REMEDIAL DESIGN/REMEDIAL ACTION QUALITY ASSURANCE PROJECT PLAN

Wausau Water Supply NPL Site
Wausau, Wisconsin

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CONESTOGA-ROVERS & ASSOCIATES

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Wausau Superfund Site

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LIST OF ACRONYMS AND SHORT FORMS

BNA	-	Base/Neutral-Acid Extractable Organic Compounds
°C	-	Degree Centigrade
CD	-	Consent Decree
CLP	-	Contract Laboratory Program
CRA	-	Conestoga-Rovers & Associates
DCE	-	1,2-Dichloroethene
DQO	-	Data Quality Objectives
GAC	-	Granular Activated Carbon
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectrometry
MDL	-	Method Detection Limit
MPP	-	Monitoring Program Plan
MS/DUP	-	Matrix Spike/Laboratory Duplicate
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
NBS	-	National Bureau of Standards
NPL	-	National Priorities List
PCB	-	Polychlorinated Biphenyl Compounds
PCE	-	Tetrachloroethylene
PE	-	Performance Evaluation
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAO	-	Quality Assurance Officer
QAPjP	-	Quality Assurance Project Plan
QC	-	Quality Control
RAS	-	Routine Analytical Services
RCRA	-	Resource Conservation and Recovery Act
RI/FS	-	Remedial Investigation/Feasibility Study
RD/RA	-	Remedial Action/Remedial Design
ROD	-	Record Of Decision
RI/FS	-	Remedial Investigation/Feasibility Study
RPD	-	Relative Percent Difference
Site	-	Wausau Superfund Site
SOP	-	Standard Operating Procedures
SVE	-	Soil Vapor Extraction
TAL	-	Target Analyte List
TCA	-	1,1,1-Trichloroethane
TCE	-	Trichloroethylene
TCL	-	Target Compound List
USEPA	-	United States Environmental Protection Agency
VOC	-	Volatile Organic Compounds
WAC	-	Wisconsin Administrative Code
WDNR	-	Wisconsin Department Of Natural Resources
ZOC	-	Zone Of Compliance

QUALITY ASSURANCE PROJECT PLAN (QAPjP)

1.0 INTRODUCTION

The Quality Assurance Project Plan (QAPjP) presents the organization, objectives, functional activities and specific quality assurance (QA) and quality control (QC) activities associated with the Remedial Design/Remedial Action (RD/RA) at the Wausau Superfund Site. This QAPjP also describes the specific protocols which will be followed for sampling, sample handling and storage, chain of custody and laboratory and field analyses. The purpose and objective of the QAPjP is to ensure that the analytical results are accurate and representative for the media sampled.

This QAPjP is prepared in accordance with USEPA QAPjP guidance document QAMS-005/80, "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" and the Region V Model QAPjP (1991).

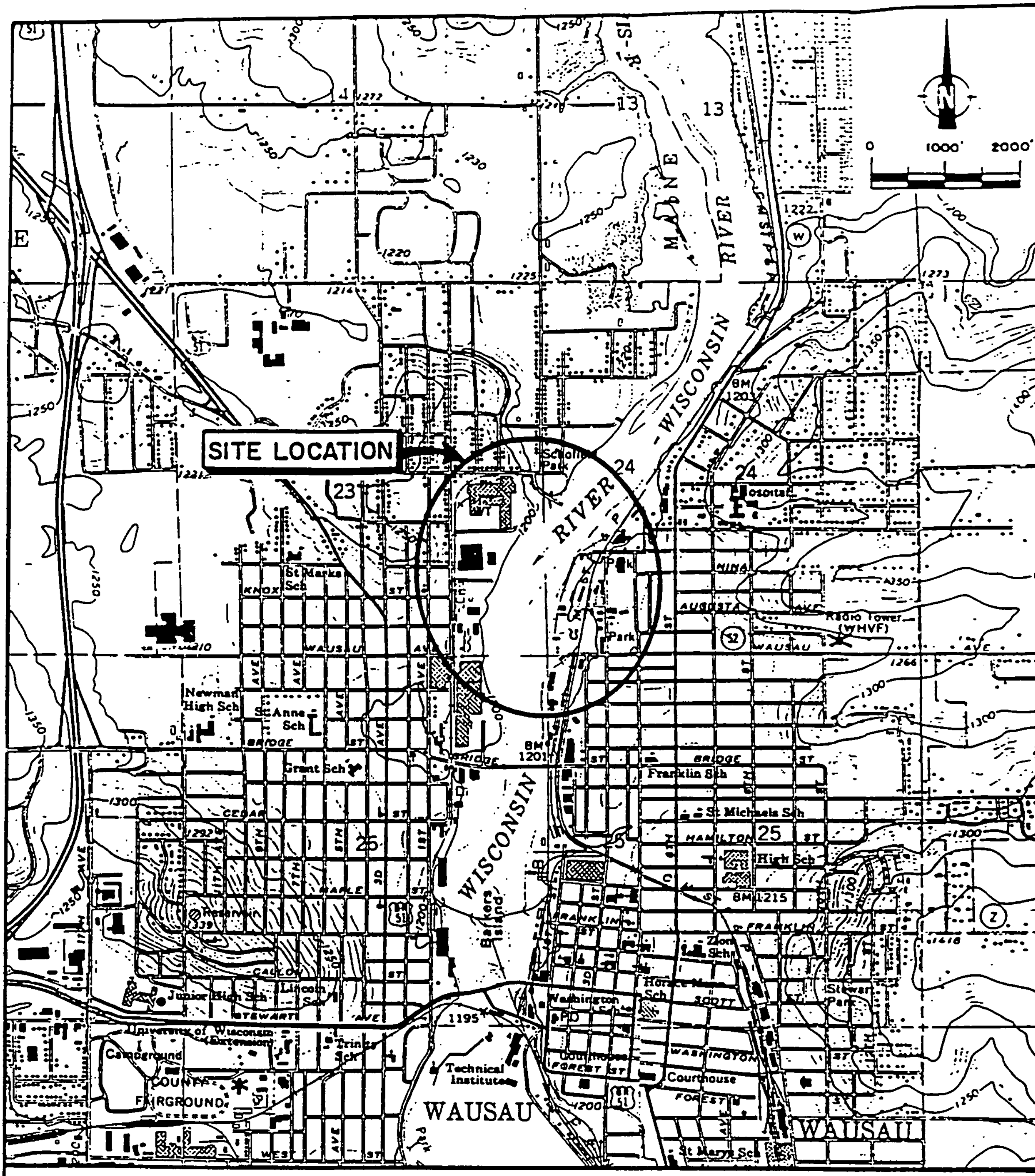
2.0 PROJECT DESCRIPTION

The following presents the Site description and background, previous investigations and existing Site conditions.

2.1 SITE DESCRIPTION

The Wausau Superfund Site (Site) is located within the City of Wausau which is located in north-central Wisconsin along the Wisconsin River, Marathon County, Wisconsin. Figure 2.1 shows the location of the Site and Figure 2.2 presents a Site plan. The Site consists of two locations separated by the Wisconsin River. The property comprising the former City of Wausau landfill is presently owned by Marathon Electric Company and is located on the west side of the Wisconsin River and is referred to as the West Site for RD/RA activities. The East Side location is owned by the Wausau Chemical Corporation and is comprised of two source areas for the Soil Vapor Extraction (SVE) remediation. These two locations are considered source areas for contaminants in the aquifer which is the source of drinking water for the City of Wausau.

The City presently operates seven production wells, six of which are located on the north side of the City. The seventh well, CW-8, is located adjacent to the Wausau Municipal Airport on the south side of the City. Plan 1 shows the location of City water supply wells within the Site. Production wells CW-6, CW-7, CW-9 and CW-10 are located west of the Wisconsin River and are collectively referred to as the west well field. Production wells CW-3 and CW-4 are located on the east side of the Wisconsin River and are referred to as the east well field. Presently, the water from CW-8 has a high concentration of iron and is used only during peak demand periods. The water from CW-4 is also used only during peak demand periods.



SOURCE U.S.G.S. WAUSAU WEST QUADRANGLE MAP.

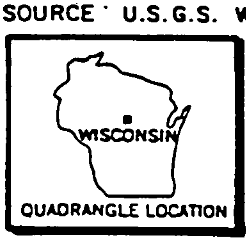


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figure 2.1
SITE LOCATION
Wausau Superfund Site

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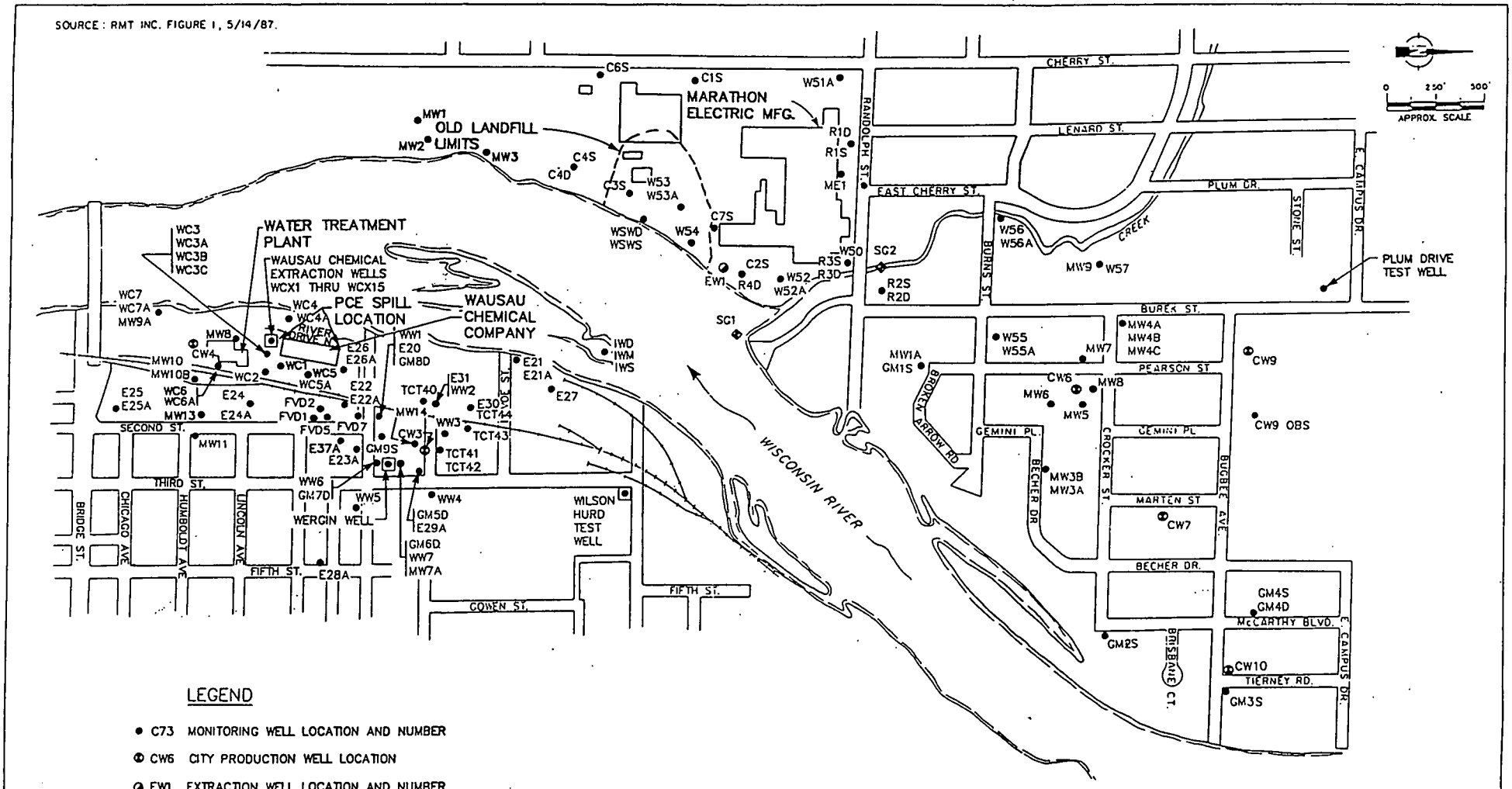


figure 2.2

SITE PLAN

Wausau Superfund Site

CRA

3978-22/05/91-2-0

The west well field is located in a predominantly residential area. Wausau Chemical Corporation is located between production wells CW-3 and CW-4. The east well field is located in a predominantly industrial section of the City. The former City of Wausau landfill is located on the south side of the Marathon Electric property, south of the City of Wausau's west well field.

2.2 SITE BACKGROUND

The City of Wausau discovered in early 1982, that its production wells CW-3, CW-4 and CW-6 were contaminated with volatile organic compounds (VOCs). Tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,2-dichloroethene (DCE) were the predominant contaminants found. TCE was the primary VOC detected at CW-6, however, PCE and DCE have also been reported (Weston, 1984). Since TCE was first detected, the concentrations at CW-6 have ranged from 26 to over 200 micrograms per liter (µg/L). Sample results from the east well field (CW-4 and CW-3) indicate PCE, TCE and DCE contamination. CW-4 has generally shown a steady decrease in concentrations of these three constituents since 1984. CW-3 has shown decreases in PCE and DCE since they were discovered. TCE concentrations, however, have remained relatively constant at concentrations ranging between 80 and 210 µg/L. Toluene, ethylbenzene and xylene were also detected in well CW-4.

The City instituted a blending program whereby uncontaminated water from CW-9 and CW-7 was blended with water from CW-3, CW-4 and CW-6 in order to decrease VOC levels to acceptable drinking water quality prior to distribution. However, the program was largely ineffective due to continuing increases in VOC concentrations and groundwater quality which exceeded regulatory limits at that time.

In the fall of 1983, the EPA awarded the City a federal grant to help fund the design and installation of research units (Granular Activated Carbon and Air Strippers) to reduce contaminants and provide sufficient water of acceptable quality to City residents. However, during the interim, the DNR requested assistance from the EPA emergency response team to evaluate possible responses to the contaminant levels in the City's drinking water supply. Under emergency response, the EPA installed and operated a temporary granular activated carbon (GAC) treatment system at CW-6 starting in July 1984. As part of the research effort, full-scale packed tower air strippers were operational in August 1984 at the City water treatment plant to treat water from wells CW-3, CW-4 and CW-6. The air stripping towers proved to be very effective for removal of the VOCs from the City's water supply. The temporary GAC system was subsequently removed from service in October 1984.

In December 1985, the Site was nominated for inclusion on the National Priorities List (NPL). A remedial investigation/feasibility (RI/FS) study was conducted for the EPA by Warzyn Engineering, Inc. The RI/FS entailed two phases of field sampling. Phase I of the field work was conducted between August 1987 and January 1988. An Operable Unit Record of Decision (ROD) and Interim Consent Decree to address the west side contamination plume was signed in September 1988. Phase II of the RI/FS field work was conducted between June and September 1988. Results of the Phase II study are summarized in the RI/FS report dated August 1989. The remedial alternative selected is outlined in the ROD issued by the EPA in September 1989. A negotiated Consent Decree incorporating the ROD in the final remedy was negotiated by the settling defendants, EPA and the WDNR in 1990. The Consent Decree was lodged with the United States District Court for the Western District of Wisconsin on November 9, 1990. The Consent Decree establishes a schedule by which settling defendants must design and construct the final remedy.

The remedial design and construction of the operable unit groundwater extraction well on the Marathon Electric Corporation's property north of the former City landfill has been completed. The approximate location of the operable unit extraction well is shown on Figure 2.2. The groundwater extraction well was put into operation on November 14, 1990 and initially extracted groundwater at an approximate flow rate of 1,600 gallons per minute (gpm). In December 1990, CRA submitted a report entitled "Extraction Well No. 1, Well Installation and Pump Testing, Marathon Electric Manufacturing Company, Wausau, Wisconsin", which summarized the installation and pump testing of the extraction well. In January 1991, CRA submitted a report entitled "Evaluation of Pumping Rate in Extraction Well No. 1, Marathon Electric Manufacturing Company, Wausau, Wisconsin". The report recommended that the pumping rate for the extraction well be reduced to approximately 800 gpm. The EPA provided written approval of the reduction in the pumping rate and on January 31, 1991, the pumping rate for the extraction well was reduced. The extraction well is currently operating at approximately 850 gpm.

2.3 ENVIRONMENTAL SETTING

Marathon County is situated near the margin of the exposed Precambrian Shield. The bedrock in the Wausau area is predominantly Precambrian igneous and metamorphic rocks of Lower and Middle Proterozoic age.

Glacial deposits underlying the Site consist of glacial outwash and alluvial sediments which have filled in the preglacial stream valley where the Wisconsin River now follows. The surface topography of the project area is controlled by the underlying Precambrian bedrock topography, glacial deposition and post-glacial erosion.

The seven production wells for the City of Wausau provide drinking water for approximately 33,000 people. These wells are screened in the glacial outwash and alluvial sand and gravel deposits which underlie and are adjacent to the Wisconsin River. This alluvial aquifer ranges from 0 to 160 feet thick and has an irregular base and lateral boundaries. The boundaries of the aquifer are defined by the relatively impermeable bedrock which underlies it and forms its lateral boundaries within a preglacial valley.

Groundwater flow within the unconfined glacial aquifer has been drastically changed by the installation and operation of the operable unit extraction well and the City production wells. Under natural conditions, groundwater would flow toward and discharge to the Wisconsin River and its tributary, Bos Creek. Under existing conditions, however, groundwater flows toward the extraction well and production wells during pumping. Prior to operation of the extraction well the natural groundwater flow directions were frequently reversed due to the City well pumping. The pumping of the east well field has appeared to have affected groundwater flow west of the Wisconsin River. Monitoring well nests located at the Marathon Electric property indicated very slight downward gradients adjacent to the Wisconsin River. Pumpage of the east well field induced recharge of surface water into the aquifer and induced groundwater below the river and on the west side of the river to flow toward CW-3. Based on water level data collected since commencing operation of the extraction well, the extraction well has created a cone of influence which extends below the river. The extraction well effectively contains and collects groundwater contamination on the west side of the river south of CW-6.

Tests performed during the RI indicated that the hydraulic conductivity of the aquifer ranges from 9.7×10^{-2} cm/sec to 2.8×10^{-1} cm/sec. Results of pump tests performed at the operable unit extraction well, as

summarized in the December 1990 CRA report, indicate hydraulic conductivity ranging from 1.9×10^{-2} cm/sec to 1.9×10^{-1} cm /sec.

2.4 SOURCE AREAS FOR CONTAMINANTS OF CONCERN

Previous investigations have identified several potential point sources of VOC contamination surrounding the City of Wausau production well fields. Table 2.1 lists the previous studies which have been conducted and supporting documents. Results of groundwater quality analyses for VOCs conducted during the RI in 1987 and 1988 show a vertical and lateral distribution of total chlorinated ethenes which suggests that a minimum of three sources are affecting the City well field; these are described below.

2.4.1 West Side Source Area

The former City landfill/Marathon Electric property occupies a former sand and gravel pit located on the west bank of the Wisconsin River. The landfill, which consists of approximately 4.5 acres, operated between 1948 and 1955 and accepted the majority of commercial, industrial and residential waste generated within the City of Wausau. The majority of the landfill is currently being used as a parking lot and is covered with a bituminous pavement; the southern portion is vegetated. The approximate limits of the sand and gravel pit and the estimated extent of the former landfill are shown on Figure 2.2.

