.3	0.19
Trichlorofluoromethane	0.5-10	89	8.1	0.08
1,2,3-Trichloropropane	0.5-10	108	14.4	0.32
1,2,4-Trimethylbenzene	0.5-10	99	8.1	0.13
1,3,5-Trimethylbenzene	0.5-10	92	7.4	0.05
Vinyl chloride	0.5-10	98	6.7	0.17
o-Xylene	0.1-31	103	7.2	0.11
m-Xylene	0.1-10	97	6.5	0.05
p-Xylene	0.5-10	104	7.7	0.13

[a]Data obtained by Robert W. Slater using column 1 with a jet separator interface and a quadrupole mass spectrometer (Sect. 11.3.1) with analytes divided among three solutions.

TABLE 5. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING THE CRYOGENIC TRAPPING OPTION AND A NARROW BORE CAPILLARY COLUMN 3[a]

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
Benzene	0.1	99	6.2	0.03
Bromobenzene	0.5	97	7.4	0.11
Bromochloromethane	0.5	97	5.8	0.07
Bromodichloromethane	0.1	100	4.6	0.03
Bromoform	0.1	99	5.4	0.20
Bromomethane	0.1	99	7.1	0.06
n-Butylbenzene	0.5	94	6.0	0.03
sec-Butylbenzene	0.5	90	7.1	0.12
tert-Butylbenzene	0.5	90	2.5	0.33
Carbon tetrachloride	0.1	92	6.8	0.08
Chlorobenzene	0.1	91	5.8	0.03
Chloroethane	0.1	100	5.8	0.02
Chloroform	0.1	95	3.2	0.02
Chloromethane	0.1	99	4.7	0.05
2-Chlorotoluene	0.1	99	4.6	0.05
4-Chlorotoluene	0.1	96	7.0	0.05
Cyanogen chloride[b]		92	10.6	0.30
Dibromochloromethane	0.1	99	5.6	0.07
1,2-Dibromo-3-chloropropane	0.1	92	10.0	0.05
1,2-Dibromoethane	0.1	97	5.6	0.02
Dibromomethane	0.1	93	6.9	0.03
1,2-Dichlorobenzene	0.1	97	3.5	0.05
1,3-Dichlorobenzene	0.1	99	6.0	0.05
1,4-Dichlorobenzene	0.1	93	5.7	0.04
Dichlorodifluoromethane	0.1	99	8.8	0.11
1,1-Dichloroethane	0.1	98	6.2	0.03
1,2-Dichloroethane	0.1	100	6.3	0.02
1,1-Dichloroethene	0.1	95	9.0	0.05
cis-1,2 Dichloroethene	0.1	100	3.7	0.06
trans-1,2-Dichloroethene	0.1	98	7.2	0.03
1,2-Dichloropropane	0.1	96	6.0	0.02
1,3-Dichloropropane	0.1	99	5.8	0.04
2,2-Dichloropropane	0.1	99	4.9	0.05
1,1-Dichloropropene	0.1	98	7.4	0.02
cis-1,3-Dichloropropene				
trans-1,3-Dichloropropene				
Ethylbenzene	0.1	99	5.2	0.03
Hexachlorobutadiene	0.1	100	6.7	0.04
Isopropylbenzene	0.5	98	6.4	0.10
4-Isopropyltoluene	0.5	87	13.0	0.26
Methylene chloride	0.5	97	13.0	0.09
Naphthalene	0.1	98	7.2	0.04

TABLE 5. (Continued)

Compound	True Conc. (µg/L)	Mean Accuracy (% of True Value)	Rel. Std. Dev. (%)	Method Dect. Limit (µg/L)
n-Propylbenzene	0.1	99	6.6	0.06
Styrene	0.1	96	19.0	0.06
1,1,1,2-Tetrachloroethane	0.1	100	4.7	0.04
1,1,2,2-Tetrachloroethane	0.5	100	12.0	0.20
Tetrachloroethene	0.1	96	5.0	0.05
Toluene	0.1	100	5.9	0.08
1,2,3-Trichlorobenzene	0.1	98	8.9	0.04
1,2,4-Trichlorobenzene	0.1	91	16.0	0.20
1,1,1-Trichloroethane	0.1	100	4.0	0.04
1,1,2-Trichloroethane	0.1	98	4.9	0.03
Trichloroethene	0.1	96	2.0	0.02
Trichlorofluoromethane	0.1	97	4.6	0.07
1,2,3-Trichloropropane	0.1	96	6.5	0.03
1,2,4-Trimethylbenzene	0.1	96	6.5	0.04
1,3,5-Trimethylbenzene	0.1	99	4.2	0.02
Vinyl chloride	0.1	96	0.2	0.04
o-Xylene	0.1	94	7.5	0.06
m-Xylene	0.1	94	4.6	0.03
p-Xylene	0.1	97	6.1	0.06

[a]Data obtained by Caroline A. Madding using column 3 with a cryogenic interface and a quadrupole mass spectrometer (Sect 11.3.3).
[b]Reference 8.

TABLE 6. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING WIDE BORE CAPILLARY COLUMN 2[a]

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
Internal Standard					
Fluorobenzene	1	-	-	-	-
Surrogates					
4-Bromofluorobenzene	2	98	1.8	96	1.3
1,2-Dichlorobenzene-d_4	3	97	3.2	95	1.7
Target Analytes					
Benzene	37	97	4.4	113	1.8
Bromobenzene	38	102	3.0	101	1.9
Bromochloromethane	4	99	5.2	102	2.9
Bromodichloromethane	5	96	1.8	100	1.8
Bromoform	6	89	2.4	90	2.2
Bromomethane	7	55	27.	52	6.7
n-Butylbenzene	39	89	4.8	87	2.3
sec-Butylbenzene	40	102	3.5	100	2.8
tert-Butylbenzene	41	101	4.5	100	2.9
Carbon tetrachloride	8	84	3.2	92	2.6
Chlorobenzene	42	104	3.1	103	1.6
Chloroethane[c]					
Chloroform	9	97	2.0	95	2.1
Chloromethane	10	110	5.0	d	
2-Chlorotoluene	43	91	2.4	108	3.1
4-Chlorotoluene	44	89	2.0	108	4.4
Dibromochloromethane	11	95	2.7	100	3.0
1,2-Dibromo-3-chloropropane[c]					
1,2-Dibromoethane[c]					
Dibromomethane	13	99	2.1	95	2.2
1,2-Dichlorobenzene	45	93	2.7	94	5.1
1,3-Dichlorobenzene	46	100	4.0	87	2.3
1,4-Dichlorobenzene	47	98	4.1	94	2.8
Dichlorodifluoromethane	14	38	25.	d	
1,1-Dichloroethane	15	97	2.3	85	3.6
1,2-Dichloroethane	16	102	3.8	100	2.1
1,1-Dichloroethene	17	90	2.2	87	3.8
cis-1,2-Dichloroethene	18	100	3.4	89	2.9
trans-1,2-Dichloroethene	19	92	2.1	85	2.3

TABLE 6. (Continued)

Compound	No.[b]	Mean Accuracy (% of True Value, 2 µg/L Conc.)	RSD (%)	Mean Accuracy (% of True Value, 0.2 µg/L Conc.)	RSD (%)
1,2-Dichloropropane	20	102	2.2	103	2.9
1,3-Dichloropropane	21	92	3.7	93	3.2
2,2-Dichloropropane[c]					
1,1-Dichloropropene[c]					
cis-1,3-Dichloropropene[c]					
trans-1,3-Dichloropropene	25	96	1.7	99	2.1
Ethylbenzene	48	96	9.1	100	4.0
Hexachlorobutadiene	26	91	5.3	88	2.4
Isopropylbenzene	49	103	3.2	101	2.1
4-Isopropyltoluene	50	95	3.6	95	3.1
Methylene chloride	27	e		e	
Naphthalene	51	93	7.6	78	8.3
n-Propylbenzene	52	102	4.9	97	2.1
Styrene	53	95	4.4	104	3.1
1,1,1,2-Tetrachloroethane	28	99	2.7	95	3.8
1,1,2,2-Tetrachloroethane	29	101	4.6	84	3.6
Tetrachloroethene	30	97	4.5	92	3.3
Toluene	54	105	2.8	126	1.7
1,2,3-Trichlorobenzene	55	90	5.7	78	2.9
1,2,4-Trichlorobenzene	56	92	5.2	83	5.9
1,1,1-Trichloroethane	31	94	3.9	94	2.5
1,1,2-Trichloroethane	32	107	3.4	109	2.8
Trichloroethene	33	99	2.9	106	2.5
Trichlorofluoromethane	34	81	4.6	48	13.
1,2,3-Trichloropropane	35	97	3.9	91	2.8
1,2,4-Trimethylbenzene	57	93	3.1	106	2.2
1,3,5-Trimethylbenzene	58	88	2.4	97	3.2
Vinyl chloride	36	104	3.5	115	14.
o-Xylene	59	97	1.8	98	1.7
m-Xylene	60	f		f	
p-Xylene	61	98	2.3	103	1.4

[a]Data obtained by James W. Eichelberger using column 2 with the open split interface and an ion trap mass spectrometer (Sect. 11.3.2) with all method analytes in the same reagent water solution.
[b]Designation in Figures 1 and 2.
[c]Not measured; authentic standards were not available.
[d]Not found at 0.2 µg/L.
[e]Not measured; methylene chloride was in the laboratory reagent blank.
[f]m-xylene coelutes with and cannot be distinguished from its isomer p-xylene, No 61.

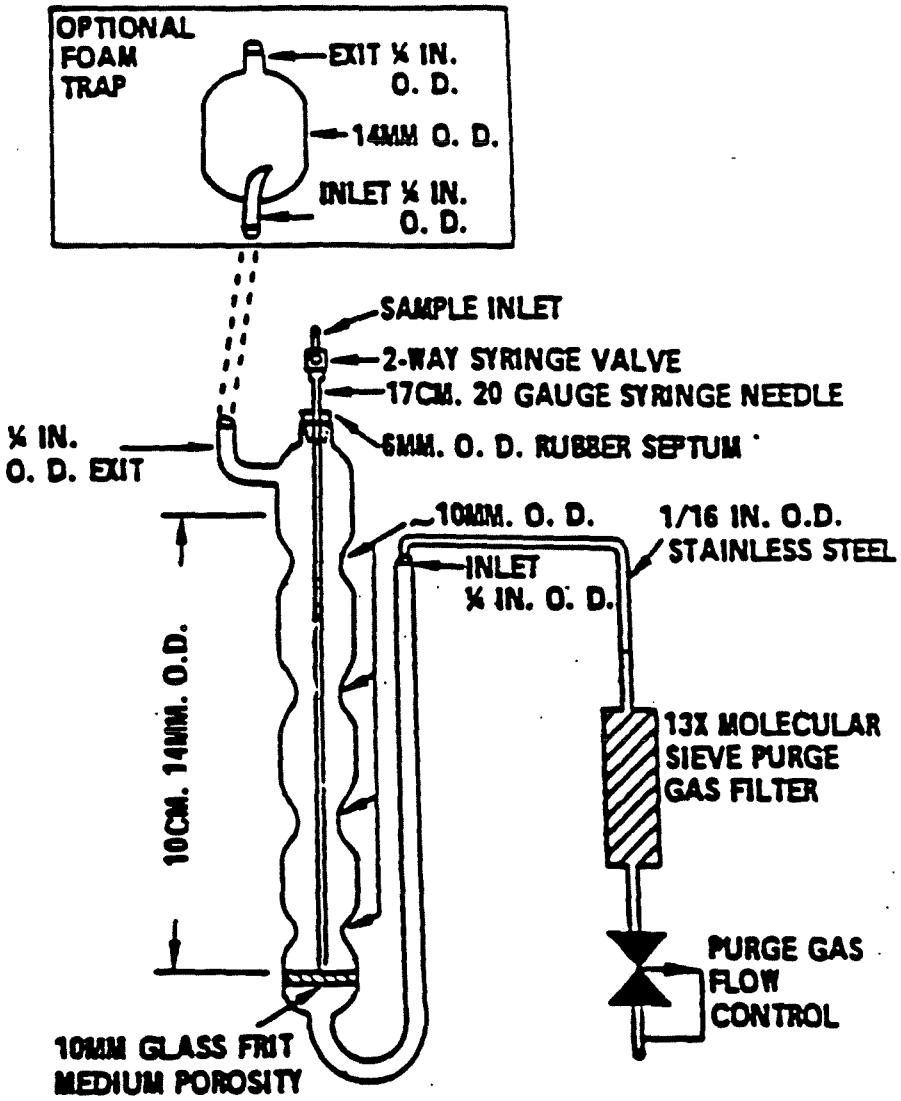


FIGURE 1. PURGING DEVICE

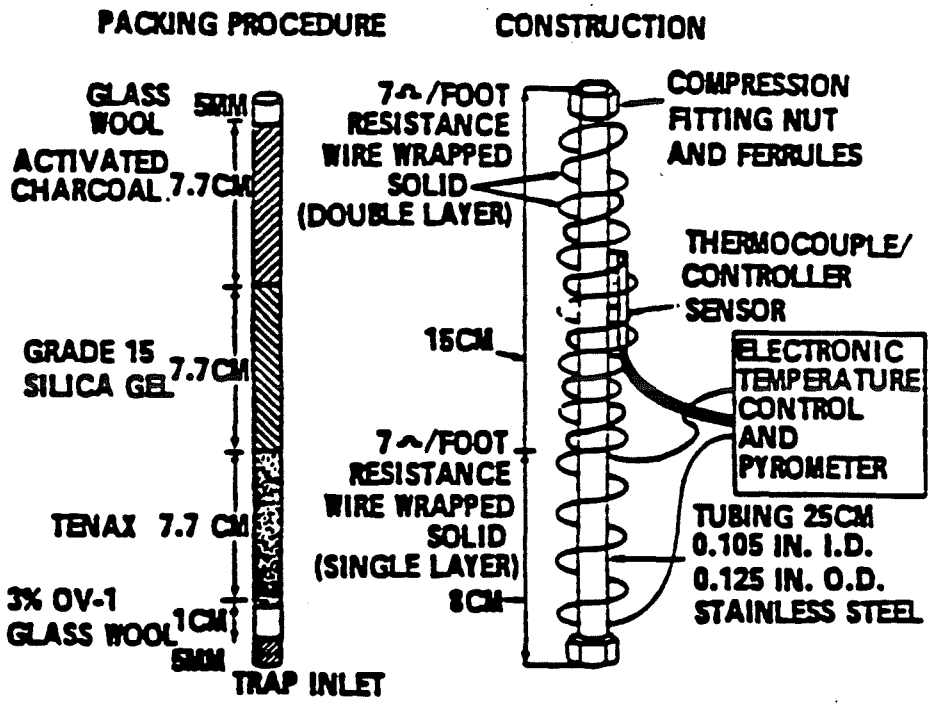


FIGURE 2. TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

FIGURE 3. NORMALIZED TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF MOST COMPOUNDS. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.

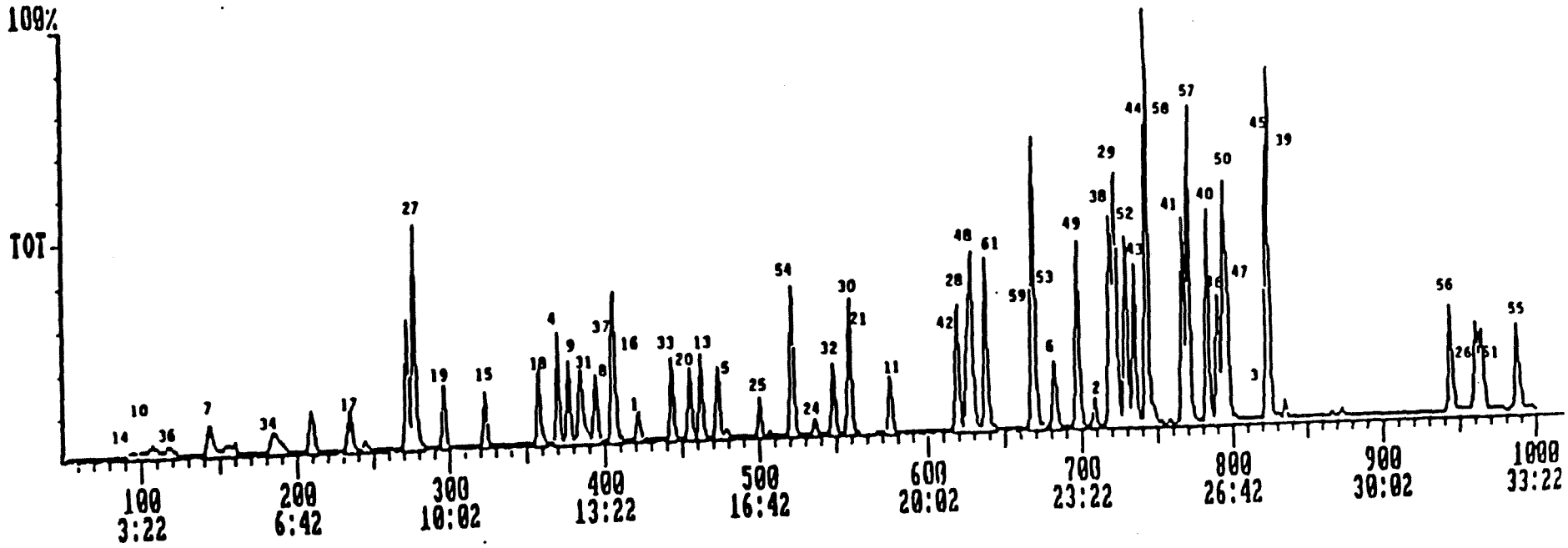
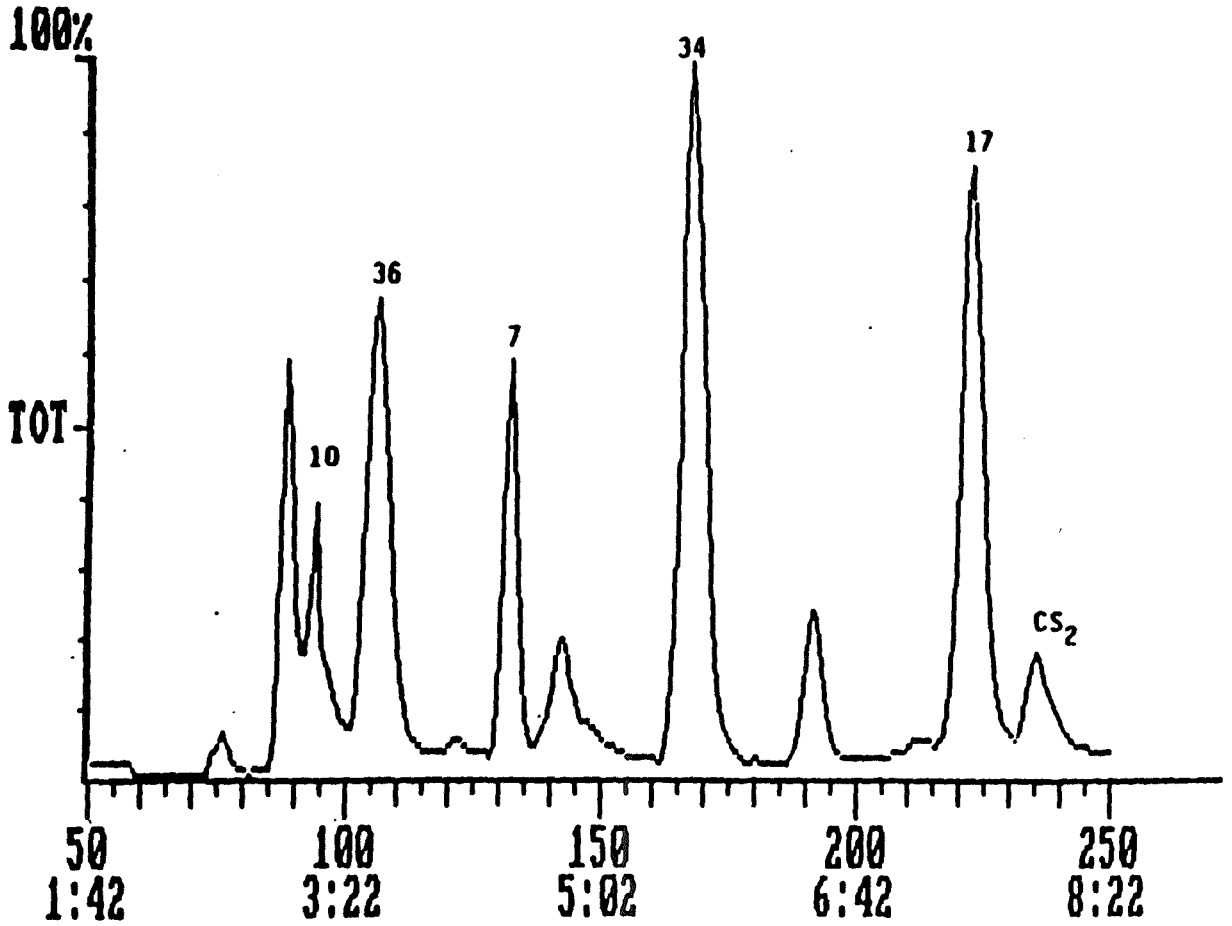


FIGURE 4. AMPLIFIED FIRST EIGHT MINUTES OF A TOTAL ION CURRENT CHROMATOGRAM FROM A VOLATILE COMPOUND CALIBRATION MIXTURE CONTAINING 25 ng (5 µg/L) OF EACH COMPONENT. THE COMPOUND IDENTIFICATION NUMBERS ARE GIVEN IN TABLE 6.



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Chicago, IL 60605
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SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :_____
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of monitoring wells, extraction wells, and residential wells for select metals with detection limits lower than those provided by the ILM03.0 SOW.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Sixteen monitoring, extraction, and residential well samples will be collected during each sampling event. The aqueous samples will be analyzed for medium to low concentrations of filterable metals. The projected number is inclusive of QA samples.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund Remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

The following metals, with the listed detection limits, will be analyzed by trace inductively coupled plasma or graphite furnace atomic absorption (GFAA) (EPA SW-846 7000 series methods);

Analyte	Detection Limits (µg/L)
Arsenic	5
Barium	200
Lead	1.5
Iron	100
Manganese	10

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe , detection limits, etc.):**

One liter of the aqueous sample will be collected and preserved with 5 ml of HNO_3 to a pH <2. Samples sho be stored at 4°C until the time of analysis.

Any sample remaining after digestion should be stored at 4°C until the validation and the acceptance sample result.

Sample holding time is 6 months from date of receipt.

Zeeman, Smith/Hieftje background correction or equivalent (not D_2) is required if GFAA analysis of arsenic is used.

Matrix modifiers are required for the analysis of arsenic.

The IDL must be shown to have been met prior to the analysis of any samples. The lab can accomplish this submitting their most recent form XI with each case.