TABLE 2.1

HISTORICAL REPORTS ON WAUSAU, WISCONSIN
WATER SUPPLY SITE

Author	*Date*	*Title*
Becher Hoppe Engineers, Inc.	1983	Groundwater Investigation (for the City of Wausau)
STS Consultants, Ltd.	July, 1984	Subsurface Exploration and Testing Program to Evaluate Groundwater Quality at the Wausau Chemical Facilities in Wausau, WI
Joseph L. Gehin	January, 1985	Wausau Water Quality Update and Performance Evaluation of CW-3 and CW-4 Air Strippers
Roy F. Weston, Inc.	September, 1985	Hydrogeological Investigation of Volatile Organic Contamination in Wausau, Wisconsin, Municipal Wells
STS Consultants, Ltd.	December, 1985	Interim Report Groundwater Extraction Program, Wausau Chemical Corp., Wausau, WI
CH_2M Hill	February, 1986	Investigation of Abandoned City of Wausau Landfill
Foth & Van Dyke & Associates	July, 1986	VOC Groundwater Investigation at the former Wausau Energy Facility in Wausau, WI
Twin City Testing Corp.	August, 1986	Existing Conditions Report and Exploration Program, Wausau East Municipal Well Field, Wausau, WI
RMT, Inc./Geraghty & Miller, Inc.	June, 1987	Hydrological Investigation of Alluvial Aquifer Beneath City Well 6, Wausau, WI

TABLE 2.1

HISTORICAL REPORTS ON WAUSAU, WISCONSIN
WATER SUPPLY SITE

Author	*Date*	*Title*
Geraghty & Miller, Inc.	March, 1987	Preliminary Data Sheets, East Side Groundwater Quality Investigation, City of Wausau, WI
Warzyn Engineering	July 24, 1989	Remedial Investigation for the US EPA Volumes 1, 2 and 3 for the Wausau NPL Site
US EPA	September 29, 1989	Record of Decision (ROD) Document Explaining Selection of Final Remedy
Conestoga-Rovers & Associates	May, 1990	Interim Remedial Alternative for Operable Unit Extraction Well for Marathon Electric Manufacturing Co.
US EPA	November 8, 1990	Consent Decree Lodged in United States District Court for the Western District of Wisconsin for the United States of America, State of Wisconsin vs City of Wausau, WI, Marathon Electric Mfg. Corp., and Wausau Chemical Co.
Conestoga-Rovers & Associates	December, 1990	Extraction Well No. 1, Well Installation and Pump Testing, Marathon Electric Manufacturing Company, Wausau, Wisconsin
Conestoga-Rovers & Associates	January, 1991	Evaluation of Pumping Rate in Extraction Well No. 1, Marathon Electric Manufacturing Company, Wausau, Wisconsin

2.4.1.1 Source Characterization

The predominant source of contamination to CW-6 and CW-3 appears to be the former City landfill/Marathon Electric property. Elevated concentrations of TCE were detected in groundwater, soil and soil gas samples obtained from the northern portion of the landfill. Soil gas TCE concentrations within the landfill ranged from below detection limits (0.01 µg/L) to 298 µg/L. Soil samples obtained from borings in the vicinity of the landfill contained TCE concentrations of approximately 200 µg/kg. Based on calculations performed during the RI, it is estimated that 270 pounds of VOCs are present in the unsaturated soils and fill at the former City landfill/Marathon Electric property. Groundwater samples obtained from the vicinity of the landfill indicate TCE concentrations range from 16 µg/L to 1900 µg/L. Also detected in the vicinity of the landfill were DCE,1,1,1-trichloroethane (TCA), chloroform and carbon tetrachloride at concentrations below 100 µg/L.

2.4.1.2 Contaminant Migration

West side monitoring wells delineate a deep (greater than 100 feet deep) north-south trending TCE plume. The vertical distribution of TCE throughout the aquifer near the old City landfill also suggests that the source of contamination lies within the northern portion of the landfill. The plume appears to have migrated northward under influence of the pumpage of CW-6 and eastward, under the Wisconsin River, toward CW-3. The highest TCE concentration (4200 µg/L) in the plume was detected approximately 550 feet south of CW-6.

TCE was also detected in the shallow aquifer between Bos Creek and CW-6. TCE contamination in this shallow aquifer appears to have resulted from the induced infiltration of surface water from Bos Creek,

which has been contaminated by the untreated discharge of water from CW-6. The induced surface water recharge of the aquifer is evident from the downward vertical gradients at monitoring well nests in that area. TCE concentrations adjacent to CW-6 discharges were found to be 100 µg/L. TCE concentrations in the ponded area downstream were approximately 70 µg/L. TCE was not detected in surface water samples collected upstream of the CW-6 discharge nor was it detected at the point where Bos Creek enters the Wisconsin River.

Prior to the summer of 1988, CW-6 was pumped directly into Bos Creek. Pumpage of CW-6 served as a barrier well to the rest of the west well field. However, the discharge of CW-6 to Bos Creek apparently created a contaminated groundwater mound between the source area and CW-6. The influence of the groundwater mound may not have fully penetrated the glacial outwash aquifer, but the RI data suggests that the mound served to effectively divide the west well field contaminant plume into northern and southern components, slowing contaminant migration away from the source.

In 1988 the City of Wausau completed a river crossing for a transport pipe to carry contaminated water from CW-6 to an air stripper on the east side of the river. The discharge of contaminated groundwater to Bos Creek was discontinued, and the City was able to put CW-6 back into service with an increase in the pumping rate. These factors would tend to increase the rate of migration from the source area towards CW-6.

In November 1990, Marathon Electric completed the installation of the operable unit extraction well on its property approximately 2100 feet south of CW-6. The extraction well is currently extracting groundwater at approximately 850 gpm. Treated groundwater is discharged to the Wisconsin River. The extraction well effectively contains and collects groundwater VOC contamination on the west side and underneath of the

Wisconsin River. The extraction well and CW-6 serve as barrier wells, providing protection for the remaining water supply wells in the west well field.

2.4.2 East Side Source Area

The Wausau Chemical Company property (Wausau Chemical) is located between CW-3 and CW-4 on the east bank of the Wisconsin River and contains the other two potential sources of VOC contamination. The facility, established in 1964, is a bulk solvent distributor and transfer station for the shipment of waste chemicals and solvents from area businesses. The facility experienced two documented PCE spills in 1983 totaling approximately 1,000 gallons. Solvents released by Wausau Chemical are apparently responsible for a large percentage of the shallow groundwater contamination in the east well field. However, there may be other sources not identified at this time. The East Side source area is comprised of two sources located on the property, one at the north loading dock and the other at the former tank area.

2.4.2.1 Source Characterization

Soil gas and soil boring data reflecting the distribution of VOCs in the unsaturated soils were collected as part of the soil gas survey and from soil borings for source characterization during the RI. This data indicates higher concentrations of contaminants in the area located in the southern portion of the facility (Wausau Chemical tank farm) with decreasing concentrations within an elongated contaminant zone trending toward the east-northeast and south. Elevated concentrations of PCE were also found in unsaturated soils near the north loading dock. The highest level of PCE in the soil gas was reported from the southern end of the facility

at a concentration of 7680 µg/L. Analysis of soil samples indicated 3500µg/kg of PCE in the vicinity of the north loading dock, and 1000 µg/kg at the south end of the property. Again, based on calculations performed during the RI, the total amount of VOCs remaining in the unsaturated soils at Wausau Chemical is approximately 260 pounds. This estimate may vary if contamination is found to exist beneath the Wausau Chemical facility building complex.

During the summer of 1984, approximately 1000 to 1500 cubic yards of solvent impacted soil was removed from the tank farm area and disposed of at a hazardous waste landfill. In October 1985, a groundwater extraction/treatment program was initiated. The groundwater remediation system consists of six submersible pumps alternatively operated in 15 extraction wells. As of January 1991, this system has removed and treated approximately 274 million gallons of impacted groundwater. Influent and effluent to the treatment system is monitored on a monthly basis to determine treatment efficiency and document compliance with WPDES permit.

2.4.2.2 Contaminant Migration

East side monitoring wells indicate three plumes within the east well field area, one deep plume apparently originating from the former City landfill on the west side of the river and two plumes originating southwest of CW-3.

The latter two plumes are restricted to the shallow portion of the aquifer (upper 40 feet) and consist of primarily PCE, TCE and DCE. Both of these plumes are apparently the result of past releases from the Wausau Chemical facility. A large, widely dispersed VOC plume extending eastward from the Wausau Chemical property was identified during the RI. The

highest concentrations of VOCs in this plume were detected in the vicinity of the Wausau Chemical tank farm behind the southern part of the building complex. A second plume was detected north of the Wausau Chemical facility in the vicinity of the northern loading dock. This plume was differentiated from the other plume by the absence of PCE degradation products.

2.5 PROJECT SCOPE AND OBJECTIVES

2.5.1 Project Scope

In accordance with the September 29, 1990 Record of Decision (ROD) and the Consent Decree (CD) entered with the court on January 24, 1991, the PRP Group is implementing the final remedial action for the Wausau Superfund Site (Site) in Wausau, Wisconsin. The remedial action consists of:

- Installation of soil vapor extraction (SVE) systems to remove VOCs in soils at each of three identified source areas;
- SVE off-gas treatment using vapor phase carbon;
- Groundwater remediation utilizing municipal supply wells and operable unit extraction wells; and
- Treatment of groundwater utilizing existing City air strippers and the operable unit extraction well treatment system.

This QAPjP has been developed in accordance with the requirements specified in Appendix four of the CD (Scope of Work) to address the quality assurance requirements necessary to assess the impact of the SVE

and groundwater remediation systems at the Site and to assure compliance with the ROD and CD.

2.5.1.1 Zone of Compliance

The Zone of Compliance (ZOC) for the Site is defined as the area in which Wisconsin Administrative Code (WAC) NR140 (October 1988) Standards must be achieved in the groundwater at specified monitoring points. For the identified VOC contaminants of concern, these levels are:

1.8 µg/L	Trichloroethylene (TCE)
1.0 µg/L	Tetrachloroethylene (PCE)
70 µg/L	1,2-Dichloroethylene (DCE)

Additionally, NR140 (October 1988) levels will apply to any other contaminants of concern identified during the monitoring for the final remedy. For compounds not listed in NR140 (October 1988), the Site groundwater standards will be identified based on the approach described in Section 2.4 of the Monitoring Program Plan (MPP). Based on the data collected during the RI/FS process, the ZOC includes the majority of the Site. The ZOC will be reevaluated based on data collected during the compliance monitoring program.

2.5.2 Monitoring Program Objectives

The Compliance Monitoring Program will be implemented as part of the final remedy at the Site to monitor the operation and performance of the SVE and groundwater remediation systems by monitoring the Site soils, soil gas, hydraulic capture and water quality

performance during systems operations. Groundwater monitoring at the Site will be broken into four zones based on the groundwater extraction systems as shown on Figure 2.3. Soil and soil gas monitoring will be separated into the two source areas based on the configuration of the SVE systems.

The objectives of the Compliance Monitoring Program are separated based on the three principal elements of the final remedy; SVE, groundwater extraction and groundwater treatment.

SVE SYSTEMS

- to monitor the long term effectiveness of the SVE systems by collection and analysis of soil and soil gas samples for VOCs;

- to monitor VOC mass removal from source areas by collection and analysis of SVE extracted air prior to carbon treatment;

- to monitor the potential for additional contaminants at the three source areas by chemical analyses at selected monitoring wells in the vicinity of the sources on an annual basis.

GROUNDWATER EXTRACTION

- to monitor the horizontal and vertical hydraulic zone of capture, within the pumped aquifer, by collection and assessment of groundwater levels;

- to monitor flow patterns at the Site, as modified by groundwater remediation operation and Wisconsin River fluctuation, by the collection and assessment of groundwater levels;

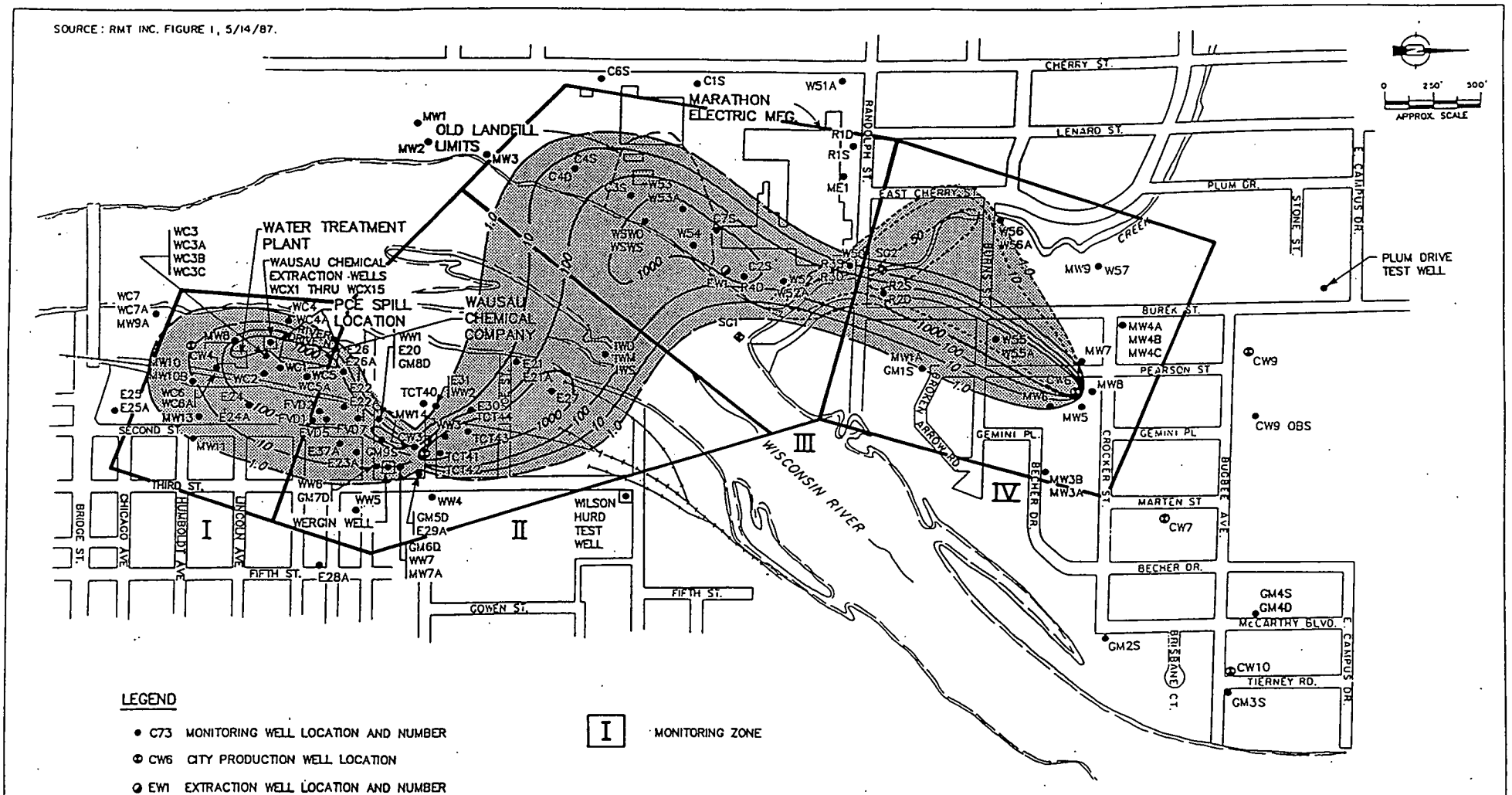


figure 2.3
MONITORING ZONES
Wausau Superfund Site

CRA

- to monitor the long term improvement in groundwater quality at the Site by the collection and chemical analysis of groundwater samples from monitoring and extraction wells;

GROUNDWATER TREATMENT

- to monitor the treatment of extracted groundwater for VOC removal efficiencies by the collection and chemical analysis of influent and effluent water samples from the treatment systems;

In order to provide representative data to satisfy the above objectives, the MPP presents the monitoring requirements to be followed during the operation of the final remedy.

Groundwater compliance monitoring is a combination of hydraulic and water quality monitoring designed to verify that the groundwater extraction wells are achieving the necessary contaminant capture and that groundwater quality is improving based on source remediation and VOC removal from the aquifer.

Groundwater VOC remediation, at a Site like Wausau, is a long-term process that can't be readily measured on a short term basis using water quality data alone. Because of the time necessary to achieve various levels of groundwater remediation, containment of contaminated groundwater is a measurable, achievable short-term objective. At Wausau, there are currently four active groundwater extraction systems designed to contain VOC contaminated groundwater during the long-term groundwater remediation program.

The best way to measure contaminant capture for the extraction wells is to measure the hydraulic gradients in proximity to the extraction wells to show that groundwater containing VOCs is flowing toward

the wells and are therefore being removed by pumping. The water level monitoring network includes the necessary monitoring points to show that necessary capture is occurring.

Actual remediation of the groundwater is a slower process that is much more difficult to measure using field data on a short-term basis. Accordingly, water quality data is measured periodically on a long-term basis to show the downward trend of VOC concentrations in groundwater. Significant VOC reductions are measured over a period of years rather than weeks or months.

The proposed groundwater monitoring network is designed to measure the long-term water quality improvement by the collection and chemical analysis of groundwater samples from a comprehensive list of wells located at the Site on an annual basis. Appreciable changes are not expected on a more frequent basis. In order to verify that significant changes aren't occurring, a group of core locations have been selected for quarterly monitoring to verify the water quality trends.

This approach has been accepted and has been shown to be effective at several other Sites including Sites in Region V.

The monitoring plan will address groundwater monitoring within the Zone of Compliance by the collection and analysis of samples from groundwater monitoring wells located from areas of higher concentration to the fringes of the Site to verify which area(s) exceed WAC NR 140 (October 1988) levels. Hydraulic data will be utilized to show that groundwater exceeding WAC NR 140 (October 1988) levels is being captured by the various extraction wells.

Extraction well performance will be evaluated utilizing water level monitoring data to define the zones of capture for each of the

extraction wells. In addition, the extraction wells will be sampled and chemically analyzed to estimate mass removal. Indicator monitoring wells in the centers of the plume will be chemically analyzed to show the reduction of VOCs in the groundwater over time.

2.6 SAMPLE NETWORK DESIGN AND RATIONALE

The sample network design and rationale for sample locations is described in detail in the MPP.

2.7 PARAMETERS TO BE TESTED AND FREQUENCY

Sample matrices, analytical parameters and frequencies of sample collection are presented in Tables 2.2.

2.8 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions made during investigation activities and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. There are five analytical levels which address various data uses and the QA/QC effort and methods required to achieve the desired level of quality.