Each calibration blank and QC audit solution must contain the same nitric acid concentration as the samples diluted samples.

The sample solutions analyzed must have their matrix concentration fully documented in the raw data.

Each analytical determination must have the resulting absorbance clearly recorded and documented in their o ar of determination.

The calibration range of the GFAA analyses can not be exceeded. Dilute any sample that does exceed calibration range.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Cust documentation, etc.). If not completed, format of results will be left to program discretion.**

The deliverables included in the SOW ILMO3.0 are required.

Current quarterly form XI, XII, and XIII for each element.

Form VIII must be modified to include the slope of each addition as well as the correlation coefficient.

Correct forms V, VI, and VII to reflect the SAS contract limits and IDL where appropriate.

10. Other (use additional sheets or attach supplementary information, as needed):

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitte to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airbill may be submitted with a record of the location of the originals, to the Region within the time frame listed in sectio 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- or conc.)
Preparation Blank	At least 1 per group of 10 or fewer samples	≤ IDL
Lab Duplicates	At least 1 per group of 10 or fewer samples	+ 25% or RPD is < or + to SAS IDL
Calibration Blank	At least 1 per group of 10 or fewer samples	≤ IDL
ICVs and CCVs	as per SOW ILM03.0	as per SOW ILM03.0
Matrix Spike/ Matrix Spike Duplicates	At least 1 per group of 20 or fewer samples	85-115% for aqueous samples and 75-125% for sediment samples
Lab Control Spike	1 per group of 10 or fewer samples	90-110% for aqueous samples and 75-125% for sediment samples

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

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SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

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B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of chloride in monitoring, extraction, and residential well samples. Results will be reported in mg/L chloride.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Sixteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium concentrations of chloride expressed in mg/L.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   1. EPA Method 325.1 (Colorimetric, Automated Ferricyanide, AA-I) 1983 ed., or

   2. EPA Method 325.2 (Colorimetric, Automated Ferricyanide, AA-II) 1983 ed.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sar manner until the validation and the acceptance of the sample result.

Sample holding time is 28 days from date of collection.

Use a standard curve between 0 and 200 mg/L or less.

The calibration curve should include 5 points or more (one of the standards must be a zero concentration).

Samples with absorbance or peak heights greater than the highest standard must be diluted and reanalyzed.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

The test procedure will be clearly identified. Bench records tabulating order of calibration standards, verificati and control standards, samples, matrix spikes, titrant blanks, etc. with resulting peak height, concentration, absorbance read-outs will be provided with copies of work-sheets used to calculate results. A photocopy of instrument readouts, (i.e., strip charts, printer tapes, etc.) must be included for all analysis. All records of analy and calculation must be legible and sufficient to recalculate all sample concentrations and QA audit results.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submit to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airbills may be submitted with a record of the location of the originals, to the Region within the time frame listed in s 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. **DATA REQUIREMENTS**

Parameter	Detection Limit	Precision Desired (+/- % or conc.
Chloride	5 mg/L	Difference in duplicate results should not exceed +/- 10% for concentrations >50 mg/L or < 2 mg/L for concentrations less than 50 mg/L. The significant figures to report depends on sensitivity of colorimetric curve or the number of significant figures in titrant volume.

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Calibration Verification Std.	At least 1 per group of 10 or fewer samples	90-110%
Lab Blank	At least 1 per group of 10 or fewer samples	< 5 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 2 mg/L
Matrix spike **	1 per group of 20 or fewer samples	85-115% Recovery

*See Section III

** Matrix spike concentrations will be greater than 30% of the sample concentration, but spiked sample shall n exceed the working range of the standard curve or titration.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

SASCHL.WP

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SAS Number

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C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for total organic carbon (TOC) in monitoring, extraction, and residential well samples. Most samples will be unfiltered, although certain aliquots can be filtered and preserved at the time of collection. Results will be reported as mg/L C.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Sixteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium concentrations of TOC expressed in mg/L C.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 415.1, the combustion method.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples will be preserved with 1 mL/L H_2SO_4 to ph <2.

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sam manner until the validation and the acceptance of the sample result.

Sample holding time is 28 days from date of receipt.

The calibration curve must include at least 5 standards (one of the standards must be a zero concentration).

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Test procedures and specific instrument conditions should be clearly identified. Bench records tabulating ord of calibration standards, lab blanks, samples, lab control standards, spikes, duplicates, etc., will be provided alon with copies of work-sheets used to calculate results. Specify the organic compound used to prepare standar and spikes. A photocopy of the instrument readout, (i.e. stripcharts, printer tapes, etc.) must be included. records of analysis must be legible and sufficient to recalculate all sample concentrations and QA audit results.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airb may be submitted with a record of the location of the originals, to the Region within the time frame listed in secti 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. <u>DATA REQUIREMENTS</u>

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Total Organic Carbon (TOC)	0.5 mg/L	Difference in duplicate results should not exceed +/- 10% for concentrations >20 mg/L or 2 mg/L for concentrations less than 20 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Calibration Verification Std.	At least 1 per group of 10 or fewer samples	90-110%
Lab Blank (1 liter of tapwater at pH <2)	At least 1 per group of 10 or fewer samples	< 0.5 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 2.0 mg/L
Matrix spike **	1 per group of 20 or fewer samples	90-110% Recovery

*See Section III

** Matrix spike concentrations will be greater than 30% of the sample concentration, but spiked sample shall n exceed the working range of the standard curve or titration.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analyti services. Should you have any questions or need any assistance, please call the Region.

SASTOC.WP

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536 S. Clark - 10th Floor
Chicago, IL 60605
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SAS Number

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B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

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1. **General description of analytical service requested:**

   Analysis for total dissolved solids (TDS) in monitoring, extraction, and residential well samples. Results will be reported in mg/L dissolved solids.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium to high concentrations of TDS.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 160.1, Filterable Residue.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples will be stored at 4°C until sample analysis. Any remaining samples should be stored in the sar manner until the validation and the acceptance of the sample result.

Sample holding time is 7 days from sample receipt.

Use standard aliquots of 100 mL; however, do not use aliquots yielding more than 200 mg residue. If resid is greater than 200 mg, repeat the analysis using a smaller aliquot.

Residue will be weighted to constant weight pursuant to Section 7.6 of Method 160.1 (weight loss is less than 0 mg or less than 4% weight loss from previous loss). Constant weights will also be obtainable on a single weig... basis if the sample is dried for a minimum of 12 hours. The final weight is to be used for calculations.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records of tare weights, final weights, additional weights to determine constant weights, volumes filtere , blanks, and duplicate samples will be provided with work sheets used to calculate results. Dates and times of when the following tasks are performed will be recorded as part of the bench record:

* determination of tare weights
* sample filtration
* determination of constant weights
* determination of residue weights

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt_1 to the Region within the time frame listed in Section 6 above. Photocopies of chain of custody forms and airbills may be submitted with a record of the location of the originals, to the Region within the time frame listed in sect 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. **DATA REQUIREMENTS**

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
TDS	20 mg/L	Difference in duplicate results should not exceed 2 mg for residues. Duplicate differences shall not exceed 10% for sample values greater than 200 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank (100 mL of filtered reagent water)	At least 1 per group of 10 or fewer samples	- 20 mg/L to + 20 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 2 mg residue
Lab Control Sample (LCS)	At least 1 per group of 20 samples	90-110% recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

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SASTDS.WP

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1. **General description of analytical service requested:**

   Analysis for Oil and Grease (O & G) in monitoring, extraction, and residential well samples. Results will be reported as mg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Sixteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium concentrations of O & G expressed in mg/L.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

EPA Method 413.2. This is a spectrophotometric method.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples will be in 1 quart or 1 liter glass bottles and preserved with 2 mL H_2SO_4 to ph <2.

Sample holding time is 28 days from date of receipt.

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sai manner until the validation and the acceptance of the sample result.

Sample volume is best calculated by weighing the sample bottle full and empty to nearest 5 grams.

A solvent blank is necessary for each solvent lot, and will be free of interferences.

Prepare a 5 point calibration curve containing a zero concentration standard for each cell between 0 and C absorbance.

Matrix spikes and laboratory blanks will be prepared from tapwater, H_2SO_4, and #2 fuel oil.

Dilute samples or select shorter cell path if samples absorbance exceeds that of the highest standard or exceeds 0.8 absorbance.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records and IR spectra of solvent blanks, samples, lab blanks, matrix spikes, standards, etc., will e provided along with copies of work-sheets used to calculate results.

The order of instrumental measurements and cell path lengths must be identified.

In case narrative and on bench records identify any problem samples as to emulsions, interferences, etc.

All records of analysis must be legible and sufficient to recalculate all sample concentrations and QA audit resu...

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitted to the Region within the time frame listed in Section 6 above. Photocopies of chain of custody forms and airb may be submitted with a record of the location of the originals, to the Region within the time frame listed in sect 6 above.

11. **Name of sampling/shipping contact:** Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Oil & Grease	0.4 mg/L	Any designated field duplicate values should not exceed +/- 25% or 0.4 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Solvent Blank (90 mL of Freon)	At least 1 per group of 10 or fewer samples	< 0.4 mg/L
Lab Blank (1 liter of tapwater at pH <2)	At least 1 per group of 10 or fewer samples	< 0.4 mg/L
Matrix Spike (1 liter of tapwater at pH <2 plus 15 to 20 mg/L or #2 fuel oil)	1 per group of 20 or fewer samples	80-120% Recovery
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	80-120% Recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

SASO&G.WP

U.S. Environmental Protection Agency-Region 5
Central Regional Laboratory
536 S. Clark - 10th Floor
Chicago, IL 60605
PHONE: (312) 353-2720 or FAX 886-2591

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for alkalinity in monitoring, extraction, and residential well samples. Results will be reported in mg/L as $CaCO_3$.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium concentrations of alkalinity expressed as mg/L as $CaCO_3$.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 310.1, Alkalinity. This is titrimetric procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sar manner until the validation and the acceptance of the sample result.

Sample holding time is 14 days from date of collection.

Sample volume or titrant normality should be adjusted so the titrant volume is greater than 10 mL, yet less th 40 mL.

Samples will be analyzed at 20 +/- 2° C unless the pH meter provides automatic temperature compensation.

9. **Analytical results required (If known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records that clearly and legibly show the order and titrant volume of the; titrant standardization, lab blank samples, lab control standards, and lab duplicates. These bench records should also show sample volumes a the volume and normality of the titrant standard in order to be able to reproduce the calculated alkalinity resul

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitte to the Photocopies of chain of custody forms and airbills may be submitted with a record of the location of t originals, to the Region within the time frame listed in section 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Alkalinity	2 mg/L as $CaCO_3$	Difference in duplicate results should not exceed +/- 10% for concentrations > 20 mg/L or 2 mg/L for concentrations less than 20 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank	At least 1 per group of 10 or fewer samples	≤ 2.0 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 2.0 mg/L
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	90-110% Recovery
Calibration Verification Standard	1 per group of 10 or fewer samples	90-110% Recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

SASALK.WP

U.S. Environmental Protection Agency-Region 5
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SAS Number

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Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for hardness in monitoring, extraction, and residential well samples. Results will be reported in mg/L as $CaCO_3$.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium concentrations of hardness, with the hardness being expressed as mg/L as $CaCO_3$.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:**

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 130.1, Hardness, Total as $CaCO_3$. This is an EDTA colorimetric procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Samples will be preserved with nitric acid to a pH <2 and stored at 4°C until the time of analysis. Any remaining samples should be stored in the same manner until the validation and the acceptance of the sample result.