DQOs have been established in accordance with the USEPA guidance document entitled "Data Quality Objectives for Remedial Response Activities - Development Process", dated March 1987, in conjunction with the document, "Data Quality Objectives for Remedial

TABLE 2.2

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WAUSAU SUPERFUND SITE*

Sample Matrix	Frequency	Field Parameters	Lab Parameters**	Estimated Number of Investigative Samples	Field (Rinsate) Blanks	Field Duplicates	MS/MSD or MS/DUP***
Groundwater - Core Locations	Quarterly****	Water Level, pH, Temp., Conductivity	Site VOC	13	2	2	1
	Prior to system startup, annually thereafter - Indicator wells	Water Level, pH, Temp., Conductivity	TCL/TAL Parameters	6	1	1	1
Groundwater - Comprehensive Locations	Prior to start-up, annually thereafter	Water level, (semi-annual), pH, Temp., Conductivity	Site VOC, Site Metals, Site BNA	66	7	7	4
Groundwater - Treatment System Influent	Monthly	pH, Temp., Conductivity	Site VOC	3	--	1:10	--
Groundwater - Treatment System Effluent	Monthly	pH, Temp., Conductivity	pH, Site VOC, Site Metals	2	--	1:10	--
	Annual	pH, Temp., Conductivity	TCL/TAL Parameters	2	--	1:10	--
Soil	Before, mid-point, and at end of SVE operation period.	pH	Site VOC	106	11	11	6

TABLE 2.2

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WAUSAU SUPERFUND SITE*

Sample Matrix	Frequency	Field Parameters	Lab Parameters**	Estimated Number of Investigative Samples	Field (Rinsate) Blanks	Field Duplicates	MS/MSD or MS/DUP***
Soil Gas	Weekly during first month, monthly for two months, quarterly thereafter, monthly PID reading.	PID	Site VOC****--on-Site	63	--	1:10	--
			Site VOC--off-Site	7 (Quarterly)	--	1	--
Exhaust Gas	Weekly during first month, monthly for two months, quarterly thereafter.	--	TCL VOC--off-Site	2	--	1:10	--

Notes:

* Two filled 40-mL preserved glass vials will be shipped with each cooler of VOC water and/or soil samples to serve as a trip blank. One pre-evacuated Summa canister will be shipped with each set of soil gas and/or exhaust gas samples to serve as a trip blank.

** See Table 4.1 for analytical methods and reporting limits.

*** Matrix spike/matrix spike duplicate (MS/MSD) analyses are required for organic parameters and matrix spike/laboratory duplicate (MS/DUP) analyses are required for inorganic parameters. Samples designated for MS/MSD analyses will be collected, with extra sample volumes for aqueous samples, at a frequency of one per group of twenty (20) or fewer investigative samples.

*** Monitoring well IWD will not be monitored during months of December, January or March, or if it is inaccessible due to weather conditions.

**** The following Site-VOC parameters will not be included in the on-Site soil gas analytical protocol: acetone, 2-butanone, chloroform, 4-methyl-2-pentanone, 1,1,2-trifluoro-1,2,2-trichloroethane, chloromethane and vinyl chloride.

Response Activities - Example Scenario RI/FS Activities at a Site with Contaminated Soils and Groundwater", dated March 1987. Reference to these documents ensures that the data base developed during the Site activities meets the objectives and quality necessary for its intended use.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different levels of analytical support:

i) Level I - Field screening or analysis using portable instruments;

ii) Level II - Field analyses using more sophisticated portable analytical instruments;

iii) Level III - All analyses performed in off-Site analytical laboratories using EPA procedures other than the Contract Laboratory Program (CLP) Routine Analytical Services (RAS);

iv) Level IV - CLP-RAS performed in a CLP analytical laboratory using CLP procedures; and

v) Level V - Non-standard analytical methods performed in an off-Site laboratory.

Chemical analyses of samples collected from the Site will require Level III analytical support. Field (on-Site) VOC analyses will require Level II support. The remaining field measurements will require Level I analytical support. Table 2.3 lists the specific investigation objectives for each data type.

TABLE 2.3

DATA QUALITY OBJECTIVES
WAUSAU SUPERFUND SITE

Matrix	*Data Type*	*Investigation Objectives*	*Data Quality Level*	*Data Uses**
Groundwater - Core Locations	Water Level	Evaluate hydraulic capture from groundwater extraction	I	MI
	pH, Temp., Conductivity, DO, Turbidity,	Characterize general water quality	I	MI
	Site VOC	Evaluate progress of remedial actions	III	MI
	TCL/TAL Parameters	Determine the presence of contaminants other	III	MI, SC
Groundwater - Comprehensive Locations	Water level	Evaluate hydraulic capture from groundwater extraction	I	MI
	pH, Temp., Conductivity, DO, Turbidity,	Characterize general water quality	I	MI
	Site VOC, Site Metals, Site	Evaluate progress of remedial actions	III	MI
Groundwater - Treatment System Influent	Site VOC	Evaluate removal efficiency and total VOC removal	III	MI

TABLE 2.3

DATA QUALITY OBJECTIVES
WAUSAU SUPERFUND SITE

Matrix	*Data Type*	*Investigation Objectives*	*Data Quality Level*	*Data Uses**
Groundwater - Treatment System Effluent	pH	Characterize general water quality	I	MI
	pH, Site VOC, Site Metals	Evaluate removal efficiency, total VOC removal and discharge	III	MI
	TCL/TAL Parameters	Evaluate discharge quality	III	MI
Soil	pH	General soil	I	MI
	Site VOC	Evaluate progress of remedial actions	III	MI
Soil Gas	PID or Colorimetric Indicator Tube	Determine when carbon requires change out	I	MI
	Site VOC --on-Site	Evaluate progress of remedial action	II	MI
	Site VOC --off-Site	Confirm progress of remedial action	III	MI, SC
Exhaust Gas	TCL VOC --off-	Evaluate VOC air	III	MI

Notes:

* Intended data uses:

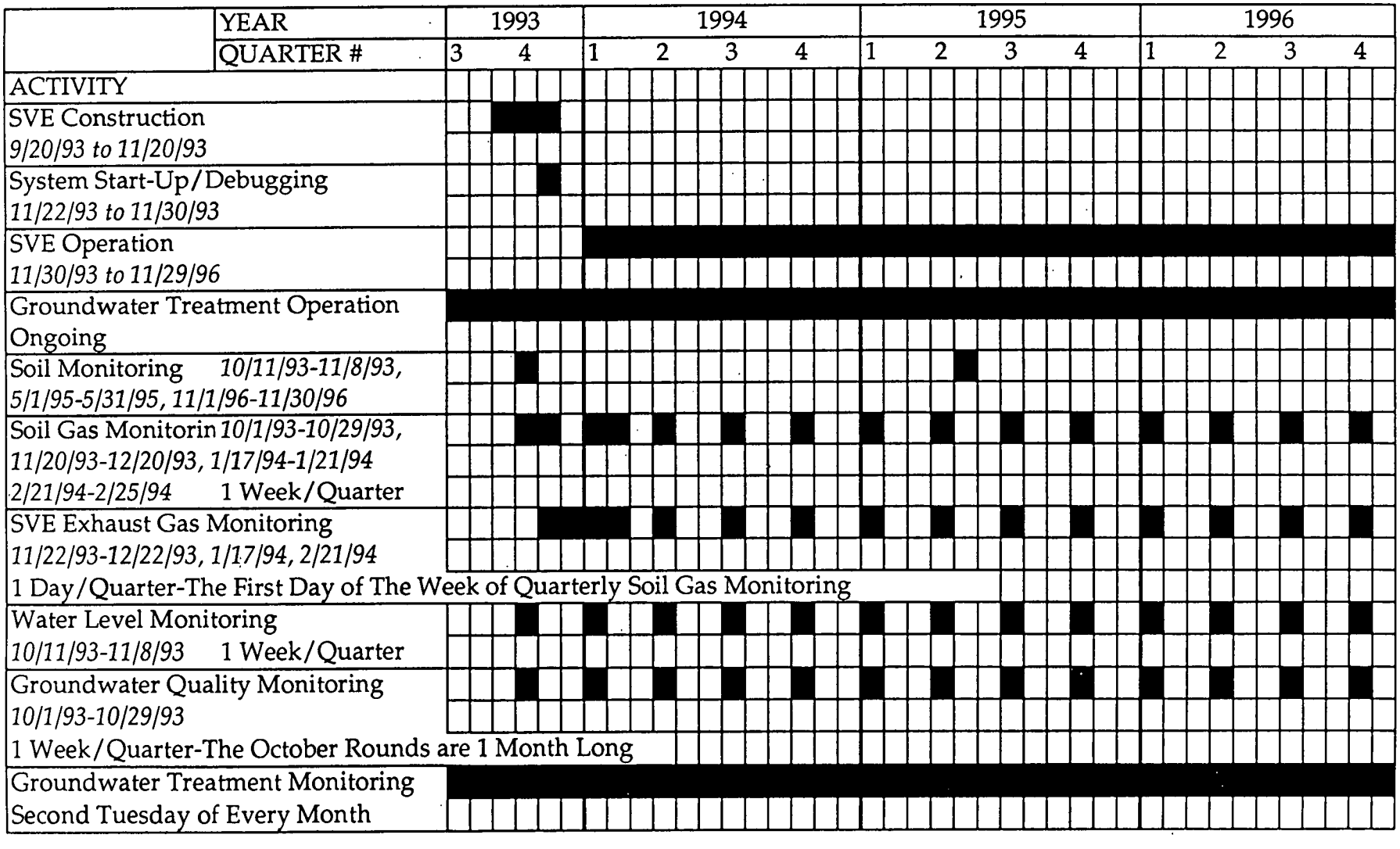
SC - Site Characterization

MI - Monitoring During Implementation of Remedial Action

2.9 PROJECT SCHEDULE

The project schedule is presented in Table 2.4.

TABLE 2.4
WAUSAU WATER SUPPLY NPL SITE
FINAL REMEDIATION PROJECT SCHEDULE



3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Conestoga-Rovers & Associates (CRA), as contractor to the Wausau PRP Group, has overall responsibility for all phases of the activities at the Site. CRA will perform or supervise all field activities and will report directly to Wausau PRP Group's project manager.

Enviroscan, Inc. (Enviroscan), will perform off-Site chemical analyses of groundwater samples for VOC, BNA, cyanide and pH. In addition, Enviroscan will analyze soil gas samples on-Site for VOC. Environmental Control Technology Corporation (Encotec) will analyze off-Site soil gas and exhaust gas samples for VOC and off-Site groundwater samples for metals and pesticides/PCBs. The laboratory addresses are as follows:

Enviroscan, Inc.
303 West Military Road
Rothschild, WI 54474

Encotec, Inc.
3985 Research Park Drive
Ann Arbor, MI 48108

All firms will provide project management as appropriate to their responsibilities. CRA will provide administrative oversight and QA/QC for all deliverables. All final project deliverables will be issued by CRA.

Figure 3.1 presents the organizational chart for the project. A summary of each of the key persons responsibilities is presented below:

Margaret Guerriero - Remedial Project Manager - USEPA

- general overview of the project to ensure that the objectives are met;
- participation on key negotiations with CRA and WDNR;
- approval of QAPjP.

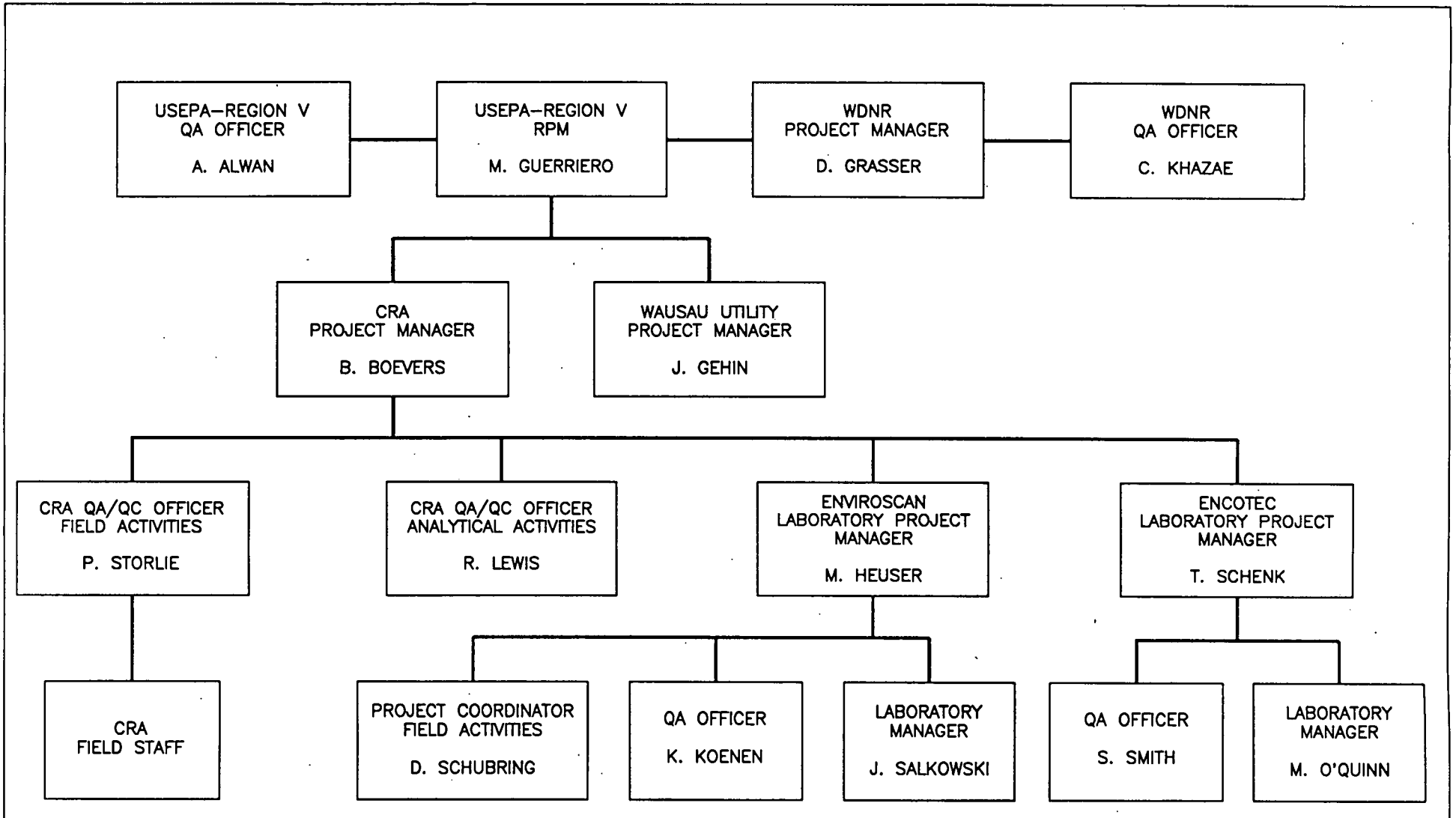


figure 3.1
PROJECT ORGANIZATION
Wausau Water Supply Site

CRA

3978(7)–AUGUST 26/93–REV.0 (C–01)(MN)

Donald Grasser - Project Manager - WDNR

- general overview of the project to ensure that the objectives are met;
- participation on key negotiations with CRA and EPA;
- approval of QAPjP.

Al Alwan-QA Manager - USEPA

- review laboratory QA/QC;
- advise on data corrective action procedures;
- approval of QAPjP.

Charlene Khazae-QA Manager - WDNR

- review laboratory QA/QC;
- advise on data corrective action procedures;
- approval of QAPjP.

Joseph Gehin - Project Manager - Wausau Water & Sewerage Utility

- general overview of the project to ensure that the objectives are met;
- participation on key negotiations with WDNR and EPA;
- approval of QAPjP; and
- managerial guidance to CRA Project Manager.

Brian Boevers - Project Manager - CRA

- data assessment;
- preparation and review of reports;
- technical representation of project activities;
- managerial guidance to technical group; and
- approval of the QAPjP.

Ruth Lewis - Quality Assurance/Quality Control (QA/QC) Officer - Analytical Activities - CRA

- systems audits - laboratory activities;
- overview and review field QA/QC;
- coordinate supply of performance evaluation samples;
- review laboratory QA/QC;
- data validation and assessment;

- advise on data corrective action procedures;
- assist in the preparation and review of reports;
- QA/QC representation of project activities; and
- approval of QAPjP.

Peter Storlie - QA Officer - Field Activities - CRA

- lead QA/QC for field activities;
- data assessment of field analyses;
- technical representation of field activities; and
- preparation of standard operating procedures (SOPs) for field activities.

Mary Christie-Heuser - Laboratory Project Manager - Enviroscan

- ensures all resources of the laboratory are available on an as-required basis;
- overview of final analytical reports; and
- approval of the QAPjP.

Timothy Schenk - Laboratory Project Manager - Encotec

- ensures all resources of the laboratory are available on an as-required basis;
- overview of final analytical reports; and
- approval of the QAPjP.

Primary responsibility for project quality rests with the CRA QA/QC Officer - Analytical Activities and QA Officer - Field Activities. Ultimate responsibility for project quality rests with the CRA Project Manager. Independent quality assurance will be provided by the Laboratory Project Manager and QA Officer prior to release of all data to CRA.

4.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analyses and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, chain-of-custody, laboratory instruments calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment and corrective action are described in other sections of this QAPjP. The purpose of this section is to address the specific objectives for accuracy, precision, completeness, representativeness and comparability.

4.1 LEVEL OF QA EFFORT

Rinsate blank, trip blank, field duplicate and matrix spike samples will be analyzed to assess the quality of the data resulting from the field sampling program. Rinsate and trip blanks will be submitted to the analytical laboratories to provide the means to assess the quality of the data resulting from the field sampling program. Rinsate blank samples are analyzed to check for procedural contamination at the Site which may cause sample contamination. Rinsate blanks are samples of reagent grade water that have been used to rinse the sampling equipment. These blanks are collected after equipment decontamination and prior to re-using the sampling equipment. Trip blanks are used to assess the potential for contamination of VOC samples due to contaminant migration during sample shipment and storage. The trip blank for aqueous and soil samples is a bottle of reagent water prepared by the laboratory which is kept unopened in the cooler throughout the process of sample collection. A trip blank for soil and exhaust gas samples is a pre-evacuated Summa Canister prepared by the laboratory which remains unopened during the sample collection process.Field duplicate samples are analyzed to check for sampling and analytical reproducibility. Field duplicate samples are obtained by alternately

filling sample containers from the same sampling device for each parameter. Matrix spikes provide information about the effect of the sample matrix on the preparation and measurement methodology. Matrix spikes are samples to which predetermined quantities of stock solutions of certain analytes are added prior to sample preparation and analysis.

The general level of the QC effort will be one field duplicate and one rinsate blank per ten investigative samples or a minimum of one per sampling Site. One matrix spike/matrix spike duplicate (MS/MSD) sample set will be analyzed for every 20 or fewer investigative samples per sample matrix for organic analyses. One matrix spike/laboratory duplicate (MS/DUP) sample set will be analyzed for every 20 or fewer investigative samples per sample matrix for inorganic analyses. One trip blank sample per shipping container will be analyzed for water, soil and soil gas samples submitted for VOC analysis. The number of field QA/QC samples to be collected are listed in Table 2.2.

The level of QC effort provided by the laboratory for soil, groundwater, soil gas and exhaust gas samples will be equivalent to those specified in the standard operating procedures (SOP) which are based on 40 CFR Part 136, Appendix A, "Chemical Methods for Analysis of Water and Wastes", USEPA-600/4-79-020, revised March 1983, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, 3rd edition, 1986 with current revisions and EPA Compendium Method TO-14, "The Determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analyses" modified for point source determinations.

Table 4.1 presents the targeted quantitation limits for the analyses.