Sample holding time is 14 days from date of collection.

Use inhibitors as necessary.

In order to avoid large titration volumes, sample volumes should be adjusted as to not contain more than 25 mg $CaCO_3$.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records that clearly and legibly show the order of; EDTA titrant standardization, lab blanks, samples, lab control standards, and lab duplicates. In order to be able to reproduce the calculated hardness, these bench records should also show sample volumes and the volume and normality of the titrant.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitted to the Region within the time frame listed in Section 6 above. Photocopies of chain of custody forms and airbills may be submitted with a record of the location of the originals, to the Region within the time frame listed in section 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Hardness	1 mg/L as $CaCO_3$	Difference in duplicate results should not exceed +/- 10% for concentrations > 10 mg/L or 2 mg/L for concentrations less than 10 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank	At least 1 per group of 10 or fewer samples	≤ 1.0 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 2.0 mg/L
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	90-110% Recovery
Calibration Verification Standard	1 per group of 10 or fewer samples	90-110% Recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Region.

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Client Request

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B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for chemical oxygen demand (COD) in monitoring, extraction, and residential well samples. Results will be reported in mg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain low concentrations of COD.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 410.2, Color. This is low-level titrimetric procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples will be preserved with sulfuric acid to a pH <2.

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sam manner until the validation and the acceptance of the sample result.

Sample holding time is 28 days from date of receipt.

Extreme care should be exercised to avoid inclusion of organic materials in the glassware or distilled water us for reagent preparation or sample dilution.

If COD values greater than 50 mg/L are found, the normality of the potassium dichromate and ferrous ammoniu sulfate solution should be increased by a factor of 10 and the samples reanalyzed.

A lab blank will be run with each set of sample analyzed.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records that clearly and legibly show the order and titrant volumes of the ferrous ammonium sulfa standardization, lab blanks, samples, lab control standards, and lab duplicates. These bench records should al show sample volumes and the volume and normality of the titrant standard in order to be able to reproduce th calculated COD results.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be sub to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airbills may be submitted with a record of the location of the originals, to the Region within the time frame listed in secti 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. **DATA REQUIREMENTS**

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
COD	5 mg/L	Difference in duplicate results should not exceed +/- 10% for concentrations > 50 mg/L or 5 mg/L for concentrations less than 50 mg/L

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank	At least 1 per group of 10 or fewer samples	≤ 5.0 mg/L
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 5.0 mg/L
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	90-110% Recovery
Calibration Verification Standard	1 per group of 10 or fewer samples	90-110% Recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

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U.S. Environmental Protection Agency-Region 5
Central Regional Laboratory
536 S. Clark - 10th Floor
Chicago, IL 60605
PHONE: (312) 353-2720 or FAX 886-2591

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for color in monitoring, extraction, and residential well samples. Results will be reported as color units.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain low color.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 110.2, Color. This is a platinum-cobalt colorimetric procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sar manner until the validation and the acceptance of the sample result.

Sample holding time is 48 hours from date of receipt.

Turbid samples should be clarified by centrifugation.

If the sample color exceeds 70 units, dilute the sample with distilled water to a point where the color is less th 70 units.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

In order to be able to reproduce the calculated color results, bench records that clearly and legibly show the estimated color and sample dilutions will be provided.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt to the Region within the time frame listed in Section 6 above. Photocopies of chain of custody forms and airbil may be submitted with a record of the location of the originals, to the Region within the time frame listed in sectio 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Color	1 color unit	Difference in duplicate results should not exceed +/- 10% for concentrations > 10 color units or 1 color units for color readings less than 10 color units

II. **QC REQUIREMENTS**

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank	At least 1 per group of 10 or fewer samples	0 color units
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 1 color unit
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	90-110 % Recovery

*See Section III

III. **ACTION REQUIRED IF LIMITS ARE EXCEEDED:**

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

SASCOL.WP

U.S. Environmental Protection Agency-Region 5
Central Regional Laboratory
536 S. Clark - 10th Floor
Chicago, IL 60605
PHONE: (312) 353-2720 or FAX 886-2591

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis for odor in monitoring well, extraction well, and residential well samples. Results will be reported as threshold odor numbers (TON).

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain little odor.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA 140.1, odor. This is a consistent series procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

In order to prevent the picking up of extraneous odors, samples must be collected in glass bottles, filled to t top and tightly capped.

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the same manner until the validation and the acceptance of the sample result.

Glassware must be cleaned shortly before use, with non-odorous soap, an acid cleaning solution, followed with rinsing with odor free water.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custo documentation, etc.). If not completed, format of results will be left to program discretion.**

In order to be able to reproduce the calculated odor results, bench records that clearly and legibly show the od responses, the number of people used to make the determination, and sample volumes used will be provided.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt to the Region within the time frame listed in Section 6 above. Photocopies of chain of custody forms and airb may be submitted with a record of the location of the originals, to the Region within the time frame listed in sectio 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Odor	1 TONs	Difference in duplicate results should not exceed 2 TONs.

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Lab Blank	At least 1 per group of 10 or fewer samples	1 TONs
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 2 TONs

*See Section III

III. **ACTION REQUIRED IF LIMITS ARE EXCEEDED:**

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

SASODO.WP

U.S. Environmental Protection Agency-Region 5
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SPECIAL ANALYTICAL SERVICES
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A. EPA Region/Client: Region V
B. RSCC Representative: Brian P. Freeman
C. Telephone Number: 312-353-2720
D. Date of Request: Date of Sampling :
E. Site Name: Region V, Onalaska Landfill
Cerclis ID# Site/Spill ID#

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of turbidity in monitoring, extraction, and residential well samples. Results will be reported in nephelometric turbidity units (NTUs).

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Fourteen aqueous samples will be collected during each sampling event. The aqueous samples will contain medium amounts of turbidity.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund remedial.

4. **Estimated date(s) of collection:** _____

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be daily shipment by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   Sample results will be required 28 days after sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   EPA Method 180.1, Turbidity. This is a nephelometric procedure.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbe detection limits, etc.):**

Samples should be stored at 4°C until the time of analysis. Any remaining samples should be stored in the sar manner until the validation and the acceptance of the sample result.

Sample holding time is 14 days from sample receipt.

Glassware used for this procedure must be kept scrupulously clean and be free of scratches and etching.

Samples with turbidities exceeding 40 units should be diluted with turbidity free water to a concentration less th 40 turbidity units.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custor documentation, etc.). If not completed, format of results will be left to program discretion.**

Bench records that clearly and legibly show sample volumes, dilutions, and the calibration curve data will be provided in order to be able to reproduce the calculated turbidity results.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills, and original data shall be submitt to the Region within the time frame listed in section 6 above. Photocopies of chain of custody forms and airbi may be submitted with a record of the location of the originals, to the Region within the time frame listed in sectic 6 above.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (+/- % or conc.)
Turbidity	1 NTUs	Difference in duplicate results should not exceed +/- 10% for concentrations > 10 NTUs or 0.02 NTUs for concentrations less than 10 NTUs

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits * (+/- % or conc)
Calibration Verification Std.	At least 1 per group of 10 or fewer samples	90-110% Recovery
Lab Blank	At least 1 per group of 10 or fewer samples	< 1 NTU
Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- 10% or 0.02 NTUs
Laboratory Control Sample (LCS)	1 per group of 20 or fewer samples	90-110% Recovery

*See Section III

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact the Region.

Please return this request to the Region as soon as possible to expedite processing of your request for special analytic services. Should you have any questions or need any assistance, please call the Region.

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APPENDIX B
FIELD TESTING PROCEDURES

Appendix B
Field Measurements and Monitoring

pH

Purpose

To provide a general guideline for field measurement of pH

Scope

Standard field pH determination techniques for use on groundwater samples.

Equipment/Materials

- pH buffer solution for pH 4, 7, and 10
- Deionized water in squirt bottle
- pH meter
- Combination electrodes
- Beakers
- Glassware that has been washed with soap and water, rinsed twice with hot water, and rinsed twice with deionized water
- 10 percent solution of HCl

Procedures/Guidelines

Calibration

Calibrate unit prior to initial daily use and at least once every 4 hours or every 5 samples, whichever is less. Calibrate with at least 2 solutions. Clean probe according to manufacturers recommendations. Duplicate samples should be run once every 10 samples or every 4 hours.

1. Place electrode in pH 7 buffer solution.

2. Allow meter to stabilize and then turn calibration dial until a reading of 7.0 is obtained.

3. Rinse electrode with deionized water and place it in a pH 4 or pH 10 buffer solution.

4. Allow meter to stabilize again and then turn slope adjustment dial until a reading of 4.0 is obtained for the pH 4 buffer solution or 10.0 for the pH 10 buffer solution.

5. Rinse electrode with deionized water and place in pH 7 buffer. If meter reading is not 7.0, repeat sequence.

Procedure

1. Before going out into the field:
   a) Check batteries.
   b) Do a quick calibration at pH 7 and 4 to check electrode.
   c) Obtain fresh solutions.

2. Calibrate meter using calibration procedure.

3. Pour the sample into a clean beaker.

4. Rinse electrode with deionized water between samples.

5. Immerse electrode in solution. Make sure the white KCl junction on the side of the electrode is in the solution. The level of electrode solution should be one inch above sample to be measured.

6. Recheck calibration with pH 7 buffer solution after every five samples.

General

1. When calibrating the meter, use pH buffers 4 and 7 for samples with pH < 8, and buffers 7 and 10 for samples with pH > 8. If meter will not read pH 4 or 10, something may be wrong with the electrode.

2. Measurement of pH is temperature dependent. Therefore, temperatures of buffers and samples should be within about 2°C. For refrigerated or cool samples, use refrigerated buffers to calibrate the pH meter.

3. Weak organic and inorganic salts and oil and grease interfere with pH measurements. If oil and grease are visible, note it on the data sheet. Clean electrode with soap and water and rinse with a 10 percent solution of HCl. Then recalibrate meter.

4. Following field measurements:

    a) Report any problems
    b) Compare with previous data
    c) Clean all dirt off meter and inside case
    d) Store electrode in pH 4 buffer

5. Accuracy and precision are dependent on the instrument used; refer to manufacturer's manual. Expected accuracy and precision are +/- 0.1 pH unit.

Attachments

pH meter calibration sheet

Key Checks/Items

- Check batteries
- Calibrate

Preventative Maintenance

- Refer to operation manual for recommended maintenance.
- Check batteries, Have a replacement set on hand.

Specific Conductivity and Temperature

Purpose

To provide a general guideline for field measurement of specific conductivity and temperature.

Scope

Standard field conductivity and temperature techniques for use on groundwater samples.

Equipment/Materials

- Conductivity meter and electrode
- Distilled water in squirt bottle
- Standard Potassium Chloride (KCl) Solution (0.01 N)

Procedures/Guidelines

Technical

Detection limit = 1 umho/cm @ 25 C; range = 0.1 to 100,000 umho/cm

Calibration

Calibrate prior to initial daily use and at least once every 4 hours or every 5 samples, whichever is less. Calibrate with standard solution. The standards should have different orders of conductance. Clean prove according to manufacturers recommendations. Duplicates should be run once every 10 samples or every 4 hours.

1. With mode switch in OFF position, check meter zero. If not zeroed, set with zero adjust.

2. Plug probe into jack on side of meter.

3. Turn mode switch to red line and turn red line knob until needle aligns with red line on dial. If They cannot be aligned, change the batteries.

4. Immerse probe in 0.01 N standard KCl solution. Do not allow the probe to touch the sample container.

5. Set the mode control to TEMPERATURE. Record the temperature on the bottom scale of the meter in°C.

6. Turn the mode switch to appropriate conductivity scale (i.e., x100, x10, or x1). Use a scale that will give a mid-range output on the meter.

7. Wait for the needle to stabilize. Multiply reading by scale setting and record the conductivity. The conductivity must then be corrected for temperature.

8. Calculate conductivity using the formula:

$$G_{25} = G_T / [1 + 0.02 (T—25)]$$

Where:

G_{25} = conductivity at 25 C, umho/cm
T = temperature of sample, °C
G_T = conductivity of sample at temperature T, umho/cm

The table below lists the values of conductivity the calibration solution would have if the distilled water were totally nonconductive, however even water of very high purity will still possess a small amount of conductivity.

Table 1
Conductivity Meter Calibration Table

Temperature (°C)	Conductivity (μmho/cm)
15	1,141.5
16	1,167.5
17	1,193.6
18	1,219.9
19	1,246.4
20	1,273.0

Table 1
Conductivity Meter Calibration Table

Temperature (°C)	Conductivity (μmho/cm)
21	1,299.7
22	1,326.6
23	1,353.6
24	1,380.8

I. Rinse the probe with deionized water

J. Run sample and rinse with deionized water when done

Attachments

Conductivity meter calibration sheet

Key Checks/Items

- Check battery
- Calibrate
- Clean probe with deionized water when done
- When reading results, note sensitivity settings

Preventative Maintenance

- Refer to operations manual for recommended maintenance.
- Check batteries. Have a replacement set on hand.

Field Filtering

Purpose

To provide a general guideline for the field filtering of water samples for dissolved metals analysis.

Scope

Standard method of field filtering techniques.

Equipment/Materials

Option 1: Disposable In-line Filter Method

- Peristaltic pump
- Peristaltic pump head tubing
- 10 percent nitric acid (HNO_3) solution.
- Distilled or deionized water
- 0.45 micron disposable filters

Option 2: Filter Stand Method

- Filter stand assembly
- 10 percent nitric acid (HNO_3) solution.
- Distilled or deionized water
- Disposable 0.45 cellulose acetate filters with compatible diameter for the filter stand assembly
- Vacuum source

Procedures/Guidelines

Reagent Preparation

1. *10 percent HNO_3 solution:* Add about 900 mL of DI water to a 1 liter Erlenmeyer flask. Using a graduated cylinder, add 100 mL concentrated HNO_3 to the DI water while stirring.

Procedure

Option 1: Disposable In-line Filter Method

1. Set up the peristaltic pump and connect to a power source (car battery or A.C. power). If the integrity of the pump head tubing is unknown or in question, replace with fresh tubing.

2. With the pump running, flush the pump tubing with 10 percent HNO_3 solution.

3. With the pump, rinse the pump tubing with analyte free distilled or deionized water. Run pump until all rinse water is removed from the line.

4. Connect the in-line filter to the outlet of the peristaltic pump. **Make sure the flow direction indicated on the filter is consistent with the flow direction indicated on the filter.**

5. Pump sample from collection vessel through the filter into a polyethylene bottle (with preservative) for shipment. If sufficient volume of the original sample exists, allow a small portion of the initial filtered sample to be discarded.

6. Remove and discard the used filter.

7. Repeat steps 1 through 3.

Option 2: Filter Stand Method

1. Attach a vacuum source (pump, syringe, etc.) to the funnel/receiver assembly.
2. Disassemble unit. Flush the entire filter system with 10 percent HNO_3 solution.
3. Rinse the entire filter system with analyte free distilled or deionized water.
4. Insert a 0.45 micron filter and reassemble unit.
5. Filter sample and transfer into a polyethylene bottle (with preservative) for shipment.
6. Disassemble unit and discard used filter.
7. Repeat steps 1 through 3.

Attachments

None.

Key Checks/Items

- 10 percent HNO_3 solution for cleaning
- All water for HNO_3 solution and rinsing must be distilled or deionized.

Key Checks/Items

- Check battery
- Zero and calibrate
- Verify sensor probe is working
- Recharge unit after use

Preventative Maintenance

A complete preventative maintenance program is beyond the scope of this document. For specific instructions, refer to the operations manual.

- A complete spare HNu should be available on site whenever field operations require this instrument.
- A spare lamp should be on hand so a defective unit can be changed without returning the unit.
- Occasional cleaning of the lamp should be performed as needed.
- Charge batteries daily.
- Occasionally allow the batteries to totally discharge before recharging to prevent battery memory from occurring.

OVA Monitoring

Purpose

To provide general guidelines for the calibration and use of the OVA (Organic Vapor Analyzer) flame ionization detector.

Scope

This is a broad guideline for the use of an OVA. For specific instructions, refer to the operations manual.

Equipment/Materials

- Instruction manual
- OVA organic vapor analyzer
- Calibration span gas (100 ppm methane in air)
- Regulator for span gas cylinder
- For continued use, a source of 99.999 percent pure hydrogen for recharging internal tank is required

Procedures/Guidelines

ONLY PROPERLY TRAINED PERSONNEL SHOULD USED THIS INSTRUMENT. FOR SPECIFIC INSTRUCTIONS, SEE INSTRUCTION MANUAL.

Start Up

1. Attach meter/probe assembly

2. Turn pump switch on and check battery by moving the ''INSTR'' switch to ''BATT'' position

3. Turn ''INSTR'' switch on and wait 5 minutes

4. Zero instrument with ''Calibrate'' knob
5. Open hydrogen gas valve

6. Depress igniter button until burner flame ignites

7. Use ''Calibrate'' knob to zero out ambient background

8. Calibrate unit with methane span gas, adjusting the ''Gas Select'' (span control) pot

9. Unit is ready to use.

Shut Down

1. Close hydrogen valve
2. Move ''INSTR'' and pump switches to off.
3. Charge unit (it will take about 1 hour of charging for each hour of operation.)

Caution

1. Hydrogen is explosive. Use caution when filling tank.

Attachments

None

Key Checks/Items

- Open hydrogen gas valve
- Light flame
- Close hydrogen gas valve when done.
- Recharge battery

Preventative Maintenance

A complete preventative maintenance program is beyond the scope of this document. For specific instructions, refer to the operations manual.

- A spare OVA should be available whenever field use of this instrument is required.

- Use only 99.999 percent pure hydrogen
- A spare supply of valve seals should be on hand so hydrogen leaks can be repaired without returning the unit.
- Charge batteries daily.
- Occasionally allow the batteries to totally discharge before recharging to prevent battery ''memory'' from occurring.

VOC Sampling—Water

Purpose

General guidelines for sampling volatile organic compounds are provided.

Scope

Standard techniques for collecting representative samples are summarized. Site specific details are discussed in the FSAP.

Equipment/Materials

- Sample vials, clean latex or surgical gloves, pH meter
- Hydrochloric acid (HCl) for preservation
- pH meter or pH indicating paper
- surgical or latex gloves

Procedures/Guidelines

1. Sample VOCs before sampling other analyte groups.

2. When sampling for VOCs, especially residential wells, evaluate the area around the sampling point for possible sources of air contamination by VOCs. Products that may give off VOCs and possible contaminate a sample include perfumes and cosmetics, skin applied pharmaceuticals, automotive products (gasoline, starting fluid, windshield deicers, carburetor cleaners, etc.) and household paint products (paint strippers, thinners, turpentine, etc.).

3. To check the amount of hydrochloric acid (HCl) that needs to be added at each location, fill a test vial (40ml) with the water to be sampled, add one drop of hydrochloric acid (HCl), gently mix, and check the pH. Repeat this cycle (if necessary) until you reach a pH of 2, counting the number of drops of HCl was required. DISCARD THE TEST VIAL and add an equal number of drops of HCl to each of the sample vials. Proceed to sample.

4. Keep the caps off of the sample vials for as short a time as possible.

5. Wear clean latex or surgical gloves.

6. Fill the sample vial immediately, allowing the water stream to strike the inner wall of the vial to minimize formation of air bubbles. DO NOT RINSE THE SAMPLE VIALS BEFORE FILLING.

7. Fill the sample vial with a minimum of turbulence, until the water forms a positive meniscus at the brim.

8. Replace the cap by gently setting it on the water meniscus. Tighten firmly, but DO NOT OVER TIGHTEN.

9. Invert the vial and tap it lightly. If you see air bubbles in the sample, do not add more sample. Use another vial to collect another sample. Repeat if necessary until you obtain a proper sample.

Attachments

None.

Key Checks/Items

- Check for possible sources of contamination
- Check pH
- Fill slowly, with as little turbulence as possible
- Check for air bubbles

MKE10015E7E.WP5

APPENDIX C
SAMPLE DOCUMENTATION AND PACKING AND SHIPPING INSTRUCTIONS

Appendix C
Sample Documentation and Packing and Shipping Instructions

Sample Documentation Instructions

Sample Identification Matrix (Figure 1)

1. Enter site name.

2. Enter project number.

3. Enter the case number and/or SAS number.

4. Enter the CRL log number.

5. Specify the sample matrix using the two- or three-digit codes listed below:

   - SS—Surface Soil
   - SB—Subsurface Soil
   - SWO—Surface Water, Onsite
   - SWC—Surface Water, Creek
   - SDO—Sediment, Onsite
   - SDC—Sediment, Creek

6. Enter the sample number.

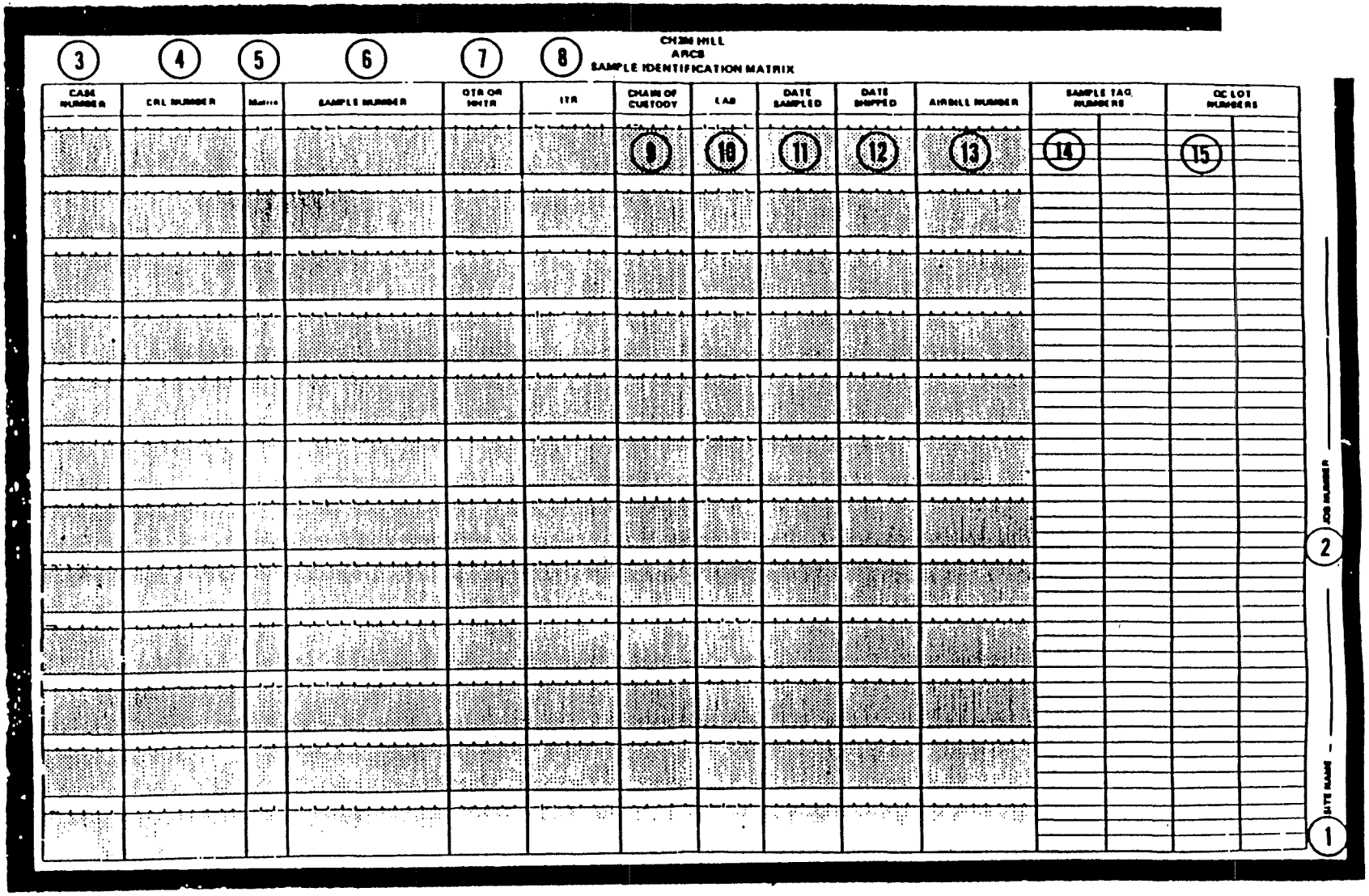
7. Enter the organic traffic label number or the SAS sample number.