TABLE 4.1

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	*Quantitation Limits*	*Quantitation Limits*	
TCL Volatile Organic Compounds	*Low Water (µg/L)*	*Low Soil (µg/Kg)*	*Med. Soil (µg/Kg)*
Chloromethane*	1	1	5
Bromomethane	1	1	5
Vinyl Chloride*	1	1	5
Chloroethane	1	1	5
Methylene Chloride*	1	1	5
Acetone*	10	10	50
Carbon Disulfide	1	1	5
1,1-Dichloroethene*	1	1	5
1,1-Dichloroethane*	1	1	5
cis-1,2-Dichloroethene*	1	1	5
trans-1,2-Dichloroethene*	1	1	5
Chloroform*	1	1	5
1,2-Dichloroethane	1	1	5
2-Butanone*	10	5	50
1,1,1-Trichloroethane*	1	1	5
Carbon Tetrachloride*	1	1	5
Bromodichloromethane	1	1	5
1,2-Dichloropropane	1	1	5
cis-1,3-Dichloropropene	1	1	5
Trichloroethene	1	1	5
Dibromochloromethane	1	1	5
1,1,2-Trichloroethane*	1	1	5
Benzene*	1	1	5
trans-1,3-Dichloropropene	1	1	5
Bromoform	1	1	5
4-Methyl-2-pentanone*	10	10	50
2-Hexanone	10	10	50
Tetrachloroethene*	1	1	5
Toluene*	1	1	5
1,1,2,2-Tetrachloroethane	1	1	5
Chlorobenzene*	1	1	5
Ethyl Benzene*	1	1	5
Styrene	1	1	5
Xylenes*	1	1	5
1,1,2-Trifluoro-1,2,2-trichloroethane*	1	1	5

TABLE 4.1 (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	
TCL Volatile Organic Compounds	*Quantitation Limits Air (ppbv)*
Benzene	1.0
Bromodichloromethane	1.0
Bromomethane	1.0
Carbon tetrachloride	1.0
Chlorobenzene	1.0
Chloroethane	1.0
Chloromethane	1.0
cis-1,2-Dichloroethene	1.0
cis-1,3-Dichloropropene	1.0
Ethylbenzene	1.0
Xylenes (total)	1.0
Methylene chloride	1.0
Styrene	1.0
Tetrachloroethene	1.0
Toluene	1.0
trans-1,3-Dichloropropene	1.0
Trichloroethene	1.0
Chloroform	1.0
Vinyl chloride	1.0
Dibromochloromethane	1.0
1,1,-Dichloroethane	1.0
1,2-Dichloroethene (total)	1.0
1,1-Dichloroethene	1.0
1,2-Dichloroethane	1.0
1,2-Dichloropropane	1.0
1,1,1-Trichloroethane	1.0
1,1,2-Trichloroethane	1.0
1,1,2,2-Tetrachloroethane	1.0
Acetone	10
2-Butanone	10
2-Hexanone	10
4-Methyl-2-pentanone	10

TABLE 4.1 (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	
TCL Base/Neutral-Acid Extractable Organic Compounds	*Quantitation Limits Water (µg/L)*
Phenol*	10
Bis(2-Chloroethyl)ether	10
2-Chlorophenol	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
4-Methylphenol	10
Bis(2-Chloroisopropyl)ether	10
2-Methylphenol	10
N-Nitroso-Di-N-Propylamine	10
Hexachloroethane	10
Nitrobenzene	10
Isophorone	10
2-Nitrophenol	10
2,4-Dimethylphenol	10
Bis(2-Chloroethoxy)methane	10
2,4-Dichlorophenol	10
1,2,4-Trichlorobenzene	10
Naphthalene*	10
4-Chloroaniline	20
Hexachlorobutadiene	10
4-Chloro-3-methylphenol	20
2-Methylnaphthalene*	10
Hexachlorocyclopentadiene	10
2,4,6-Trichloropentadiene	10
2,4,5-Trichlorophenol	10
2-Chloronaphthalene	10
2-Nitroaniline	50
Dimethylphthalate	10
Acenapthylene	10
3-Nitroaniline	50
Acenaphthene	10
2,4-Dinitrophenol	50
4-Nitrophenol	50
Dibenzofuran	10
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
Diethylphthalate	10
Carbazole	10

TABLE 4.1 (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	
4-Chlorophenyl phenyl ether	10
Fluorene*	10
4-Nitroaniline	10
4,6-Dinitro-2-methylphenol	50
N-Nitrosodiphenylamine	10
4-Bromophenyl phenyl ether	10
Hexachlorobenzene	10
Pentachlorophenol*	50
Phenanthrene*	10
Anthracene	10
Di-n-butylphthalate	10
Fluoranthene	10
Pyrene	10
Butyl benzyl phthalate	10
3,3-Dichlorobenzidine	20
Benzo(a)anthracene	10
bis(2-ethylhexyl)phthalate*	10
Chrysene	10
Di-n-octyl phthalate	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Indeno(1,2,3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(ghi)perylene	10

TABLE 4.1 (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	*Quantitation Limits*
TCL Pesticides/PCBs	*Water (µg/L)*
Aldrin	0.01
alpha-BHC	0.01
beta-BHC	0.01
delta-BHC	0.01
Lindane	0.01
Chlordane	0.01
4,4-DDD	0.01
4,4-DDE	0.01
4,4-DDT	0.01
Dieldrin	0.01
Endosulfan I	0.01
Endosulfan II	0.01
Endosulfan Sulfate	0.01
Endrin	0.01
Endrin Aldehyde	0.01
Heptachlor	0.01
Heptachlor Epoxide	0.01
Toxaphene	0.10
PCB-1016	0.10
PCB-1221	0.10
PCB-1232	0.10
PCB-1242	0.10
PCB-1248	0.10
PCB-1254	0.10
PCB-1260	0.10
Methoxychlor	0.50

TABLE 4.1 (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	*Quantitation Limits*
TAL Inorganic Parameters	*Water (µg/L)*
Aluminum	16
Antimony	75
Arsenic	1.4
Barium*	1
Beryllium	0.2
Cadmium	2
Calcium	19
Chromium*	6
Cobalt	5
Copper	5
Iron*	3
Lead	2
Magnesium	41
Manganese*	2
Mercury	0.2
Nickel	10
Potassium	1200
Selenium	5
Silver	6
Sodium	42
Thallium	5
Vanadium	6
Zinc*	4
Cyanide	10
pH	**

Notes:

* - Site Target Compounds/Parameters
** - Not Applicable

4.2 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.

4.3 COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

Completeness is a measure of the amount of valid (usable) data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that the laboratory will provide data meeting QC acceptance criteria for 95 percent or greater for all samples tested using the analytical methods. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness} = \frac{\text{Valid (Usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

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 development of this network, consideration has been given to the historical operations, existing analytical data and physical setting and processes. The rationale of the sampling network is discussed in detail in the MPP. Representativeness will be satisfied by insuring that the MPP is followed, proper sampling techniques are used, proper analytical

procedures are followed and holding times of the samples are not exceeded in the laboratory.

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.

5.0 SAMPLING PROCEDURES

The procedures and protocols for collecting samples and for performing related field activities are described in the following sections.

5.1. EQUIPMENT CLEANING AND DECONTAMINATION

The procedures detailed below will be followed for all sampling equipment before and between sampling events.

5.1.1 Drill Rig/Soil Sampling Equipment

Upon mobilization of the drill rig to the Site, and prior to commencing drilling, the rig and all associated equipment will be thoroughly steam cleaned to remove oil, grease, mud and other foreign matter. Cleaning will take place in the designated on-Site decontamination area. Subsequently, before initiating drilling at each borehole, the augers, cutting bits, drill steel and associated equipment will be steam cleaned to prevent cross-contamination from the previous drilling location.

Decon water will be collected and discharged to the sanitary sewer. Cleaning of soil sampling equipment (e.g. split spoon samplers) will be accomplished by flushing and wiping the components to remove all visible sediments followed by:

i) clean with tap water and laboratory detergents, using a brush if necessary, to remove particulate matter and surface films;

ii) rinse thoroughly with tap water;

iii) rinse with isopropanol (pesticide grade);

iv) allow the equipment to air dry as long as possible;

v) final distilled water rinse; and

vi) wrap with aluminum foil, if appropriate, to prevent contamination if the equipment is going to be stored or transported.

Following final rinse, openings will be visually inspected to verify they are free of soil particulates and other solid material which may contribute to possible sample cross-contamination.

Fluids used for cleaning will not be recycled. All wash water and rinse water will be collected and discharged to the sanitary sewer. Decontamination fluids (isopropanol) will be collected and stored in containers for disposal in accordance with WDNR and EPA Region V regulations.

Soil borings will be backfilled with remaining soil cuttings, if no confining layers have been encountered, to a depth of three feet bgs. The upper three feet will be backfilled with a cement/bentonite grout mixture in accordance with WDNR requirements. Borehole abandonment will be documented using WDNR Well/Drillhole/Borehole Abandonment form (Form 3300-5B).

5.1.2 Aqueous Sampling Equipment

The aqueous sampling equipment cleaning and decontamination procedures are as follows:

1) Washed thoroughly with Alconox or equivalent;

2) Rinsed with potable water;

3) Rinsed with isopropanol (pesticide grade);

4) Allowed to air dry;

5) Wrap with new aluminum foil; and

6) A final distilled water rinse prior to purging.

Fluids used for cleaning will not be recycled. All wash water and rinse water will be collected and discharged to the sanitary sewer. Decontamination fluids (isopropanol) will be collected and stored in containers for disposal in accordance with WDNR and EPA Region V regulations.

5.2 SUBSURFACE SOIL SAMPLING PROTOCOL

All soil samples will be collected with a split spoon sampler fitted with a removable, sealable brass liner. The soil samples collected in the split-spoon samplers will be prepared in the following manner for chemical analyses:

1) The sampling tool and all other instruments used in extracting the soil samples for chemical analyses will be precleaned using the prescribed rinse sequence (Section 5.1). A new pair of disposable latex gloves will be used for each sample handled. Disposable gloves and rinsings will be collected and contained for proper disposal.

2) Each soil sample for chemical analyses will be obtained and prepared in the following manner:

   Upon opening of the split spoon sampler, the brass liner will immediately be trimmed and removed from the spoon. Aluminum

foil and an air tight plastic cap will be placed over the each end of the brass tube.

3) Containers for sample collection (e.g., rinse blanks) will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

4) Soil samples will be labeled noting the sampling location, depth, time and sampler's initials. A separate hard-cover field book will be maintained to document all soil samples and sampling events (including: date and time collected, sample handling and storage, preservation and labeling, field measurements, characteristics of each sample taken, and weather conditions).

5) Samples will be placed on ice or cooler packs in laboratory supplied coolers after collection and labeling.

5.3 GROUNDWATER SAMPLING PROTOCOL

The order of sample collection for each sample fraction will be as follows:

1) VOC fraction
2) Metals fraction
3) BNA fraction
4) Pesticide/PCB fraction
5) Cyanide fraction

5.3.1 Monitoring Well Sampling

All monitoring wells will be sampled according to the following protocols:

1) New disposable latex gloves will be used when sampling each well. Additional glove changes will be made for each sampling.

2) The sampler will measure and record the depth to water in each well to the nearest 0.01 foot using an electric tape or plopper.

3) Prior to sampling, each well will be purged, using a slow flow rate teflon bladder stainless steel pump fitted with teflon purging and air supply lines attached to a nylon rope. A minimum of three times the standing water volume in the well will be removed, or until conductivity, temperature, pH, turbidity, dissolved oxygen and redox potential stabilize in the purge water. In the event that a well is purged dry prior to achieving three well volumes, groundwater will be permitted to recover to a level sufficient for sample collection. The time that the well was purged dry will be noted and well recovery will be monitored. Upon recovery, a bladder pump will then be used for sample collection. A bailer will be used to collect the sample if it is physically impossible to use a bladder pump. Prior to use in each well, the bailer or bladder pump will be precleaned as follows:

   1) Washed thoroughly with Alconox or equivalent;
   2) Rinsed with potable water;
   3) Rinsed with isopropanol (pesticide grade);
   4) Allowed to air dry;
   5) Wrap with new aluminum foil; and
   6) A final distilled water rinse prior to purging.

All waste groundwater, not used for samples, will be collected and discharged to the sanitary sewer. Waste groundwater from the west side monitoring well sampling will be discharged to the Interim Action treatment manhole if it is in closer proximity than the sanitary sewer.

4) Field measurements of pH, conductivity , temperature, turbidity, dissolved oxygen and redox potential will be recorded prior to sample collection. Calibration of field instruments will be conducted as specified in Section 7.0.

5) After the required standing well water has been purged, water samples will be collected using a teflon bladder stainless steel pump, fitted with teflon purging and air supply lines, attached to a nylon rope. The groundwater samples will be collected from the purge line of the bladder pump used to purge the well. New nylon rope, where applicable, will be used for each monitoring well.

   Initially, unfiltered and filtered monitoring well samples will be submitted to the laboratory for metals analyses. Field filtered samples will be collected using a 0.45 micron filter. After one year from initiation of the monitoring program, EPA, WDNR and CRA project management will decide whether filtered and/or unfiltered samples will be submitted for future metals analyses. The decision will be based on the data generated during the first year of monitoring.

6) Containers for sample collection will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

7) All disposable gloves and nylon ropes will be placed in DOT approved 55-gallon drums and stored at a designated area. All drummed waste will be disposed of in accordance with State and Federal regulations. All rinsings will be handled as discussed in item (3), above.

8) Samples will be labeled noting the well location, date, time and sampler's initials. A separate hard-cover bound field notebook will be maintained describing the sampling history (including: date and time of collection, sample handling and storage, preservation and labeling, field measurements, details pertaining to well purging and characteristics of each sample taken, and weather conditions).

9) Samples will be placed on ice or cooler pack in laboratory supplied coolers after collection and labeling.

5.3.2 Well Head Sampling

The production and extraction well (influent) head sampling will be conducted in accordance with the following protocols:

1) New disposable latex gloves will be used when collecting the water samples.

2) The samples will be collected by the grab sample method directly into the precleaned sample containers. The samples will be collected at the well head directly from sampling ports.

3) Containers for sample collection will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

4) Samples will be labeled noting the sampling location, date, time and sampler's initials. A separate hard-cover field book will be maintained to document all samples and sampling events. Weather conditions at the time of sampling will be noted.

5) Samples will be placed on ice or cooler packs in laboratory supplied coolers after collection and labeling.

5.3.3 Treated Groundwater Effluent Sampling

The treated groundwater (effluent) samples will be collected in accordance with the following protocols:

1) New disposable latex gloves will be used when collecting the sample.

2) The samples will be collected by the grab sample method directly into the precleaned sample containers. The Marathon Electric extraction sample will be collected from the rip rap lined discharge structure immediately prior to the point where the treated groundwater enters the Wisconsin River. The City of Wausau sample will be collected from the effluent from the air stripping towers.

3) Containers for sample collection will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance

for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

4) Samples will be labeled noting the sampling location, date, time and sampler's initials. A separate hard-cover field book will be maintained to document all samples and sampling events. Weather conditions at the time of sampling will be noted.

5) Samples will be placed on ice or cooler packs in laboratory supplied coolers after collection and labeling.

5.4 SVE EXHAUST GAS SAMPLING

Off-Site Sample Analysis

The SVE exhaust gas samples will be collected from the exhaust side of the SVE vacuum blower upstream from the first activated carbon unit and from downstream of the second carbon unit. The samples will be collected in accordance with the following protocols:

1) New disposable latex gloves will be used when collecting the sample.

2) The samples will be collected by attaching a pre-evacuated, 6-liter Summa gas canister to the exhaust sampling port using Swageloc compression tube connectors.

3) The samples will be collected while the vacuum blower is operating at its nominal flow rate and pressure by opening both the sample port valve and the Summa canister valve.

4) The valves will be left open until the pressure on the canister has equilibrated with that on the SVE exhaust line as indicator by a pressure gauge on the intake of the canister.

5) The valve on the canister will be closed and then the valve on the exhaust port will be closed.

6) Canisters for sample collection will be prepared using standard laboratory validated cleaning procedures that meet or exceed the requirements of the specific method. QA/QC samples will be collected as specified in Table 2.2.

7) The canister will be labeled with the location, time, date, sampler name and exhaust pressure. A separate hard-cover field book will be maintained to document all samples and sampling events. Weather conditions at the time of sampling will be noted.

5.5 SOIL GAS SAMPLING

On-Site Sample Analysis

Soil gas samples will be collected from all of the permanent monitoring probes for on-Site field laboratory analysis according to the following protocols:

1) New disposal latex gloves will be used when collecting the sample.

2) Samples will be collected after the SVE system has been shut-off at least 48 hours for the quarterly sampling. Samples collected during the weekly and monthly sampling will be collected while the SVE system is operating.

3) The soil gas sample will be collected by inserting a syringe needle through the silicone tube and into the sampling valve outlet port.

4) The glass sampling syringe will be purged three times prior to collecting a soil gas sample for analysis. The sample will be drawn after a minimum of five probe volumes have been purged from the probe and before the vacuum pump is turned off.

5) After the syringe sample has been collected, the vacuum pump will be turned off and the sampling valve is shut.

6) The silicone tube will then be removed from the sampling valve and a 100 ml. glass syringe is connected.

7) The sampling valve will again be opened and another sample is drawn for field screening, if necessary.

8) On-Site analysis of syringe samples will be conducted as quickly as possible to minimize any VOC losses. Glass/Teflon syringes and syringe valves or needle plugs are used to maintain sample integrity between sample collection and analysis

Off-Site Sample Analysis

Soil gas samples will be collected from the permanent monitoring probes according to the following protocols:

1) New disposable latex gloves will be used when collecting the sample.

2) Samples will be collected after the SVE system has been shut-off at least 48 hours.

3) Samples will be collected by attaching a pre-evacuated Summa gas canister and portable vacuum pump with a T-connector to the probe with the valves on the probe and canister closed.

4) The probe will be evacuated for a sufficient time to remove three probe volumes of gas at standard temperature and pressure. The probe evacuation volume will be calculated based on the volume of the tubing leading to the sampling interval and the approximate pore volume of the sand pack in the sampling interval.

5) After purging is complete but prior to shutting off the vacuum pump, the valve between the pump and the T-connector will be closed. The vacuum pump will then be shut off.

6) With the probe valve open and the canister valve shut, the probe will be allowed to equilibrate to ambient pressure.

7) After the vacuum gauge on the probe has read zero vacuum for one minute, the valve on the Summa canister will be opened to collect the sample. Sampling will be complete after the vacuum gauge on the probe has read zero vacuum for one minute and the valves on the canister and the probe will be closed.

8) Canisters for sample collection will be prepared using standard laboratory validated cleaning procedures that meet or exceed the requirements of the specific method. QA/QC samples will be collected as specified in Table 2.2.

9) The canister will be labeled with the location, time, date and sampler name. A separate hard-cover field book will be maintained to document all samples and sampling events. Weather conditions at the time of sampling will be noted.

Sample containers will be delivered to the Site in sealed shipping containers. Container, preservation, shipping and packaging requirements for samples will be in accordance with Table 5.1.

TABLE 5.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WAUSAU SUPERFUND SITE

Analysis	Containers	Preservation	Holding Time*	Sample	Shipping	Packaging
A. Groundwater						
Site/TCL VOC	Three 40 mL volatile organic analysis (VOA) vials	HCl to pH <2, Iced, 4°C	14 days to analysis	Fill completely, no air bubbles	Overnight Courier or Hand Deliver	Foam Liner or equivalent
Site/TCL BNA	Two 1-L amber glass	Iced, 4°C	7 days to extraction; 40 days to analysis	Fill to neck of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
TCL Pesticides/PCB	Two 1-L amber glass	Iced, 4°C	7 days to extraction; 40 days to analysis	Fill to neck of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
Site/TAL Metals	One 1-liter plastic bottle	HNO3 to pH < 2, Iced, 4°C	6 months to analysis (28 days-Mercury)	Fill to shoulder of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
Cyanide	One 500-mL plastic bottle	NaOH to pH > 12, Iced, 4°C	14 days to analysis	Fill to shoulder of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
pH	One 250-ml plastic bottle	Iced, 4°C	24 hours to analysis	Fill to shoulder of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent

TABLE 5.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WAUSAU SUPERFUND SITE

Analysis	Containers	Preservation	Holding Time*	Sample	Shipping	Packaging
B. Soil						
Site VOC	Two 4-ounce wide-mouth glass jars	Iced, 4 ℃	14 days	Fill completely, no headspace	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
C. Soil Gas & Exhaust Gas						
Site VOC/TCL VOC	One 6-liter Summa Passivated Canister	NA	30 days	***	Overnight Courier or Hand Deliver	Bubble Pack or equivalent

Notes:

* Holding time periods are based from time of sample collection to completion of analysis.

** Extra volume (three times the standard volume) will be required for aqueous samples submitted for MS/MSD analysis.

*** For soil gas and exhaust gas samples submitted for VOC analyses, samples are collected by opening the canister valve for a specified period of time or by using a calibrated critical orifice as a sampling device.

6.0 SAMPLE CUSTODY AND DOCUMENT CONTROL

It is USEPA and Region V Policy to follow the USEPA Region V sample custody, or the chain-of-custody protocols as described in "NEIC Policies and Procedures", EPA-330/9-78-DDI-R, revised August 1991. This custody is in three parts: Sample collection, Laboratory analysis and Final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area.

A sample or evidence file is under your custody if they:

i) are in your possession;

ii) are in your view, after being in your possession;

iii) are in your possession and you place them in a secured location; or

iv) are in a designated secure area.

6.1 FIELD CHAIN-OF-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.

6.1.1 Field Procedures

1) 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.

2) All bottles will be labeled with unique sample numbers.

3) Sample labels are to be completed for each sample using waterproof ink unless prohibited by weather conditions.

A unique sample numbering system will be used to identify each collected sample. This system will provide a tracking number to allow retrieval and cross-referencing of sample information. A listing of the sample identification numbers with written descriptions of sample location, type and date will be maintained by CRA field personnel. A typical example of a sample numbering system to be used as follows:

Example	S-041693-AA-XXX		
where:	S	-	Designates sample type (S - Soil, W - Groundwater, A -Soil Gas/Exhaust Gas)
	041693	-	date of collection
	AA	-	sampler initials
	XXX	-	sequential number starting with 001

6.1.2 Field Logbooks/Documentation

The field logbook will provide the means of recording data collecting activities performed. As such, entries will be described in as much detail as possible so that persons going to the Site could reconstruct a particular situation without reliance on memory.

The title page of each logbook will contain the following:

i) person to whom the logbook is assigned;

ii) logbook number;

iii) project name;

iv) project start date; and

v) end date.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the Site, field sampling or investigation team personnel and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in ink and no erasures will be made. If an incorrect entry is make, the information will be crossed out with a single strike mark and initialed. Whenever a sample is collected, or a measurement is made, a detailed description of the location of the station, which includes compass and distance taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in the MPP and Section 5.0 of this document. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. A sample identification number will be assigned during sample collection. Field QC samples (blanks and duplicates), which will receive an entirely separate sample identification number, will be submitted blind to avoid laboratory bias of field QC samples.

6.1.3 Transfer of Custody and Shipment Procedures

1) Samples are accompanied by a properly completed chain-of-custody form. A example of a chain-of-custody form and seal are included in Attachment B. The sample numbers and locations will be listed on the chain-of-custody form. 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 the laboratory, or to/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 secured with strapping tape and 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 chain-of-custody record 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 goldenrod copies will be retained by the sampler for returning 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. Commercial carriers are not required to sign off on the custody form as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

6.2 LABORATORY CHAIN-OF-CUSTODY PROCEDURES

The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number and customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be noted.

Laboratory custody procedures and document control for those samples analyzed by the laboratory will be carried out as specified in the appropriate SOP in Attachment C.

6.3 STORAGE OF SAMPLES

After the sample custodian has prepared the log book, the chain-of-custody will be checked to ensure that all samples are stored in the appropriate locations. All samples will be stored within an access controlled location and will be maintained at 4°C until completion of all analytical work or, as a minimum, for 30 days after receipt of the final report by CRA.

6.4 FINAL EVIDENCE FILES CUSTODY PROCEDURES

Evidential files for the entire project will be maintained by CRA and will consist of the following:

i) project plan;

ii) project log books;

iii) field data records;

iv) sample identification documents;

v) chain-of-custody records;

vi) preliminary data;

vii) correspondence;

viii) references, literature;

ix) final data packages;

x) miscellaneous - photos, maps, drawings, etc.; and

xi) final report.

The evidentiary file materials will be the responsibility of the evidentiary file custodian with respect to maintenance and document removal.

The laboratory will be responsible for maintaining analytical log books and laboratory data. Raw laboratory data files will be inventoried and maintained by the laboratory for a period of five years, at which time CRA will advise the laboratory regarding the need for additional storage.

7.0 CALIBRATION PROCEDURES AND FREQUENCY

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

7.1 LABORATORY INSTRUMENTS

Calibration of laboratory equipment will be based on approved written procedures. Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing quality control activities. These records will be filed at the location where the work is performed and may be subject to QA audit. For all instruments, the laboratory will maintain a factory-trained repair staff with in-house spare parts or will maintain service contracts with vendors.

The records of calibration will be kept as follows:

1) If possible, each instrument will have record of calibration permanently affixed with an assigned record number.

2) A label will be affixed to each instrument showing description, manufacturer, model numbers, date of last calibration and by whom calibrated (signature), due date of next calibration and compensation or correction figures, as appropriate.

3) A written stepwise calibration procedure will be available for each piece of test and measurement equipment.

4) Any instrument that is not calibrated to the manufacturer's original specification will display an appropriate warning tag.

Calibration procedures are detailed in laboratory SOPs for the specified analytical methods (Attachment C).

7.2 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 during the field sampling will be examined to certify that it is in proper operating condition. This includes checking the manufacturer's operating manual 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 of field instruments is governed by the specific SOP for the applicable field method (Attachment C). Calibration of field instruments will be conducted at the intervals specified by the manufacturer or more frequently as conditions dictate. The field equipment will be calibrated, operated and maintained in a manner consistent with the manufacturer's guidelines and USEPA standard methods.

8.0 ANALYTICAL PROCEDURES

The samples collected for analyses will be analyzed according to the USEPA method from which the laboratory specific SOP (see Attachment C) was derived. Table 8.1 presents the analytical method SOPs designated for this project.

TABLE 8.1
SUMMARY OF ANALYTICAL METHOD SOPS
WAUSAU SUPERFUND SITE

Matrix	Method (SOP Number)[1]	Analysis
Groundwater	SOP for SW 8260 (ES 500)	Site/TCL VOC
	SOP for SW 8270 (ES 501)	Site/TCL BNA
	SOP for SW 6010/7000 Series	Site/TAL Metals
	SOP for SW 6010 &6020 (ARLICP.sop & MTLICP.sop)	Aluminum
		Antimony
		Barium
		Beryllium
		Cadmium
		Calcium
		Chromium
		Cobalt
		Copper
		Iron
		Lead
		Magnesium
		Manganese
		Nickel
		Potassium
		Silver
		Sodium
		Thallium
		Vanadium
		Zinc
	SOP for SW 7061 (MTLHYD.mth)	Arsenic
	SOP for SW 7741 (MTLHYD.mth)	Selenium
	SOP for SW 7471 (MTLHG.mth)	Mercury

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1 Methods were derived from:

SW - "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, November 1986 and current revisions.

TO - "The Determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analyses", EPA Compendium Method TO-14, modified for point source determinations.

EPA - "Methods for Chemical Analysis of Water and Wastes", USEPA-600/4-79-020, revised March 1983.

TABLE 8.1
SUMMARY OF ANALYTICAL METHOD SOPS
WAUSAU SUPERFUND SITE

Matrix	Method (SOP Number)[1]	Analysis
Groundwater (Con'd)	SOP for SW 9012 (ES A134)	Cyanide
	SOP for SW 8080 (8080PEST.sop)	TCL
Pesticides/PCB		
	SOP for EPA 150.1 (ES 168)	pH
	CRA Field SOP #1	pH
	CRA Field SOP #2	Conductivity
	CRA Field SOP #3	Temperature
	CRA Field SOP #4	Dissolved Oxygen
	CRA Field SOP #5	Turbidity
	CRA Field SOP #6	Redox Potential
	CRA Field SOP #7	HNu
	CRA Field SOP #8	Indicator Tube
Soil	SOP for SW 8260 (ES 500)	Site/TCL VOC
Soil Gas;	SOP for SW 8021 (ES 521)	Site VOC (on-Site)
Exhaust Gas	SOP for TO-14 (TO-14LL.sop)	TCL VOC (off-Site)

9.0 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

This section presents the internal quality control checks and frequency procedures which will be employed for field and laboratory measurements.

9.1 FIELD QC

Quality control of field sampling will involve collecting field duplicates, field (rinsate) blanks and trip blanks in accordance with the applicable procedures described in Section 4.1, and the level of effort indicated in Table 2.2.

9.2 LABORATORY QC (ON-SITE & OFF -SITE LABORATORY)

Specific procedures related to internal laboratory QC samples (namely, calibration checks, method blanks, matrix spike/matrix spike duplicates, matrix spike/laboratory duplicates, surrogate spikes, QC check samples) are detailed in the following subsections. Current control limits associated with internal laboratory QC are provided in Attachment D. Updated limits will be provided with each data package received from the laboratory.

9.2.1 Initial and Continuing Calibration Checks

The compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. The initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analytical run, while the continuing calibration checks document that the

initial calibration is still valid, and that satisfactory maintenance and adjustment of the instrument on a day-to-day basis is achieved. The specific control criteria and action requirements for these calibrations will be assessed as specified in the laboratory specific SOP for analysis.

9.2.2 Method Blank Samples

A method blank sample will be analyzed by the laboratory at a frequency of one blank per twenty analyses or, in the event that an analytical round consists of less than twenty samples, one method blank sample will be analyzed. The method blank sample will be carried through the entire preparation and analytical procedure. The specific method blank criteria will be assessed as specified in the laboratory specific SOP for analysis.

9.2.3 Matrix Spike/Matrix Spike Duplicates and Matrix Spike/Laboratory Duplicates

A matrix spike/matrix spike duplicate (MS/MSD) or matrix spike/laboratory duplicate (MS/DUP) sample set will be analyzed at a minimum frequency of one per twenty investigative samples for soil and groundwater matrices. Acceptable criteria and compounds that will be used for matrix spikes are identified in the appropriate SOP (see Section 8.0). Percent spike recoveries will be used to evaluate analytical accuracy while percent relative standard deviation between the matrix spike/matrix spike duplicate or unspiked sample/laboratory duplicate will be used to assess analytical precision.

9.2.4 Surrogates

Surrogates are used in all GC and GC/MS analyses. Every blank, standard, and environmental sample including MS/MSD samples will be spiked with surrogate compounds prior to sample analysis for VOC, base/neutral-acid extractable organic compounds (BNA), pesticides and polychlorinated biphenyl compounds (PCB).

Surrogates will be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries will be compared to the control limits set by procedures specified in the method for analytes falling within the quantitation limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates out of the quantitation limit; assessment of analytical quality in these cases will be based in the quality control embodied in the check, matrix spike and matrix spike duplicate samples.

9.2.5 Blind Check Samples

As supplied by the agencies, an analytical batch may contain a blind check sample. In general, the blind check sample will be obtained from EPA Region V and supplied to CRA. The analytes employed in this check sample will be a representative subset of the analytes of interest.

Standard deviations and relative standard deviations will be calculated for the percent recovery of analytes from the check samples. These are defined in Section 13.2.

10.0 DATA REDUCTION, VALIDATION AND REPORTING

The project laboratories (off-Site and on-Site) will perform analytical data reduction and validation in-house under the direction of the laboratory QA officer. The laboratory QA officer will be responsible for assessing data quality and advising of any data which were rated "preliminary" or "unacceptable" or other qualifications based on laboratory QC criteria. Data reduction, validation and reporting by the laboratory will be conducted as detailed in the following. It should be noted, however, that "sign-off" will be required following completion of each step.

1) Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst.

2) The area supervisor reviews the data for attainment of quality control criteria presented in the referenced analytical methods.

3) Upon completion of all reviews and acceptance of the raw data by the laboratory operations manager, a report will be generated and sent to the laboratory quality assurance officer.

4) The laboratory QA officer will complete a thorough inspection of all reports.

5) The QA officer and area supervisor will decide whether any sample re-analysis is required.

6) Upon acceptance of the preliminary reports by the QA officer, final reports will be generated and signed by the laboratory manager.

The data packages supplied by the project laboratories will be consistent and will include the following:

1) Case narrative that includes summary of analytical methods used and description of any unusual action or conditions;

2) laboratory sample results.

3) dates of sample receipt, preparation and analysis;

4) method blank sample analysis summary;

5) surrogate and matrix spike recovery (if applicable) data and control limits;

6) check sample data and control limits;

7) laboratory duplicate data (if applicable) and control limits;

8) dilution factors identified (as required);

9) practical quantitation limits (PQL) for each method;

10) executed chain-of-custody forms;

11) calibration results; and

12) raw data (i.e., chromatograms, spectra, tuning results)

CRA QA/QC Officer - Analytical Activities will conduct an evaluation of data reduction and reporting by the off-Site laboratories. These evaluations will consider items 1 through 12 listed above as well as field QA/QC results (i.e., rinsate blanks, trip blanks, field duplicates). The material will be checked for legibility, completeness, correctness and the presence of requisite dates, initials, and signatures. The results of these checks will be assessed and reported to the CRA project managers noting any

discrepancies and their effect upon the acceptability of the data. All information garnered for QA/QC checks will be discussed in the final report.

Validation of the analytical data from off-Site analyses will be performed by the CRA QA/QC Officer - Analytical Activities based on the QC criteria outlined in "National Functional Guidelines for Organic Data Review", December 1990 (Revised June 1991) and "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analyses", July 1988. Items 1 through 12 and field QA/QC results will be assessed in accordance with the applicable criteria outlined in the guidance documents. The results of these data validations will be reported to the CRA project managers, noting any discrepancy and their effect upon acceptability of the data.

The field GC data will be reduced and assessed by Enviroscan's field analyst. Preliminary results will be reported to CRA upon request. The analyst will perform a second review of the data before issuing a final report to CRA. The report will include numerical sample results and the associated quality control data. Field GC data (on-Site analyses) will be reviewed by CRA's Field QA/QC Officer. The data will be checked for legibility, completeness and any inconsistent data. Any discrepancies and their effect on the acceptability of the data will be noted in a memo to the CRA Project Manager. A formal data validation of field GC data will not be performed.

Raw data from other field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. In addition, field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

Field and laboratory data will accompany the progress reports that are submitted to the regulatory agencies on a scheduled basis.

The data report will be generated from a database prepared by CRA. In addition, copies of actual laboratory data may also be included with the report.

11.0 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 RD/RA Work Plan (and Appendices) and QAPjP. The audits of field and laboratory activities include two separate, independent parts; internal and external audits.

11.1 FIELD AUDITS

A internal audit of field activities (sampling and measurements) will be conducted by the CRA QA/QC Officer - Field Activities prior to any investigatory sampling. The audit will include examination of field sampling records, field instrument operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, etc. These audits would be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the project. The audits would involve review of field measurement records, instrumentation calibration records and sample documentation.

External audits of field activities may be conducted by WDNR or USEPA Region V, as required.

11.2 LABORATORY AUDITS

The internal performance and system audits of the Enviroscan laboratory will be conducted by the CRA QA/QC Officer - Analytical Activities. A systems audit will be conducted prior to any investigatory sample analyses. Additional audits will be conducted as

deemed necessary by either the owner, CRA project manager or the CRA QA/QC Officer - Analytical Activities and will include examination of laboratory documentation of sample receiving, sample log-in, sample storage, chain-of-custody procedure, sample preparation and analysis, instrument operating records, etc. Blind QC samples may be prepared and submitted along with project samples to the laboratory for analysis throughout the project. The QA officer will evaluate the analytical results of these blind performance samples to ensure the laboratories maintain a good performance.

A internal performance and system audit of Encotec laboratory is not scheduled at this time. The audit will be conducted during the course of the project, if deemed necessary.

External audits of laboratory activities may be conducted by WDNR or U.S. EPA Region V, as required.

12.0 PREVENTIVE MAINTENANCE

All analytical instruments to be used in this project will be serviced by the laboratory or field personnel at regularly scheduled intervals in accordance with the manufacturers recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of the laboratory or field personnel will be performed by the equipment manufacturer or its designated representative.

Daily checks of each instrument will be by the laboratory or field personnel who have been assigned responsibility for that instrument. Manufacturer's recommended procedures will be followed in every case.

Routine preventative maintenance procedures are outlined in the specific method SOPs (Attachment C).

13.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA, PRECISION, ACCURACY, COMPLETENESS AND SENSITIVITY

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy and completeness achieved during the associated sample analyses.

13.1 LABORATORY DATA (ON-SITE & OFF-SITE ANALYSES)

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

13.1.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD for organic analyses and between laboratory duplicates for inorganic analyses. The relative percent difference (%RPD) will be calculated for each pair of duplicate analysis.

13.1.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 4.0 and 10.0 of the QAPjP using the analytical results of reagent/preparation blanks, method blanks, MS/MSD samples, calibration check samples and field QA/QC samples.

13.1.3 Completeness

Completeness will be assessed by comparing the number of valid results (as determined by CRA QA/QC Officer - Analytical Activities) to the total possible number of results using the following formula:

$$\text{Completeness} = \frac{\text{Valid (Usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

The required level of completeness for laboratory analyses will be 95 percent.

13.1.4 Sensitivity

The achievement of method detection and practical quantitation limits depends on instrumental sensitivity and matrix effects. Therefore, it is important to monitor the instrumental sensitivity to ensure the data quality through constant instrument performance. The instrumental sensitivity will be monitored through the analysis of method blank, calibration check sample and laboratory control sample results.

13.2 FIELD DATA

Field data will be assessed by CRA's Field QA/QC Officer. The Field QA/QC Officer will assess the accuracy of field measurements using daily instrument calibration, calibration check and method blank data (if applicable). Precision will be assessed on the basis of reproducibility of multiple readings from a single sample. Data completeness will be calculated using the completeness calculation (Section 13.1.3).

13.3 STATISTICAL EVALUATIONS

In examination of data and determination of its precision and accuracy, standard statistical formulae will be used.

13.3.1 Arithmetic Mean

The arithmetic mean is the average obtained by dividing a sum by the number of its addends. A number of recovery results are averaged together to improve the accuracy of the measurement. Figure 13.1, equation 1 summarizes the formula to be used to determine the arithmetic mean.