8. Enter the inorganic traffic label number.

9. Enter the chain-of-custody number.

10. Indicate the laboratory to be doing the analysis (abbreviations may be used as they are shown on the current laboratory list).

11. Enter the date the sample was taken: month, day, year (no hyphen or slash, e.g., 081292).



NOTE: For purposes of illustration this form has been reproduced at 60% of original size.

FIGURE 1

12. Enter the shipping date.

13. Enter the airbill number of the shipment.

14. List sample tag numbers corresponding to sample containers shipped under the traffic label number listed in either box 7 or 8.

15. List the QC lot numbers of the containers matching the tag numbers listed in Item 14.

Note: The date recorded on this form must be suitable for computer entry. Each entry must be flush left and must not exceed the number of digits allowed in each section. If portions of samples are to be sent to more than one laboratory for analysis, allow an entire line for each laboratory to accommodate for the additional traffic report, chain-of-custody, and airbill numbers.

Sample Tag (Figure 2)

1. Enter date of sampling.

2. Enter time of sampling (military time only).

3. Specify ''grab'' or ''composite'' sample with an ''X.''

4. Enter CH2M HILL sample identification code.

5. Obtain signature of sample team leader.

6. Indicate preservative used (if any) with an ''X.''

7. Specify all parameters for analysis by placing an ''X'' to the right of each one.

8. Indicate the sample number (for CLP Lab) or CRL log number (for CRL).

9. Indicate case number and/or SAS number (e.g., Case No. 1234 and/or SAS No. 5678E).

10. Leave BLANK (for laboratory use only).

11. Enter any desired analyses not listed on menu (e.g., PCBs, ammonia, sulfide, etc.) and mark box with an ''X.''

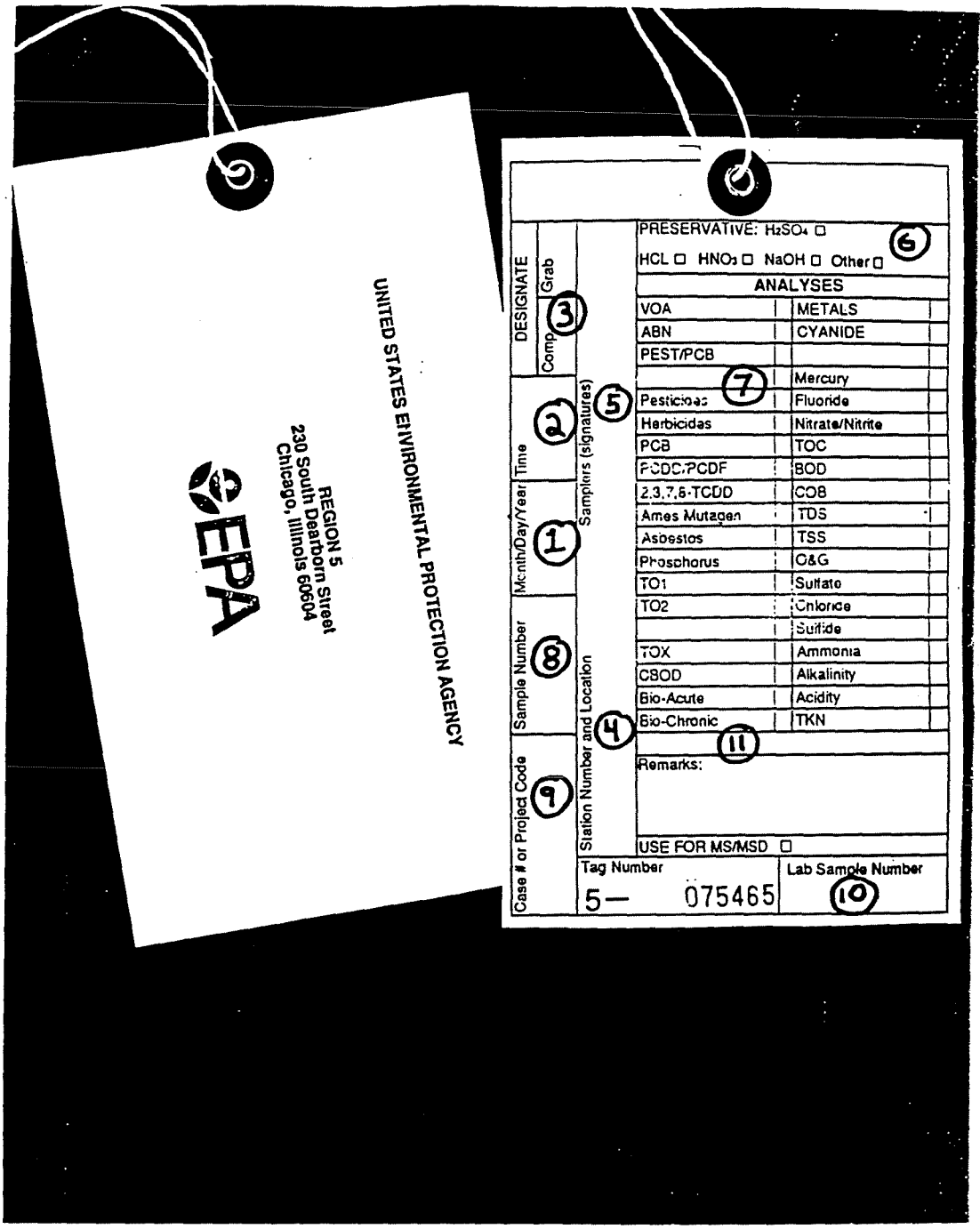


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FIGURE 2

Inorganic Traffic Report (Figure 3)

1. Enter assigned laboratory case number.

2. Enter assigned laboratory SAS number, if applicable.

3. Check the code that describes the activity being performed.

4a. Enter site name.

4b. Enter city and state of site.

4c. Enter spill ID No. (obtained from the PM or Data Coordinator).

5. Enter EPA region number (e.g., V).

6. Enter sample team leader's company/office.

7. Enter sample team leader's name.

8. Enter laboratory name and address, and laboratory contact.

9. Indicate date of shipment.

10. Indicate airbill number corresponding to sample shipment.

11. Indicate the shipment carrier (i.e., Federal Express).

12. Enter the ITR Label Number.

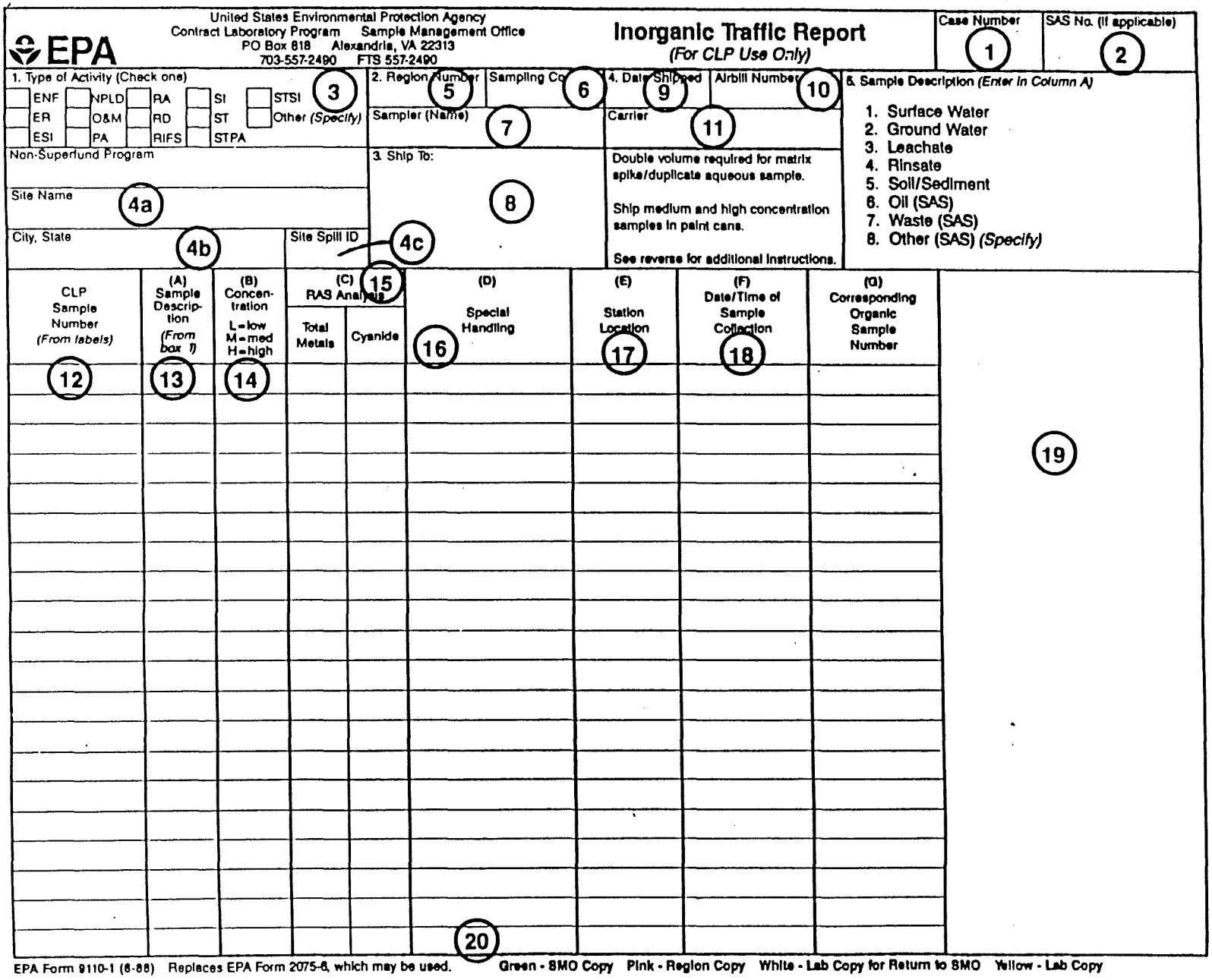
13. Indicate sample description with a number (e.g., 1, 2, 3, 4, 5, 6, 7, 8) from box 5 on ITR.