13.3.2 Standard Deviation

The standard deviation is the square root of the average squared difference between the individual values and the average value. A number of recovery results are evaluated to find the numerical variation in the data which is then used in the determination of the percent relative standard deviation. Figure 13.1 equation 2 summarizes the formula to be used to determine the standard deviation.

13.3.3 Percent Relative Standard Deviation (%RSD)

The percent relative standard deviation is the percentage obtained by dividing the standard deviation of the values by the arithmetic mean of the values multiplied by 100. The %RSD is calculated on a series of measurements to evaluate an instruments analytical precision (e.g., initial calibration). Figure 13.1, equation 3 summarizes the formula to be used to determine %RSD.

Equation 1 Determination of Arithmetic Mean ($\bar{X}$)

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where n = number of measurements
x_i = value of measurements

Equation 2 Determination of Standard Deviation (σ_{n-1})

$$\sigma_{n-1} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}}$$

where n = number of measurements
x_i = value of measurements

Equation 3 Determination of Percent Relative Standard Deviation (% RSD)

$$\% \text{ RSD} = \frac{\sigma_{n-1}}{\bar{X}} \times 100$$

where σ_{n-1} = standard deviation
$\bar{X}$ = arithmetric mean

Equation 4 Determination of Percent Recovery (%R)

$$\%R = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result or Background
SA = Spike Added

Equation 5 Determination of Relative Percent Difference (RPD)

$$RPD = \left(\frac{|R_1 - R_2|}{\frac{R_1 + R_2}{2}} \right) \times 100$$

where R_1 = value of first result
R_2 = value of second result

figure 13.1
STATISTICAL FORMULAE
QUALITY ASSURANCE PROJECT PLAN
WAUSAU SUPERFUND SITE
Wausau, Wisconsin

13.3.4 Percent Recovery (%R)

The percent recovery of a parameter is the percentage obtained by dividing the amount recovered by the true amount added multiplied by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Figure 13.1, equation 4 summarizes the formula to be used to determine the percent recovery.

13.3.5 Relative Percent Difference (RPD)

The relative percent difference is the percentage obtained by dividing the difference between two numbers by their arithmetic mean multiplied by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (e.g., matrix spike/matrix spike duplicate). Figure 13.1, equation 5 summarizes the formula to be used to determine RPD.

14.0 CORRECTIVE ACTION

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

For non-compliance problems, a formal corrective action program will be determined an implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the CRA Project Manager, who will notify the EPA RPM. If the problem is analytical in nature, information on these problems will promptly communicated to the EPA QAS by the EPA RPM. Implementation of corrective action will be confirmed in writing through the same channels.

Any non-conformance with the established quality control procedures in the QAPjP will be identified and corrected in accordance with the QAPjP.

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by a stop-work order from the USEPA RPM.

14.1 SAMPLE COLLECTION/FIELD MEASUREMENT

Technical staff and project personnel will be responsible for reporting all suspected technical or QA non-conformances or suspected deficiencies of any activity or issued document by reporting the situation to CRA's Field QA/QC Officer. He will be responsible for assessing the suspected problems in consultation with CRA's QA/QC Officer-Analytical Activities on

making a decision based on the potential for the situation to impact the data quality. If it is determined that the situation warrants a reportable non-conformance requiring corrective action, then a non-conformance report will be initiated by CRA's Field QA/QC Officer. He will be responsible for ensuring that corrective action for non-conformances are initiated by:

- evaluating all reported non-conformances;
- controlling additional work on non-conforming items;
- determining disposition or action to be taken;
- maintaining a log of non-conformances;
- reviewing non-conformance reports and corrective actions taken;
- ensuring non-conformance reports are included in the final site documentation project files.

If appropriate, the CRA Field QA/QC Officer will ensure that no additional work that is dependent on the non-conforming activity is performed until the corrective actions are completed.

Corrective action for the field measurements may include:

- repeat measurement to check the error;
- check for all proper adjustments for ambient conditions such as temperature;
- check the batteries;
- recalibration;

- replace the instrument or measurement devices; and

- stop work (if necessary).

The CRA Field QA/QC Officer or his designee is responsible for all Site activities. In this role, he 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 CRA Field QA/QC Officer of the anticipated change and implements the necessary changes after obtaining the approval of the CRA Field QA/QC Officer.

The CRA Field QA/QC Officer for the Site is responsible for controlling, tracking and implementing the identified changes. Reports on all changes will be distributed to all affected parties which include the EPA RPM.

14.2 LABORATORY ANALYSES

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy;

- blanks contain target analytes above acceptable levels;

- undesirable trends are detected in spike recovery or RPD data;

- there are unusual changes in detection limits;

- deficiencies are detected by the QA department during internal or external audits or from results of performance evaluation samples; or

- inquiries concerning data quality are received.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedures for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, etc.. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, manager and/or QA department for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the QA department. Specific corrective action procedures for specific analytical methods are outlined in the method SOPs (Attachment C).

15.0 QUALITY ASSURANCE REPORT TO MANAGEMENT

Management will receive reports on the performance of the measurement system and data quality following each sampling round and at the conclusion of the project.

Minimally, these reports will include:

1) assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

2) results of system audits; and

3) QA problems and recommended solutions.

4) amendments to QAPjP.

The CRA QA/QC Officer - Analytical Activities will be responsible within the organizational structure for preparing these reports. The final report for the project will also include a separate QA section which will summarize data quality information contained in the periodic QA/QC reports to management, and details an overall data assessment and validation in accordance with the data quality objectives outlined in this QAPjP.

ATTACHMENT A

CONTAINER REQUIREMENTS

EPA/540/R/93/051

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MAY 2 --

MEMORANDUM

SUBJECT: Revision of "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers"

FROM: Joan F. Fisk, Chief,
Analytical Methods Implementation Section,
Analytical Operations Branch,
Hazardous Site Evaluation Division (OS-230)

TO: Addressees

In September, 1989 you received OSWER Directive #9240.0-05 from Henry Longest II with the memorandum titled "Decentralization of the Superfund Bottle Repository Functions". The purpose of this transmittal is to provide you with a revised version of the "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers" that addresses problems brought up once the original document was put into use. This revised version has been through extensive review provided by the Regions through the Contract Laboratory Technical Project Officers who circulated the draft for comments.

The Analytical Operations Branch plans to transmit this document formally with an amended directive number, but since we have had so many urgent requests for it, we decided that this early distribution to you would be of great assistance in your procuring of bottles. We would appreciate any comments that you have as soon as possible, so that if we have overlooked any deficiencies we can remedy them prior to the transmittal as a directive.

Addressees:

Contract Laboratory Program Technical Project Officers
Regional Sample Control Centers
Superfund Branch Chiefs

cc:

Director, Waste Management Division
Regions I, IV, V, VII, VIII
Director, Emergency and Remedial Response Division
Region II
Director, Hazardous Waste Management Division
Regions III, VI
Director, Toxic and Waste Management Division
Region IX
Director, Hazardous Waste Division
Region X
Director, Environmental Services Division
Regions I-X
Joan Barnes, AOB
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Frank Rzasa, CMD
Bill Topping, PCMD
Lloyd Guerci, OWPE
Susan Bromm, OWPE
Russ Wyer, HSCD
Hans Crump-Wiesner, ERD
Penny Hansen, SAB

SPECIFICATIONS

AND

GUIDANCE

FOR OBTAINING

CONTAMINANT-FREE SAMPLE CONTAINERS

APRIL, 1990

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SECTION I

INTRODUCTION

In August 1989, the Environmental Protection Agency's (EPA) Office of Emergency and Remedial Response (OERR) decentralized Superfund's Sample Container Repository program (OSWER Directive #9240.0-05). In conjunction with the decentralization of Superfund's bottle program, OERR issued initial "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers" (August 1989) to assist the Regions in obtaining appropriate sample containers from commercially available suppliers.

This document revises the initial specifications and provides a single source of standardized specifications and guidance on appropriate cleaning procedures for preparing contaminant-free sample containers that meet all Contract Laboratory Program (CLP) detection/quantitation limits, including those for newly established low concentration analyses. Although the specifications and guidance procedures contained in this document are based on CLP low concentration requirements, they also are suitable for use in other analytical programs. Specific needs of EPA Regions will dictate which cleaning procedures are used by the designated bottle preparer.

Major revisions in this document include:

- Allowing the use of polypropylene closures as an alternative to phenolic closures;
- Specifying the use of CLP Inorganic Low Concentration Contract Required Detection Limits (CRDL);
- Specifying the use of CLP Organic Low Concentration Contract Required Quantitation Limits (CRQL);
- Including procedures for the cleaning of containers for fluoride and nitrate/nitrite analyses;
- Including procedures for the quality control analysis of fluoride and nitrate/nitrite; and
- Specifying the use of CLP Inorganic and Organic Low Concentration analytical methods for quality control analyses.

OERR and the EPA Regions decided to use the most stringent CLP requirements available to set the specifications for obtaining contaminant-free sample containers. As a result, the CLP Inorganic and Organic Low Concentration Statement of Work (SOW) requirements were selected as the basis for these specifications. Major factors in this decision included the desire to have a single set of bottle cleaning specifications that met or exceeded all analytical requirements and the related need to avoid potential misuse of cleaned bottles (e.g., using a container cleaned by a multi-concentration

procedure for a low concentration sample). OERR will reevaluate this decision if the low concentration requirements are deemed to be too stringent.

Specifications and guidance for preparing contaminant-free sample containers are provided in the sections that follow and are intended to describe one approach for obtaining cleaned, contaminant-free sample containers for use by groups performing sample collection activities under Superfund and other hazardous waste programs. Although other cleaning procedures may be used, sample containers must meet the criteria specified in Section II. In certain instances, the user of the sample containers may require exact adherence to the cleaning procedures and/or quality control analysis described in this document. In other instances, the user may require additional or different cleaning procedures and/or quality control analysis of the sample containers. The specific needs of the bottle user will determine the requirements for the cleaning and quality control analysis of the sample containers.

Most environmental sampling and analytical applications offer numerous opportunities for sample contamination. For this reason, contamination is a common source of error in environmental measurements. The sample container itself represents one such source of sample contamination. Hence, it is vital that sample containers used within the Superfund program meet strict specifications established to minimize contamination which could affect subsequent analytical determinations. Superfund sampling and analysis activities require all component materials (caps, liners, septa, packaging materials, etc.) provided by the bottle preparer to meet or exceed the criteria limits of the bottle specifications listed within Section II.

Section III provides guidance on cleaning procedures for preparing contaminant-free sample containers that meet the specifications contained in Section II. The procedures provided in this section are intended to provide sample containers that meet all current CLP Low Concentration Inorganic and Organic detection/quantitation levels.

In selecting cleaning procedures for sample containers, it is important to consider all of the parameters of interest. Although a given cleaning procedure may be effective for one parameter or type of analysis, it may be ineffective for another. When multiple determinations are performed on a single sample or on a subsample from a single container, a cleaning procedure may actually be a source of contamination for some analytes while minimizing contamination in others. It should be the responsibility of the bottle supplier to verify that the cleaning procedures actually used satisfy the quality control requirements set forth in Section IV.

Two aspects of quality assurance (i.e., quality control and quality assessment) must be applied to sample containers as well as to the analytical measurements. Quality control includes the application of good laboratory practices and standard operating procedures especially designed for the cleaning of sample containers. The cleaning operation should be based on protocols especially designed for specific contaminant problems. Strict adherence to these cleaning protocols is imperative.

Quality assessment of the cleaning process depends largely on monitoring for adherence to the respective protocols. Because of their critical role in the quality assessment of the cleaning operation, protocols must be carefully designed and followed.

Guidance is provided in Section IV on design and implementation of quality assurance and quality control protocols.

SECTION II

SAMPLE CONTAINER AND COMPONENT MATERIAL SPECIFICATIONS

This Section identifies sample containers commonly used in the Superfund program and provides specifications for contaminant-free sample containers for each bottle type.

A. CONTAINER MATERIAL

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interferences with analytes of interest, cost, and availability.

Container types A through L (Figure 1, pages 6-7) are designated as the type of sample containers that have been used successfully in the past. Kimax or Pyrex brand borosilicate glass is inert to most materials and is recommended where glass containers are used (i.e., pesticides and other organics). Conventional polyethylene is recommended when plastic is acceptable because of its lower cost and lower adsorption of metal ions. The specific sampling situation will determine the use of plastic or glass.

While the sample containers shown in Figure 1 are utilized primarily for Superfund sampling activities, they also may be used for sampling activities under other programs, such as the Resource Conservation and Recovery Act (RCRA).

B. MAXIMUM CONTAMINANT LEVEL SPECIFICATIONS FOR SAMPLE CONTAINERS

The CLP, through a series of technical caucuses, has established inorganic Contract Required Detection Limits (CRDL) and organic Contract Required Quantitation Limits (CRQL) which represent the minimum detectable quantities needed to support the hazardous substance identification and monitoring requirements necessary for remedial and other actions at hazardous waste sites.

The philosophy used for determining the maximum permissible amount of contamination in a sample container was to consider the number of aliquots of sample that are available in the container and assume that the contamination present would be uniformly distributed in all of the aliquots. This assumption, and the assumption that there should be no more than one-half the CRDL or CRQL contributed by the container, resulted in the establishment of contamination limits by container type.

For inorganic sample containers, the CRDLs listed in Table 1, page 8, are the specifications for maximum trace metal contamination. Concentration at or above these limits on any parameter should preclude these containers from use in collecting inorganic samples.

The CRQL specifications for organic sample containers are listed in Table 2, pages 9-13. When the CRQL in Table 2 is multiplied by the appropriate factor listed below, the resulting value then represents the maximum concentration allowed for particular sample containers based on organic CLP sample sizes for routine analyses.

Container type	Multiple of CRQL
A	1.0
B	0.5
D	10.0
E	8.0
F	4.0
G	2.0
H	0.5
J	0.5
K	2.0

C. GROSS CONTAMINATION

Gross contamination is defined as greater than two hundred times the acceptable concentration values in Tables 1 or 2, unless the cleaning procedure is successful in reducing the amount of contamination to within specifications. If this is not achieved, the grossly contaminated materials should be discarded and replaced to prevent cross contamination with other batches of containers.

The bottle preparer should inspect all materials to ensure conformance with the required specifications.

FIGURE 1

SAMPLE CONTAINER
SPECIFICATIONS

Container Type	Specifications
A	Container: 80-oz amber glass, ring handle bottle/jug, 38-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 38-430 size; 0.015-mm teflon liner. Total Weight: 2.45 lbs.
B	Container: 40-mL glass vial, 24-mm neck finish. Closure: white polypropylene or black phenolic, open-top, screw cap, 15-cm opening, 24-400 size. Septum: 24-mm disc of 0.005-in teflon bonded to 0.120-in silicon for total thickness of 0.125-in. Total Weight: 0.72 oz.
C	Container: 1-L high-density polyethylene, cylinder-round bottle, 28-mm neck finish. Closure: white polyethylene cap, white ribbed, 28-410 size; F217 polyethylene liner. Total Weight: 1.89 oz.
D	Container: 120-mL wide mouth, glass vial, 48-mm neck finish. Closure: white polypropylene cap, 48-400 size; 0.015-mm teflon liner. Total Weight: 4.41 oz.
E	Container: 16-oz tall, wide mouth, straight-sided, flint glass jar, 63-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 63-400 size; 0.015-mm teflon liner. Total Weight: 9.95 oz.
F	Container: 8-oz short, wide mouth, straight-sided, flint glass jar, 70-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 58-400 size; 0.030-mm teflon liner. Total Weight: 7.55 oz.

FIGURE 1

SAMPLE CONTAINER
SPECIFICATIONS
(Continued)

Container Type	Specifications
G	Container: 4-oz tall, wide mouth, straight-sided, flint glass jar, 48-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 48-400 size; 0.015-mm teflon liner. Total Weight: 4.70 oz.
H	Container: 1-L amber, Boston round, glass bottle, 33-mm pour-out neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 33-430 size; 0.015-mm teflon liner. Total Weight: 1.11 lbs.
J	Container: 32-oz tall, wide mouth, straight-sided, flint glass jar, 89-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap, 89-400 size; 0.015-mm teflon liner. Total Weight: 1.06 lbs.
K	Container: 4-L amber glass, ring handle bottle/jug, 38-mm neck finish. Closure: white polypropylene or black phenolic, baked polyethylene cap. 38-430 size; 0.015-mm teflon liner. Total Weight: 2.88 lbs.
L	Container: 500-mL high-density polyethylene, cylinder-round bottle, 28-mm neck finish. Closure: white polypropylene cap, white ribbed, 28-410 size; F217 polyethylene liner. Total Weight: 1.20 oz.

TABLE 1

INORGANIC ANALYTE
SPECIFICATIONS

	Analyte	Contract Required Detection Limits[1] (µg/L)
1.	Aluminum	100
2.	Antimony	5
3.	Arsenic	2
4.	Barium	20
5.	Beryllium	1
6.	Cadmium	1
7.	Calcium	500
8.	Chromium	10
9.	Cobalt	10
10.	Copper	10
11.	Iron	500
12.	Lead	2
13.	Magnesium	500
14.	Manganese	10
15.	Mercury	0.2
16.	Nickel	20
17.	Potassium	750
18.	Selenium	3
19.	Silver	10
20.	Sodium	500
21.	Thallium	10
22.	Vanadium	10
23.	Zinc	20
24.	Cyanide	10
25.	Fluoride	200
26.	Nitrate/Nitrite	100

1 CRDLs are based on the CLP Inorganic Low Concentration SOW (1990)

TABLE 2

ORGANIC COMPOUND
SPECIFICATIONS

	Volatiles	CAS Number	Contract Required Quantitation Limits[1] (µg/L)
1.	Chloromethane	74-87-3	1
2.	Bromomethane	74-83-9	1
3.	Vinyl Chloride	75-01-4	1
4.	Chloroethane	75-00-3	1
5.	Methylene Chloride	75-09-2	2
6.	Acetone	67-64-1	5
7.	Carbon Disulfide	75-15-0	1
8.	1,1-Dichloroethene	75-35-4	1
9.	1,1-Dichloroethane	75-34-3	1
10.	cis-1,2-Dichloroethene	156-59-4	1
11.	trans-1,2-Dichloroethene	156-60-5	1
12.	Chloroform	67-66-3	1
13.	1,2-Dichloroethane	107-06-2	1
14.	2-Butanone	78-93-3	5
15.	Bromochloromethane	74-97-5	1
16.	1,1,1-Trichloroethane	71-55-6	1
17.	Carbon Tetrachloride	56-23-5	1
18.	Bromodichloromethane	75-27-4	1
19.	1,2-Dichloropropane	78-87-5	1
20.	cis-1,3-Dichloropropene	10061-01-5	1
21.	Trichloroethene	79-01-6	1
22.	Dibromochloromethane	124-48-1	1
23.	1,1,2-Trichloroethane	79-00-5	1
24.	Benzene	71-43-2	1
25.	trans-1,3-Dichloropropene	10061-02-6	1
26.	Bromoform	75-25-2	1
27.	4-Methyl-2-pentanone	108-10-1	5
28.	2-Hexanone	591-78-6	5
29.	Tetrachloroethene	127-18-4	1
30.	1,1,2,2-Tetrachloroethane	79-34-5	1

1 CRQLs are based on the CLP Organic Low Concentration SOW (1990)

TABLE 2

ORGANIC COMPOUND
SPECIFICATIONS
(Continued)

	Volatiles	CAS Number	Contract Required Quantitation Limits[1] (µg/L)
31.	1,2-Dibromoethane	106-93-4	1
32.	Toluene	108-88-3	1
33.	Chlorobenzene	108-90-7	1
34.	Ethylbenzene	100-41-4	1
35.	Styrene	100-42-5	1
36.	Xylenes (total)	1330-20-7	1
37.	1,3-Dichlorobenzene	541-73-1	1
38.	1,4-Dichlorobenzene	106-46-7	1
39.	1,2-Dichlorobenzene	95-50-1	1
40.	1,2-Dibromo-3-chloropropane	96-12-8	1

1 CRQLs are based on the CLP Organic Low Concentration SOW (1990)

TABLE 2

ORGANIC COMPOUND
SPECIFICATIONS
(Continued)

	Semivolatiles	CAS Number	Contract Required Quantitation Limits[1] (µg/L)
1.	Phenol	108-95-2	5
2.	bis-(2-Chlorethyl)ether	111-44-4	5
3.	2-Chlorophenol	95-57-8	5
4.	2-Methylphenol	95-48-7	5
5.	2,2'-oxybis-(1-Chloropropane)	108-60-1	5
6.	4-Methylphenol	106-44-5	5
7.	N-Nitroso-di-n-dipropylamine	621-64-7	5
8.	Hexachloroethane	67-72-1	5
9.	Nitrobenzene	98-95-3	5
10.	Isophorone	78-59-1	5
11.	2-Nitrophenol	88-75-5	5
12.	2,4-Dimethylphenol	105-67-9	5
13.	bis-(2-Chloroethoxy)methane	111-91-1	5
14.	2,4-Dichlorophenol	120-83-2	5
15.	1,2,4-Trichlorobenzene	120-82-1	5
16.	Naphthalene	91-20-3	5
17.	4-Chloroaniline	106-47-8	5
18	Hexachlorobutadiene	87-68-3	5
19.	4-Chloro-3-methylphenol	59-50-7	5
20.	2-Methylnaphthalene	91-57-6	5
21.	Hexachlorocyclopentadiene	77-47-4	5
22.	2,4,6-Trichlorophenol	88-06-2	5
23.	2,4,5-Trichlorophenol	95-95-4	20
24.	2-Chloronaphthalene	91-58-7	5
25.	2-Nitroaniline	88-74-4	20
26.	Dimethylphthalate	131-11-3	5
27.	Acenaphthylene	208-96-8	5
28.	2,6-Dinitrotoluene	606-20-2	5
29.	3-Nitroaniline	99-09-2	20
30.	Acenaphthene	83-32-9	5

1 CRQLs are based on the CLP Organic Low Concentration SOW (1990)

TABLE 2

ORGANIC COMPOUND
SPECIFICATIONS
(Continued)

	Semivolatiles	CAS Number	Contract Required Quantitation Limits[1] (µg/L)
31.	2,4-Dinitrophenol	51-28-5	20
32.	4-Nitrophenol	100-02-7	20
33.	Dibenzofuran	132-64-9	5
34.	2,4-Dinitrotoluene	121-14-2	5
35.	Diethylphthalate	84-66-2	5
36.	4-Chlorophenyl-phenylether	7005-72-3	5
37.	Fluorene	86-73-7	5
38.	4-Nitroaniline	100-01-6	20
39.	4,6-Dinitro-2-methylphenol	534-52-1	20
40.	N-Nitrosodiphenylamine	86-30-6	5
41.	4-Bromophenyl-phenylether	101-55-3	5
42.	Hexachlorobenzene	118-74-1	5
43.	Pentachlorophenol	87-86-5	20
44.	Phenanthrene	85-01-8	5
45.	Anthracene	120-12-7	5
46.	Di-n-butylphthalate	84-74-2	5
47.	Fluoranthene	206-44-0	5
48	Pyrene	129-00-0	5
49.	Butylbenzylphthalate	85-68-7	5
50.	3,3'-Dichlorobenzidine	91-94-1	5
51.	Benz[a]anthracene	56-55-3	5
52.	Chyrsene	218-01-9	5
53.	bis-(2-Ethylhexyl)phthalate	117-81-7	5
54.	Di-n-octylphthalate	117-84-0	5
55.	Benzo[b]fluoranthene	205-99-2	5
56.	Benzo[k]fluoranthene	207-08-9	5
57.	Benzo[a]pyrene	50-32-8	5
58.	Indeno(1,2,3-cd)pyrene	193-39-5	5
59.	Dibenz[a,h]anthracene	53-70-3	5
60.	Benzo[g,h,i]perylene	191-24-2	5

1 CRQLs are based on the CLP Organic Low Concentration SOW (1990)

TABLE 2

ORGANIC COMPOUND
SPECIFICATIONS
(Continued)

	Pesticides/PCBs	CAS Number	Contract Required Quantitation Limits[1] (µg/L)
1.	alpha-BHC	319-84-6	0.01
2.	beta-BHC	319-85-7	0.01
3.	delta-BHC	319-86-8	0.01
4.	gamma-BHC (Lindane)	58-89-9	0.01
5.	Heptachlor	76-44-8	0.01
6.	Aldrin	309-00-2	0.01
7.	Heptachlor epoxide	1024-57-3	0.01
8.	Endosulfan I	959-98-8	0.01
9.	Dieldrin	60-57-1	0.02
10.	4,4'-DDE	72-55-9	0.02
11.	Endrin	72-20-8	0.02
12.	Endosulfan II	33213-65-9	0.02
13.	4,4'-DDD	72-54-8	0.02
14.	Endosulfan sulfate	1031-07-8	0.02
15.	4,4'-DDT	50-29-3	0.02
16.	Methoxychlor	72-43-5	0.10
17.	Endrin ketone	53494-70-5	0.02
18	Endrin aldehyde	7421-36-3	0.02
19.	alpha-Chlordane	5103-71-9	0.01
20.	gamma-Chlordane	5103-74-2	0.01
21.	Toxaphene	8001-35-2	1.0
22.	Aroclor-1016	12674-11-2	0.20
23.	Aroclor-1221	11104-28-2	0.20
24.	Aroclor-1232	11141-16-5	0.40
25.	Aroclor-1242	53469-21-9	0.20
26.	Aroclor-1248	12672-29-6	0.20
27.	Aroclor-1254	11097-69-1	0.20
28.	Aroclor-1260	11096-82-5	0.20

1 CRQLs are based on the CLP Organic Low Concentration SOW (1990)

SECTION III

SAMPLE CONTAINER PREPARATION AND CLEANING PROCEDURES

This Section is provided as guidance for the preparation of sample containers that meet the contaminant-free specifications contained in Section II. There are various procedures for cleaning sample containers depending upon the analyses to be performed on the sample. The following cleaning procedures are modeled after those specified for the Superfund Sample Container Repository program.

A. Cleaning Procedure for Container Types: A, E, F, G, H, J, and K

1. Sample Type: Semivolatile Organics, Pesticides, Metals, Cyanide, and Fluoride in Soils and Water.

   a. Wash glass bottles, teflon liners, and caps with hot tap water using laboratory grade nonphosphate detergent.

   b. Rinse three times with copious amounts of tap water to remove detergent.

   c. Rinse with 1:1 nitric acid (reagent grade HNO_3, diluted with ASTM Type I deionized water).

   d. Rinse three times with ASTM Type I organic free water.

   e. Oven dry bottles, liners and caps at 105-125°C for one hour.

   f. Allow bottles, liners, and caps to cool to room temperature in an enclosed contaminant-free environment.

   g. Rinse bottles with pesticide grade hexane (for pesticide determinations) or pesticide grade methylene chloride (for semivolatile organics determinations) using 20 mL for 1/2 gallon containers; 10 mL for 32-oz and 16-oz containers; and 5 mL for 8-oz and 4-oz containers.

   h. Oven dry bottles, liners, and caps at 105-125°C for one hour.

   i. Allow bottles, liners, and caps to cool to room temperature in an enclosed contaminant-free environment.

   j. Place liners in lids and cap containers.

   k. Label each container with lot number and pack in case.

   l. Label exterior of each case with lot number.

   m. Store in contaminant-free area.

2. Sample Type: Nitrate/Nitrite in Soils and Water.

a. Substitute reagent grade sulfuric acid (H_2SO_4) for nitric acid in step A.1.c.

b. Follow all other steps in the cleaning procedure described in part A.1 above.

B. Cleaning Procedure for Container Types: B, D

1. Sample Type: Purgeable (Volatile) Organics in Soils and Water.

a. Wash glass vials, teflon-backed septa, teflon liners, and caps in hot water using laboratory grade nonphosphate detergent.

b. Rinse three times with copious amounts of tap water to remove detergent.

c. Rinse three times with ASTM Type I organic-free water.

d. Oven dry vials, caps, septa, and liners at 105-125°C for one hour.

e. Allow vials, caps, septa and liners to cool to room temperature in an enclosed contaminant-free environment.

f. Seal 40-mL vials with septa (teflon side down) and cap.

g. Place liners in lids and cap 120-mL vials.

h. Label each vial with lot number and pack in case.

i. Label exterior of each case with lot number.

j. Store in contaminant-free area.

C. Cleaning Procedure for Container Types: C, L

1. Sample Type: Metals, Cyanide, and Fluoride in Soils and Water.

a. Wash polyethylene bottles and caps in hot tap water using laboratory-grade nonphosphate detergent.

b. Rinse three times with copious amounts of tap water to remove detergent.

c. Rinse with 1:1 nitric acid (reagent grade HNO_3, diluted with ASTM Type I deionized water).

d. Rinse three times with ASTM Type I deionized water.

e. Invert and air dry in contaminant-free environment.

f. Cap bottles.

g. Label each container with lot number and pack in case.

h. Label exterior of each case with lot number.

i. Store in contaminant-free area.

2. Sample Type: Nitrate/Nitrite in Soils and Water.

a. Substitute reagent grade sulfuric acid (H_2SO_4) for nitric acid in step C.1.c.

b. Follow all other steps in the cleaning procedure described in part C.1 above.

SECTION IV

SAMPLE CONTAINER QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

A. Quality Assurance

The objectives of this Section are to: (1) present procedures for evaluating quality assurance (QA) information to ensure that specifications identified in Section II have been met; and (2) discuss techniques for the quality control (QC) analysis of sample containers to be used in conjunction with the cleaning procedures contained in Section III.

Major QA/QC activities should include the inspection of all incoming materials, QC analysis of cleaned lots of containers, and monitoring of the containers' storage area. Complete documentation of all QC inspection results (acknowledging acceptance or rejection) should be kept as part of the permanent bottle preparation files. QA/QC records (e.g., preparation/QC logs, analytical data, data tapes, storage log) should also be stored in a central location within the facility.

Documentation indicating that the container lot has passed all QA/QC requirements should be provided by the bottle vendor to the bottle purchaser with each container lot. Documentation should include a signed and dated cover statement affirming that all QA/QC criteria were met or exceeded and copies of raw data from applicable analyses of the QC containers. Minimum documentation that should be provided with each lot of containers follows:

- A statement that "Sample container lot _____ meets or exceeds all QA/QC criteria established in 'Specifications and Guidance for Obtaining Contaminant-Free Sample Containers'";
- Reconstructed Ion Chromatographs (RICs) from volatile and semivolatile organics determinations;
- GC chromatographs from pesticides determinations;
- ICP, hydride-ICP, or ICP-MS instrument readouts from metals determinations;
- AA raw data sheets and instrument readouts from metals determinations; and
- Cyanide, fluoride, and nitrate/nitrite raw data sheets and instrument readouts from these detrminations.

1. Incoming Materials Inspection:

A representative item from each case of containers should be checked for conformance with specifications provided in Section II. Any deviation should be considered unacceptable. A log of incoming shipments should be maintained to identify material type, purchase order number, and delivery date. The date

of incoming inspection and acceptance or rejection of the material should also be recorded on this log.

2. Quality Control Inspection of Cleaned Lots of Containers:

Following container cleaning and labeling, two containers should be selected from each container lot to be used for QC purposes. The two categories of QC containers should be as follows:

a. Analysis QC Containers:

One QC container per lot should be designated as the analysis QC container. The sample container preparer should analyze the analysis QC container(s) to check for contamination prior to releasing the associated container lot for shipment. The QC analyses procedures specified in the Quality Control Analysis part of this Section for determining the presence of semivolatile and volatile organics, pesticides, metals, cyanide, fluoride, and nitrate/nitrite should be utilized.

For each representative analysis QC container(s), the appropriate QC number should be assigned to the related lot of containers. For example, the QC number could be a six-digit number sequentially assigned to each lot that has undergone QC analysis. Under this numbering scheme, the first alphabetical character would be the container type letter from Figure 1, the next four digits would be assigned sequentially in numerical order starting with "0001" for the first lot to undergo QC analyses, and the last character would be either a "C" to indicate clearance or an "R" to indicate rejection.

If the representative analysis QC container(s) passes QC inspection, the related lot of containers should be released, and the appropriate QC number should be entered in the preparation/QC log to indicate clearance of the lot for shipment.

If the analysis QC container(s) are found to be contaminated per the specified QC analysis procedures, the appropriate QC rejection number should be assigned and entered in the preparation/QC log. Any container labels should be removed and the entire lot returned for reprocessing under a new lot number. Excessive QC rejection for a particular container type should be noted for future reference.

A laboratory standard and a blank should be run with each QC analysis. All QC analysis results should be kept in chronological order by QC report number in a central QC file. The QC numbers assigned should be documented in the preparation/QC log, indicating acceptance or rejection and date of analysis.

A container lot should not be released for shipment prior to QC analysis and clearance. Once the containers have passed QC inspection, the containers should be stored in a contaminant-free area until packaging and shipment.

b. Storage QC Containers:

One QC container per lot should be designated as the storage QC container. The storage QC container should be separated from the lot after cleaning and labeling and should be stored in a designated contaminant-free area for one year. The date the container is placed in the storage area should be recorded in the storage QC container log.

If contamination of the particular container lot comes into question at any time following shipment, the storage QC container should be removed from the storage area and analyzed using the QC analysis procedures for that container type (see Quality Control Analysis, this Section). Upon removal, containers should be logged out of the storage area.

The designated storage area should be monitored continuously for volatile contaminants. A precleaned, 40-mL vial that has passed a QC inspection should be filled with ASTM Type I organic-free water and be placed in the storage area. This vial should be changed at one-week intervals. The removed vial should be subjected to analysis for volatile organics as described in the Quality Control Analysis part of this Section. Any peaks indicate contamination. Identify contaminants, if present, and include the results in a report to all clients who purchased bottles in the past month from the affected lot(s).

B. Quality Control Analysis

The types of QC analyses correlate with the types of containers being analyzed and their future use in sample collection. The QC analyses are intended for the determination of:

- Semivolatile organics and pesticides;
- Volatile organics;
- Metals;
- Cyanide;
- Fluoride; and
- Nitrate/Nitrite.

QC analyses should be performed according to the container type and related sample type and utilize the specific method(s) described below.

1. Determination of Semivolatile Organics and Pesticides:

Container Types: A, E, F, G, H, J, and K

a. Sample Preparation:

- Add 60 mL of pesticide-grade methylene chloride to the container, and shake for two minutes.

- Transfer the solvent to a Kuderna-Danish (KD) apparatus equipped with a three-ball Snyder column. Concentrate to less than 10 mL on a steam bath. Split the solvent into two 5 mL fractions for semivolatile and pesticide determinations.

- Add 50 mL of pesticide-grade hexane (for pesticide determinations only) to the KD apparatus by slowly pouring down through the Snyder column. Concentrate to less than 10 mL to effect solvent replacement of hexane for methylene chloride.

- Concentrate the solvent to 1 mL using a micro-Snyder column.

- Prepare a solvent blank by adding 60 mL of the rinse solvent used in step "g" of the cleaning procedure for container types A, E, F, G, H, J, and K (Section III page 14) directly to a KD apparatus, and proceed as above.

b. Semivolatile Organics Sample Analysis:

- Instrument calibration should be performed as described in the current CLP Low Concentration Organics SOW with the following exceptions:

  (1) If problems are encountered meeting the %RSD criteria on the initial calibration for semivolatiles, the high concentration point should be deleted and a four-point calibration used.

  (2) The low concentration standard should be used for the continuing calibration standard for semivolatile analyses.

  (3) The percent difference window should be widened to ± 30 percent for all compounds.

- Inject 1 µL of solvent into a gas chromatograph/mass spectrometer (GC/MS).

- GC/MS operating conditions are listed in Figure 3 (page 28).

- Any peaks found in the container solvent that are not found in the solvent blank or with peak heights or areas not within + 50 percent of the blank peak height or area should be cause for rejection.

- Identify and quantitate any contaminant(s) that cause rejection of a container lot.

- A standard mixture of the 9 semivolatile organic compounds listed in Table 3 (page 27) with concentrations in the 5-20 ppb range should be analyzed to ensure that sensitivities are achieved that will meet contract required quantitation limits.

- A solvent blank should be run with each analysis.

c. Pesticides Sample Analysis:

- Instrument calibration should be performed as described in the current CLP Low Concentration Organics SOW.

- Inject 1 μL of solvent into a gas chromatograph (GC) equipped with an electron capture detector (ECD).

- GC/ECD operating conditions are listed in Figure 4 (page 29).

- Any peaks found in the container solvent that are not found in the solvent blank or with peak heights or areas not within + 50 percent of the blank peak height or area should be cause for rejection.

- A standard mixture of the 7 pesticide compounds listed in Table 3 (page 27) with concentrations in the 0.01 to 1 ppb range should be analyzed to ensure that sensitivities are achieved that will meet contract required quantitation limits.

- A solvent blank should be run with each analysis.

2. Determination of Volatile Organics:

Container Types: B and D

a. Sample Preparation:

- Fill the container with ASTM Type I organic-free water.

b. Sample Analysis:

- Instrument calibration should be performed as described in the current CLP Low Concentration Organics SOW with the following exceptions:

  (1) If problems are encountered meeting the %RSD criteria on the initial calibration for volatiles, the high concentration point should be deleted and a four-point calibration used.

(2) The low concentration standard should be used for the continuing calibration standard for volatile analyses.

(3) The percent difference window should be widened to ± 30 percent.

- GC/MS operating conditions are listed in Figure 5 (page 30).

- Any peaks not found in the blank or with peak heights or areas not within + 50 percent of the blank peak height or area should be cause for rejection.

- Identify and quantitate any contaminant(s) that cause rejection of a container lot.

- A standard mixture of the 5 volatile organic compounds listed in Table 3 (page 27) with concentrations in the 1-5 ppb range should be analyzed to ensure that sensitivities are achieved that will meet contract required quantitation limits.

- A blank should be run by analyzing an aliquot of the ASTM Type I water used above.

3. Determination of Metals:

Container Types: A, C, E, F, G, H, J, K and L

a. Sample Preparation:

- Add 50 mL of ASTM Type I deionized water to the container, and acidify with 0.5 mL reagent-grade HNO_3. Cap and shake well.

- Treat the sample as a dissolved metals sample. Analyze the undigested water using the current CLP Low Concentration Inorganics SOW.

b. Sample Analysis:

- Instruments used for the analysis of the samples should meet the contract required detection limits in Table 1.