14. Specify sample concentration with an L, M, or H indicating contamination level.

15. Check required analyses.

16. Specify special handling to notify laboratory if sample is a blank, MS/MSD or field duplicate.

17. Enter CH2M HILL sample number.



EPA

United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Inorganic Traffic Report

(For CLP Use Only)

Case Number (1) | SAS No. (If applicable) (2)

1. Type of Activity (Check one) (3)
ENF | NPLD | RA | SI | STSI
ER | O&M | RD | ST | Other *(Specify)*
ESI | PA | RIFS | STPA

2. Region Number (5) | Sampling Co (6)

Sampler (Name) (7)

4. Date Shipped (9) | Airbill Number (10)

Carrier (11)

Non-Superfund Program

Site Name (4a)

City, State (4b) | Site Spill ID (4c)

3. Ship To: (8)

Double volume required for matrix spike/duplicate aqueous sample.

Ship medium and high concentration samples in paint cans.

See reverse for additional instructions.

5. Sample Description *(Enter in Column A)*
1. Surface Water
2. Ground Water
3. Leachate
4. Rinsate
5. Soil/Sediment
6. Oil (SAS)
7. Waste (SAS)
8. Other (SAS) *(Specify)*

CLP Sample Number *(From labels)* (12)	(A) Sample Description *(From box 1)* (13)	(B) Concentration L=low M=med H=high (14)	(C) RAS Analysis (15) Total Metals	(C) RAS Analysis (15) Cyanide	(D) Special Handling (16)	(E) Station Location (17)	(F) Date/Time of Sample Collection (18)	(G) Corresponding Organic Sample Number	(19)
					(20)				

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FIGURE 3

18. Enter the date/time of sample collection.

19. Leave BLANK (for laboratory use only).

20. Write at bottom of form if shipment is **complete** or is **not complete**.

Organic Traffic Report (Figure 4)

1. Enter assigned laboratory case number.

2. Enter assigned laboratory SAS number, if applicable.

3. Check the code that describes the activity being performed.

4a. Enter site name.

4b. Enter site city and state.

4c. Enter spill ID No. (obtained from the PM or Data Coordinator).

5. Enter EPA region number (e.g., V).

6. Enter sample team leader's company/office.

7. Enter sample team leader's name.

8. Enter laboratory name and address and laboratory contact.

9. Indicate date of shipment.

10. Indicate airbill number corresponding to sample shipment.

11. Indicate the shipment carrier (i.e., Federal Express).

12. Enter the OTR Label Number.

13. Specify sample description with a number (e.g., 1, 2, 3, 4, 5, 6, 7, 8) from box 5 on OTR.

14. Specify the sample concentration with an L, M, or H, indicating contamination level.

EPA

United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Organic Traffic Report
(For CLP Use Only)

Case Number (1) | SAS No. (if applicable) (2)

1. Type of Activity (Check one) (3)
☐ ENF ☐ NPLD ☐ RA ☐ SI ☐ STSI
☐ ER ☐ O&M ☐ RD ☐ ST ☐ Other *(Specify)*
☐ ESI ☐ PA ☐ RIFS ☐ STPA

2. Region Number (5) | Sampling Co (6)

Sampler (Name) (7)

4. Date Shipped (9) | Airbill Number (10)

Carrier (11)

5. Sample Description *(Enter in Column A)*
1. Surface Water
2. Ground Water
3. Leachate
4. Rinsate
5. Soil/Sediment
6. Oil (SAS)
7. Waste (SAS)
8. Other (SAS) *(Specify)*

Non-Superfund Program

Site Name (4a)

City, State (4b) | Site Spill ID (4c)

3. Ship To: (8)

Triple volume required for matrix spike/duplicate aqueous sample.

Ship medium and high concentration samples in paint cans.

See reverse for additional instructions.

CLP Sample Number *(From labels)* (12)	(A) Sample Description *(From box 1)* (13)	(B) Concentration L=low M=med H=high (14)	(C) RAS Analysis (15) VOA	BNA	Pest/ PCB	(D) Special Handling (16)	(E) Station Location (17)	(F) Date/Time of Sample Collection (18)	(G) Corresponding CLP Inorganic Sample Number	(19)
						(20)				

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FIGURE 4

15. Check required analyses.

16. Specify special handling to notify laboratory if sample is a blank, MS/MSD or field duplicate (replicate).

17. Enter CH2M HILL sample number.

18. Enter the date/time of sample collection.

19. Leave BLANK (for laboratory use only).

20. Write at bottom of form if shipment is **complete** or is **not complete**.

SAS Packing List (Figure 5)

1. Enter assigned SAS case number.

2. Enter EPA region number (e.g., V).

3. Enter sample team leader's name.

4. Enter sample team leader's company/office and phone number.

5. Enter date sample was taken.

6. Enter date of shipment.

7. Enter site name.

8. Enter laboratory name and address.

9. Enter name of laboratory contact.

10. List SAS sample numbers, which should include the SAS number.

11. Specify sample matrix, concentration, tag number, and analysis to be performed (e.g., low concentration soil sample for PCB analysis, tag No. 5-48246).

12. Leave BLANK (for laboratory use only).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS Number (1)

SPECIAL ANALYTICAL SERVICE
PACKING LIST

Sampling Office: (2)	Sampling Date(s): (5)	Ship To: (8)	For Lab Use Only
Sampling Contact: (3) (name) (4) (phone)	Date Shipped: (6)		Date Samples Rec'd:
	Site Name/Code: (7)	Attn: (9)	Received By:

	Sample Numbers	Sample Description i.e., Analysis, Matrix, Concentration	Sample Condition on Receipt at Lab
1.			
2.			
3.			
4.			
5.			
6.			
7.			
8.			
9.			
10.	(10)	(11)	(12)
11.			
12.			
13.			
14.			
15.			
16.			
17.			
18.			
19.			
20.			
			For Lab Use Only

White - SMO Copy, Yellow - Region Copy, Pink - Lab Copy for return to SMO, Gold - Lab Copy

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FIGURE 5

Chain-of-custody Record (Figure 6)

1. Enter first six digits of the CRL sample identification code.

2. Leave blank.

3. Obtain full signature of sample team leader and signed initials of active team members (including paperwork person).

4. Enter last three digits of the CRL sample identification code.

5. List sampling dates for all samples.

6. List sampling times for all samples (military time only).

7. Indicate ''grab'' or ''composite'' sample with an ''X.''

8. List CH2M HILL sample numbers.

9. Enter number of containers per sample.

10. List analyses individually.

11. Enter column heading for traffic label number and list serial numbers for corresponding sample identification codes.

12. Write in the words ''CASE No. '': or ''SAS No. '': and enter the correct number.

13. Enter column heading for ''tag number'' and list tag numbers for each sample container.

14. Obtain signature of sample team leader and carry out chain-of-custody procedures.

15. State carrier service and airbill number, lab service, and custody seal numbers.

Combined Chain-of-custody and Traffic Report Forms (Figure 7)

A. Project Code: Leave blank.

B. Account Code: Leave blank.

ENVIRONMENTAL PROTECTION AGENCY
Office of Enforcement

CHAIN OF CUSTODY RECORD

REGION 5
230 South Dearborn Street
Chicago, Illinois 60604

PROJ. NO. (1)	PROJECT NAME (2)	NO. OF CONTAINERS	(10)	(12) REMARKS
SAMPLERS: (Signature) (3)				
STA. NO. (4)	DATE (5)	TIME (6)	COMP	GRAB (7)	STATION LOCATION (8)	(9)	(11)	(13)

Relinquished by: (Signature) (14)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks (15)	

Distribution: White — Accompanies Shipment, Pink — Coordinator Field Files; Yellow — Laboratory File

5- 20445

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FIGURE 6

COMBINED CHAIN OF CUSTODY AND TRAFFIC REPORT FORMS

EPA — United States Environmental Protection Agency, Contract Laboratory Program, Sample Management Office, PO Box 818 Alexandria, VA 22313, 703-557-2490 FTS 557-2490

Organic Traffic Report & Chain of Custody Record (For Organic CLP Analysis)

SAS No. (if applicable) (M) — Case No. (M)

1. Project Code (A)	Account Code (B)	2. Region No. (G)	Sampling Co. (H)
Regional Information (C)		Sampler (Name) (I)	
Non-Superfund Program (D)		Sampler Signature (I)	
Site Name (E)		3. Type of Activity (J): SF, PRP, ST, FED, PA, SS, LSI, NPLD, CLEM, REMA, REM, OIL, UST	
City, State (F)	Site Spill ID (F)		

4. Date Shipped (K)	Carrier (K)
Airbill Number (K)	
5. Ship To (L)	

6. Preservative *(Enter in Column D)*
1. HCl
2. HNO3
3. $NaHSO_4$
4. H_2SO_4
5. Other (SAS) *(Specify)*
6. Ice only
N. Not preserved

7. Sample Description *(Enter in Column A)*
1. Surface Water
2. Ground Water
3. Leachate
4. Rinsate
5. Soil/Sediment
6. Oil (SAS)
7. Waste (SAS)
8. Other (SAS) *(Specify)*

CLP Sample Numbers (from labels)	A Enter # from Box 7	B Conc. Low Med High	C Sample Type: Comp./Grab	D Preservative from Box 6	E RAS Analysis VOA	BNA	Pest/PCB	High ARO/TOX	F Regional Specific Tracking Number or Tag Numbers	G Station Location Number	H Mo/Day/Year/Time Sample Collection	I Sampler Initials	J Corresp. CLP Inorg. Samp. No.	K Designated Field QC
(N)	←			(O)				→	(P)	(Q)	(R)	(S)	(T)	(U)

Shipment for Case complete? (Y/N) (V)	Page 1 of ___ (W)	Sample used for a spike and/or duplicate (X)	Additional Sampler Signatures (Y)	Chain of Custody Seal Number (Z)

CHAIN OF CUSTODY RECORD

Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
← (AA) →					
Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date / Time	Received by: *(Signature)*
Received by: *(Signature)*	Date / Time	Received for Laboratory by: *(Signature)*	Date / Time	Remarks Is custody seal intact? Y/N/none	

EPA Form 9110-2 (Rev. 5-91) Replaces EPA Form (2075-7), previous edition which may be used

DISTRIBUTION:
Blue - Region Copy Pink - SMO Copy White - Lab Copy Yellow - Lab Copy for Return to SMO

Split Samples ☐ Accepted ☐ Declined *(Signature)* (BB)

FIGURE 7

C. Regional Information: If sampling is in support of oversight activities, indicate here. If not—leave blank.

D. NonSuperfund Program: If sampling is not done under the Superfund program, enter the name of the program (e.g., RCRA).

E. Site Name, City, State: Complete as instructed.

F. Site Spill ID: Enter ID code provided by the office.

G. Region No.: Enter "Region 5."

H. Sampling Company: Enter "CH2M HILL."

I. Sampler Information: Complete as instructed.

J. Type of Activity:

SF—Superfund lead
PRP—PRP lead
ST—State lead
FED—Federal lead
PA—Preliminary assessment
SSI—Screening site investigation
LSI—Listing site investigation
RIFS—Remedial Investigation/Feasibility Study
RD—Remedial design
O&M—Operation & Maintenance
NPLD—National Priorities List delete
CLEM—Classic emergency
REMA—Removal assessment
REM—Removal
OIL—Oil response
UST—Underground storage tank response

K. Shipping Information: Complete as instructed.

L. Ship To: Enter lab name, address and sample recipient/custodian.

M. SAS/Case No.: Complete as instructed.

N. Sample Numbers: For routine organic/inorganic samples, enter the CLP numbers from the ''stick-on'' labels. For SAS samples, enter the SAS sample numbers (SAS number plus a unique sequential numeric suffix).

O. Sample Information: Complete as instructed.

P. Regional Specific Tracking Number or Tag Number: Enter sample tag number(s).

Q. Station Location Number: Enter sample identifier (as defined in the QAPP).

R. Time/Date: Complete as instructed. Use military time.

S. Sampler Initials: OPTIONAL.

T. Corresponding CLP Organic/Inorganic Sample Number: Enter CLP sample number (from ''stick-on'' labels) of corresponding sample from same location. Not applicable to SAS forms.

U. Designated Field QC: Indicate QC status when applicable (field blanks, trip blanks, duplicates, MS/MDS, etc.).

V. Sampling Status: Is the sampling for this Case/SAS complete? Circle one.

W. Page 1 of : Record number of documents enclosed in cooler.

X. MS/MSD and/or Duplicate: List samples.

Y. Additional Samplers Signatures: OPTIONAL.

Z. Chain-of-custody Seal No.: Enter the numbers that appear on the custody seals to be used to seal the cooler (there should be two).

AA. ''Relinquished by'' and ''Time/Date'': Complete as instructed. Use military time.

BB. Split Samples: PRP representative (PRP contractor) shall sign off here if work is oversight.

Distribution: The **Lab Copy** and **Lab Copy for Return to SMO** are included with the shipment. The **Region Copy** and **SMO Copy** are returned to the office.

Notice of Transmittal (Figure 8)

1. Enter name of team leader.

2. Enter team leader's firm name.

3. Enter CH2M HILL project number.

4. Enter case number.

5. Enter date.

6. Enter number of samples shipped.

7. Enter matrix of samples.

8. Enter the site name in words.

9. Enter the location of the site (city, state).

Central Regional Laboratory Sample Data Report (Figure 9)

The Central Regional Laboratory Sample Data Report is filled out by the CH2M HILL Sample Documentation Coordinator. A separate report is filled out for each laboratory that receives samples.

1. Enter the case number or SAS number.

2. Enter the site name.

3. Enter the laboratory name.

4. Enter the date shipped.

5. Enter the Superfund D.U. number.

6. Enter the EPA RPM.

7. Enter the CERCLIS number.

8. Enter the page numbers.

NOTICE OF TRANSMITTAL

DATE:

TO: CH2M HILL - REM/FIT Office, Reg. V-X (WI)
310 West Wisconsin Avenue, Suite 700
P.O. Box 2090
Milwaukee, Wisconsin 53201

Attn.: Shirley Stringer

FROM: ① (name) / ② (firm)

CH2M HILL PROJECT #: ③

Enclosed are appropriate copies of the sample documentation forms completed under Case # ④ for the ⑤, 19⑤ shipment of ⑥ (qty) ⑦ (matrix) samples from the ⑧ site located in ⑨, ⑨.

GLT85/15

FIGURE 8

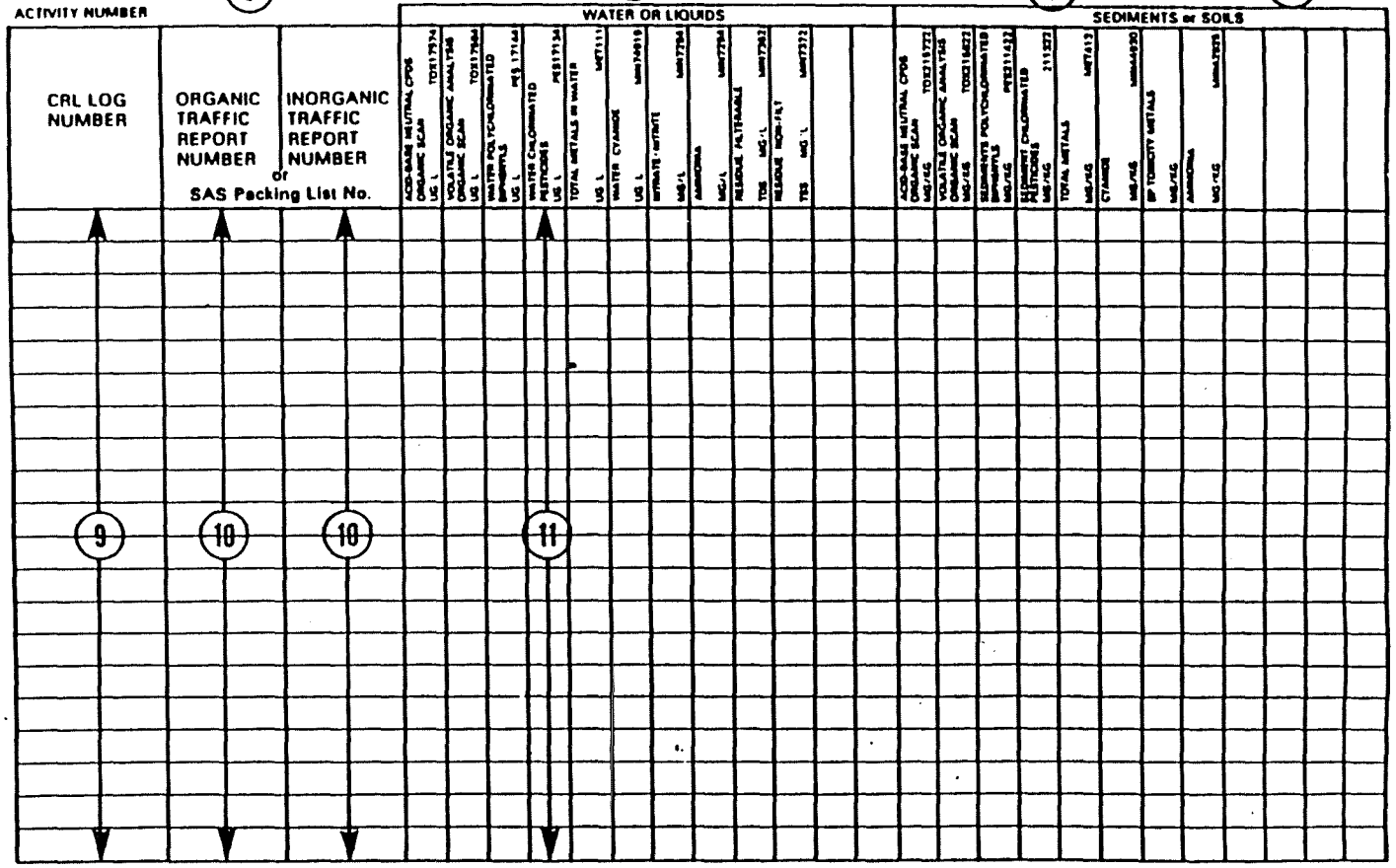
CENTRAL REGIONAL LABORATORY SAMPLE DATA REPORT
ORGANICS/INORGANICS

THIS FORM IS TO BE USED FOR SAMPLES SENT TO CONTRACT ONLY

CASE NUMBER/SAS No. (1) SITE NAME (2) LABORATORY (3) DATE SHIPPED (4)

SUPERFUND DU NUMBER (5) EPA RPM or OSC IS M S I/ICES) (6) CERCLIS NUMBER (7) PAGE (8) OF

ACTIVITY NUMBER



NOTE: For purposes of illustration forms are reproduced at 70% of original size.

FIGURE 9

9. Enter the CRL numbers.

10. Enter the organic or inorganic traffic report number or the SAS packing list number.

11. Check the appropriate boxes for the analyses to be performed.

Packaging and Shipping Procedures

Low-Concentration Samples

1. Prepare coolers for shipment.

    - Tape drains shut.
    - Affix ''This Side Up'' labels on all four sides and ''Fragile'' labels on at least two sides of each cooler.
    - Place mailing label with laboratory address on top of coolers.
    - Fill bottom of coolers with about 3 inches of vermiculite or use performed poly-foam liner.
    - Place appropriate traffic reports, SAS packing lists, or regional field sheets and chain-of-custody records with corresponding custody seals on top of each cooler.

2. Arrange decontaminated sample containers in groups by sample number.

3. Mark volume levels on bottles with a grease pencil.

4. Secure appropriate sample tags around lids of containers with string or wire.

5. Secure container lids with strapping tape.

6. Arrange containers in front of assigned coolers.

7. Affix appropriate adhesive labels from assigned traffic report to each container. Protect with clear label protection tape.

8. Seal each container within a separate plastic bag.

9. Arrange containers in coolers so that they do not touch.

10. If ice is required to preserve the samples, cubes should be repackaged in double zip-loc bags and placed on and around the containers (especially on VOA vials).

11. Fill remaining spaces with vermiculite (or place poly-foam liner cover on top of samples).

12. Sign chain-of-custody form (or obtain signature) and indicate the time and date it was relinquished to Federal Express.

13. Separate copies of forms. Seal proper copies within a large zip-loc bag and tape to inside lid of cooler. Distribute remaining copies as indicated in the following sections.

14. Close lid and latch.

15. Carefully peel custody seals from backings and place intact over lid openings (right front and left back). Cover seals with clear protection tape (Figure 10).

16. Tape cooler shut on both ends, making several complete revolutions with strapping tape. **Do not** cover custody seals (see Figure 10).

17. Relinquish to Federal Express. Place airbill receipt inside the mailing envelope and send to the sample documentation coordinator along with the other documentation.

18. Telephone the SMO in Alexandria, Virginia.

    (Note: This step should be omitted for samples sent to the CRL).

    Ms. Leslie Braun (subject to change)
    703/557-2490

    Provide the following information:

    - Your name
    - Project name
    - Case number
    - Number of samples sent to each laboratory for analysis
    - Airbill numbers

This must be done IMMEDIATELY following sample shipment. If the SMO is closed at that time, call in the information first thing the next day.

Medium- and High-Concentration Samples

Medium- and high-concentration samples are packaged using the same techniques used to package low-concentration samples, with several additional restrictions. First, a special airbill including a Shipper's Certification for Restricted Articles is required (Figures 10 and 11). Second, ''Flammable Liquid N.O.S.'' or ''Flammable Solid N.O.S.'' labels must be placed on at least two sides of the cooler. Third, sample containers are packaged in metal cans with lids before being placed in the cooler, as indicated below.

1. Place approximately ½ inch of vermiculite in the bottom of the can.

2. Position the sample jar in the zip-loc bag so that the sample tags can be read through the plastic bag.

3. Place the jar in the can and fill the remaining volume with vermiculite.

4. Close the can and secure the lid with metal clips.

5. Write the traffic report number on the lid.

6. Place ''This Side Up'' and ''Flammable Liquid N.O.S.'' (or ''Flammable Solid N.O.S.'') labels on the can.

7. Place the cans in the cooler.

Special Instructions for Shipping Samples by Federal Express (Figures 11 and 12)

1. Label cooler as hazardous shipment.

   - Write shipper's address on outside of cooler. If address is stenciled on, just write "shipper" above it.
   - Write or affix sticker saying "This Side Up" on two adjacent sides.
   - Write or affix sticker saying "ORM-E" with box around it on two adjacent sides. Below ORM-E, write NANo. 9188.
   - Label cooler with "Hazardous Substance, N.O.S." and "liquid" or "solid," as applicable.

2. Complete the special shipping bill for restricted articles (Figures 10 and 11).

   - Under *Proper Shipping Name*, write "Hazardous Substance, N.O.S." and "liquid" or "solid," as applicable.
   - Under *Class*, write "ORM-E."
   - Under *Identification No.*, write NA No. 9188.