- The rinse solution should be analyzed before use on the bottles that are designated for analysis to ensure that a contaminated solution is not used for rinsing the bottles.

- Calibration verification standards should be analyzed at the beginning, end, and every ten samples within an analysis run (a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements). The verification standards should be three to five times the values in Table 1. The percent recovery factor for the

verification standards should be between 90 to 110 percent or ± 10 percent of the actual value of the verification standard.

- Calibration blanks should be analyzed at the beginning, end, and every ten samples within an analysis run. A calibration blank is a solution made up exactly like the sample preparation solution. The calibration blank should be below the values in Table 1.

- A set of standards in the expected working range should be analyzed with each analytical run. The acid matrix of the standards, blank, and quality control samples should match that of the samples.

- Concentrations at or above the detection limit for each parameter (listed in Table 1) should be cause for rejection of the lot of containers. NOTE: Sodium detection limit for container types A, E, F, G, H, J, and K is 5000 µg/L unless the containers will be used for low concentration analyses, then the detection limit is 500 µg/L.

4. Determination of Cyanide:

Container Types: A, C, E, F, G, H, J, K and L

a. Sample Preparation:

- Place 250 mL of ASTM Type I deionized water in the container. Add 1.25 mL of 6N NaOH (for container types F and G use 100 mL ASTM Type I deionized water and 0.5 mL 6N NaOH). Cap the container and shake vigorously for two minutes.

b. Sample Analysis:

- Analyze an aliquot as described in the current CLP Low Concentration Inorganics SOW.

- The detection limit should be 10 µg/L or lower.

- A blank should be run by analyzing an aliquot of the ASTM Type I water used above.

- A set of standards in the expected working range, a quality control sample, and blank should be prepared exactly as the sample.

- The detection of contaminants of 10 µg/L cyanide (or greater) should be cause for rejection of the lot of containers. NOTE: Contamination could be due to the container, the cap, or the NaOH.

5. Determination of Fluoride:

Container Types: A, C, E, F, G, H, J, K and L

a. Sample Preparation:

- Place 250 mL of ASTM Type I deionized water in the container (for container types F and G use 100 mL ASTM Type I deionized water). Cap the container and shake vigorously for two minutes.

b. Sample Analysis:

- Analyze an aliquot as described in the current CLP Low Concentration Inorganics SOW.
- The detection limit should be 200 µg/L or lower.
- A blank should be run by analyzing an aliquot of the ASTM Type I water used above.
- A set of standards in the expected working range, a quality control sample, and blank should be prepared exactly as the sample.
- The detection of contaminants of 200 µg/L (or greater) fluoride should be cause for rejection of the lot of containers. NOTE: Contamination could be due to the container or the cap.

6. Determination of Nitrate/Nitrite:

Container Types: A, C, E, F, G, H, J, K and L

a. Sample Preparation:

- Place 250 mL of ASTM Type I deionized water in the container (for container types F and G use 100 mL ASTM Type I deionized water). Cap the container and shake vigorously for two minutes.

b. Sample Analysis:

- Analyze an aliquot as described in the current CLP Low Concentration Inorganics SOW.
- The detection limit should be 100 µg/L or lower.
- A blank should be run by analyzing an aliquot of the ASTM Type I water used above.

- A set of standards in the expected working range, a quality control sample, and blank should be prepared exactly as the sample.

- The detection of contaminants of 100 $\mu g/L$ (or greater) nitrate/nitrite should be cause for rejection of the lot of containers. NOTE: Contamination could be due to the container or the cap.

C. Preparation and Labeling

Sampling for environmental specimens requires that sample containers be transported to field sites prior to sample collection. As a result, considerable time may elapse between the receipt of sample containers and collection of the samples. Because of the large number of samples taken at any one site, accounting for all sample containers can become extremely difficult. The following guidance on the identification and tracking of sample containers is based on procedures that have been used successfully in the CLP bottle program.

1. Each shipment should be inspected to verify that the requested number of cleaned and prepared sample containers have been supplied and meet the requirements specified in Section II (Tables 1 and 2). If any shipment fails to meet the required specifications, it should be discarded and replaced with a supply of sample containers that meet the required criteria.

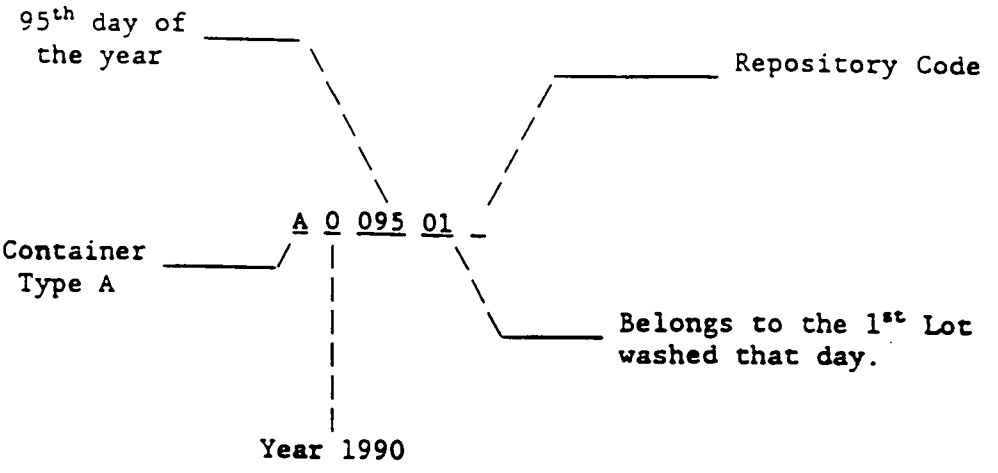
2. The sample containers should be removed and prepared in accordance with the methods designated below:

   a. Allocate the appropriate number of sample containers (Figure 1) to a designed container lot.

   b. Recommended lot size for each container should be based on the recommended number of items per case.

3. A permanent eight-digit lot number should be assigned to each lot of sample containers for identification and tracking purposes throughout the life of the containers. Figure 2 provides an example of a lot number sequence.

FIGURE 2



Lot Number Sequence

a. The first digit represents the container type in Section II (Figure 1).

b. The second digit represents the last digit of the calendar year.

c. The next three digits represents the day of the year on which the sample containers were washed.

d. The sixth and seventh digits represent the daily lot number.

e. The final digit represents the identification of the person who prepared the lot.

4. The lot number for each container should be entered, along with the date of washing, type of container, and number of containers per lot, into the preparation/QC log book.

5. Lot numbers printed with solvent resistant ink on a nonremovable label should remain with the corresponding containers throughout the cleaning procedure.

6. After sample container cleaning and drying, the label should be affixed to the containers in a permanent manner.

7. At least one face should be clearly marked, excluding the top and bottom faces, of each case of sample containers with the assigned lot numbers.

TABLE 3

STANDARD MIXTURES OF ORGANIC COMPOUNDS TO VERIFY SENSITIVITY

Volatiles	Semivolatiles	Pesticides
Methylene Chloride	Nitrobenzene	Gamma-BHC
Acetone	4-Chloroaniline	Heptachlor
2-Butanone	2,6-Dinitrotoluene	Aldrin
Trichloroethene	Diethylphthalate	Dieldrin
Toluene	4-Bromophenyl-phenylether	Endrin
	Hexachlorobenzene	4,4'-DDT
	Pentachlorophenol	Aroclor 1260
	Di-n-butylphthalate	
	bis(2-Ethylhexyl)phthalate	

FIGURE 3

GC/MS OPERATING CONDITIONS FOR SEMIVOLATILE ORGANICS QC ANALYSIS

OPERATOR: _____ DATE: _____

JOB NUMBER: _____ SAMPLE IDENTIFICATION: Container Lot number

SOLVENT: Methylene Chloride _____ ANALYTICAL METHOD: CLP Low Concentration SOW

Semivolatile Organics Fraction

COLUMN

Type Fused Silica Capillary or equiv.

Length 30 m

Diameter 0.25 mm or 0.32 mm ID

Liquid Phase (% wt)

J&W Scientific DB-5 or equivalent

Support N/A

Mesh N/A

CARRIER GAS Helium

Rotameter _____

Inlet Pressure, psig _____

Linear Velocity cm/sec 25-30

SCAVENGER GAS _____

SPLIT _____

FID GLASS

Hydrogen, mL/min N/A

Air, mL/min _____

CHART SPEED, cm/min _____

DETECTOR Mass Spectrometer

Range 35-500 a.m.u.

Attenuation _____

TEMPERATURE, °C

Detector _____

Injection Port 250-230°C

Column

Initial 40°/3 min

Program 10°/min

Final 290°C

INSTRUMENT _____

FIGURE 4

GC/ECD OPERATING CONDITIONS FOR PESTICIDES QC ANALYSIS

OPERATOR: _____ DATE: _____

JOB NUMBER: _____ SAMPLE IDENTIFICATION: Container Lot number

SOLVENT: Hexane ANALYTICAL METHOD: CLP Low Concentration SOW

Pesticide Fraction

COLUMNS (Two are required)

Type Fused Silica Capillary or equiv.

Length 30 m

Diameter 0.53 mm ID

Liquid Phase (% wt)

J&W Scientific DB-1710 and DB-608 or equivalent

Support N/A

Mesh N/A

CARRIER GAS Helium or Hydrogen

Rotameter _____

Inlet Pressure, psig _____

Flow Rate, mL/min 5

SCAVENGER GAS _____

SPLIT _____

FID GLASS

Hydrogen, mL/min N/A

Air, mL/min N/A

CHART SPEED, cm/min 1 cm/min

DETECTOR Electron Capture

Range _____

Attenuation 16

TEMPERATURE, °C

Detector 350°C

Injection Port ≥ 200°C

Column

Initial 150°/30sec

Program 5-6°/min

Final 275°C

INSTRUMENT _____

FIGURE 5

GC/MS OPERATING CONDITIONS FOR VOLATILES QC ANALYSIS

OPERATOR: _____ DATE: _____

JOB NUMBER: _____ SAMPLE IDENTIFICATION: Container Lot number

SOLVENT: Methanol _____ ANALYTICAL METHOD: CLP Low Concentration SOW

_____ Volatile Organics Fraction

COLUMN

Type Fused Silica Capillary or equiv.

Length 30 m

Diameter 0.53 mm ID

Liquid Phase (% wt)

J&W Scientific DB-624, Suppelco VOCAL or equivalent

Support N/A

Mesh N/A

CARRIER GAS Helium or Nitrogen

Rotameter _____

Inlet Pressure, psig _____

Flow Rate, mL/min 15

SCAVENGER GAS _____

SPLIT _____

FID GLASS

Hydrogen, mL/min N/A

Air, mL/min N/A

CHART SPEED, cm/min _____

DETECTOR Mass Spectrometer

Range 35-300 a.m.u.

Attenuation _____

TEMPERATURE, °C

Detector _____

Injection Port _____

Column

Initial 10°/1-5 min

Program 6°/min

Final 160°C/all cmpds. elute

INSTRUMENT _____

ATTACHMENT B

CHAIN-OF-CUSTODY
RECORD/LABEL

CRA Consulting Engineers
CONESTOGA-ROVERS & ASSOCIATES
651 Colby Drive, Waterloo, Ontario Canada N2V 1C2

SHIPPED TO (Laboratory name):

CHAIN OF CUSTODY RECORD

PROJECT Nº:

PROJECT NAME:

SAMPLER'S SIGNATURE _____ (SIGN)

SEQ. Nº.	SAMPLE Nº.	DATE	TIME	SAMPLE LOCATOIN	SAMPLE TYPE	Nº OF CONTAINERS	REMARKS
				TOTAL NUMBER OF CONTAINERS			

SAMPLE

ANTICIPATED CHEMICAL HAZARDS:

RELINQUISHED BY: [1] (SIGN)	DATE/TIME	RECEIVED BY: ② (SIGN)
RELINQUISHED BY: [2] (SIGN)	DATE/TIME	RECEIVED BY: ③ (SIGN)
RELINQUISHED BY: [3] (SIGN)	DATE/TIME	RECEIVED BY: ④ (SIGN)
ADDITIONAL SIGNATURE SHEET REQUIRED ☐		

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY BY: (SIGN)	DATE/TIME
CONDITION OF SEAL UPON RECEIPT: GENERAL CONDITION OF COOLER:		COOLER OPENED BY: (SIGN)	DATE/TIME

WHITE – CRA OFFICE COPY
YELLOW – RECEIVING LABORATORY COPY
PINK – CRA LABORATORY COPY
GOLDEN ROD – SHIPPERS

Nº 29472

CRA Consulting Engineers
CONESTOGA-ROVERS & ASSOCIATES LIMITED
651 Colby Drive, Waterloo, Ontario Canada N2V 1C2

*SHIPPER:*_____

*DATE SHIPPED:*_____

DO NOT OPEN
SEALED CONTAINER

DO NOT OPEN
SEALED CONTAINER

*SHIPPER:*_____

*DATE SHIPPED:*_____

CRA Consulting Engineers
CONESTOGA-ROVERS & ASSOCIATES LIMITED
651 Colby Drive, Waterloo, Ontario Canada N2V 1C2

ATTACHMENT C

METHOD SOP'S

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
ES 168	Determination of pH
ES 500	Determination of volatile organic compounds by gas chromatography- mass spectrometry
127	Tuning the ITS 40 GC-ITMS-DS system
ES 501	Determination of semi-volatile organic compounds by gas chromatography-mass spectrometry
120	Tuning the INCOS 50B GC/MS/DS system
ES 404	Extraction Method for EPA 525/625/8270 for Water/Wastewater
ES 408	Extraction Method for EPA 8270 for Soil Samples
ES A134	Determination of Total Cyanide
ES 521	On-Site VOC Analysis of Soil Gas Samples
ES 524	Soil Gas Sampling Procedure
111	Sample Receiving (Enviroscan)
SMPLCOC.sop	Sample Receiving (ENCOTEC)
TO14LL.SOP	Method for the determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canisters and Analysis by Gas Chromatography/Ion Trap Mass Spectrometry
EXT&PREP.sop	General Requirements for Organic Extraction and Sample Preparation

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
SEPFUNEX.sop	Separatory Funnel Liquid-Liquid Extraction
EXCLN608.sop	Florisil Cleanup - Organochlorine Pesticides/PCB Analysis
8080PEST.sop	Method for the Determination or Organochlorine Pesticides and PCBs by Gas Chromatography/Electron Capture Detection (GC/ECD)
PCBID.sop	Standard Operating Procedure for Identification and Quantitation of Polychlorinated Biphenyls (PCBs)
1AQDIG.mth	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by Flame-AA or ICP (DIG)
1AQMS.mth	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by ICPMS (DIGMS)
HYDPREP.mth	Preparation of Metals Digestates for Analysis by Hydride Atomic Absorption (HAS, HSE)
CVAQPREP.mth	Preparation of Aqueous Samples for Analysis for Mercury by Cold Vapor (HGP)
ARLICP.mth	Analysis of Total and Dissolved Metals by the ARL 3560 Simultaneous ICP
MTLICPMS.sop	Analysis of Total and Dissolved Metals by the Perkin-Elmer ELAN 5000 ICP/MS
MTLHYD.mth	Use of Hydride Generation in Analysis for Arsenic and/or Selenium (AS, SE)
MTLHG.mth	Analysis for Mercury by Cold Vapor (HG)

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
Field SOP No. 1	Procedures for Measuring pH
Field SOP No. 2	Procedures for Measuring Conductivity
Field SOP No. 3	Procedures for Measuring Temperature
Field SOP No. 4	Procedures for Measuring Dissolved Oxygen
Field SOP No. 5	Procedures for Measuring Turbidity
Field SOP No. 6	Procedures for Measuring Oxidation Reduction Potential (ORP)
Field SOP No. 7	Procedures for HNu Photoionization Detector
Field SOP No. 8	Procedures for Colorimetric Indicator Tubes

ENVIROSCAN

ENVIRONMENTAL AND
ANALYTICAL SERVICES

July 27, 1993

Ruth Lewis
Conestoga-Rovers & Associates
1801 Old Highway 8, Suite #114
St. Paul, Minnesota 55112

Dear Ms. Lewis:

Enclosed are the method updates requested in your 7/16/93 fax (reference # 3978). The field screening method updates for On-Site VOC of Soil Gas Samples (ES-521) and the Gas Sampling Procedure (ES-524) are not enclosed.

SOP #114 and 115 have been changed to ES-404 and ES-408. This update is reflected in the text of method ES-501.

The method detection limit (MDL) study for volatiles is not included. As Mary Christie discussed with you, we have not completed an MDL study at this time. We are reporting our low calibration standard as our quantitation limit. If this is unacceptable, we will complete an MDL study prior to the receipt of the samples.

If you have any questions concerning the enclosed methods, please contact me (715) 359-7226. Thank you.

Sincerely,

Karla M Coenen

Karla M. Coenen
Quality Assurance Manager

303 West Military Road Rothschild, WI 54474 (715) 359-7226
An Affiliate of the Black Clawson Co.

ENVIROSCAN

Environmental And Analytical Services

303 West Military Road, Rothschild, WI 54474
Telephone (715) 359-7226 • FAX (715) 355-3221

Telefax Correspondence

To: Ruth Lewis

Company: Conestoga Rovers & Associates

Telefax No.: 612-639-0923

Telephone No.: 612-639-0913

Date: 8/19/93

From: Karla M. Coenen

Total Number Of Pages, Including This Page: 1

Reference:

Ruth-
The modifications indicated by the EPA and WDNR which were not included in the SOP updates for the QAPP are as follows:

- The MDL studies for volatiles by GC/MS and the On-Site VOC analysis

- The On-Site VOC (ES-521) procedure lacked updating or clarifying the following information in the SOP:

  1. It did not provide the protocol for checking and monitoring the flow rate. The procedure completed is that the flow is checked at the beginning of each analysis day using a digital flow meter at the FID jet. The value obtained must agree with manufacturers recommendations. The flow rates are monitored through the day by the stability or shifting of retention times.

  2. It also did not provide the parameters for the check standard which must be within 30%. The procedure is that all compounds in the attached table of the method or being analyzed for be within $\pm$30% of the true value.

  3. The procedure did not make any changes concerning comment (B,1,g) in which it states that the calibration should include as a minimum one concentration in the field for all the compounds of interest. Our laboratories feels that it is the role of the check standard to confirm the calibration is still within operating parameters and adding a point to the calibration once in the field is unnecessary. If required, we will conform to the recommendation of one standard being completed in the field.

If you have any questions or comments about the above information, please contact me. Thank you.

Karla Coenen

Determination of: pH

Method: Electrometric

Reagents: Standard Buffer Solutions

Interferences: Temperature
Material which coats the electrode surface.

References:
APHA, 1989. Standard Methods for the Examination of Water and Wastewater, 17th Edition. American Public Health Association, Washington, D.C.

USEPA, 1983. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Cincinnati, OH.

USEPA, 1986. Test Methods for Evaluating Solid Wastes, SW-846, 3rd Edition. U.S. Environmental Protection Agency, Washington, D.C.

Issued: 1980
Revised: 1991
Revised: 7/93

Discussion

The pH of a sample is determined electrometrically using a combination electrode. This method is applicable to both liquid or solid samples.

Interferences

Temperature of the sample will affect the response of the pH electrode. This can be compensated for electrically on most pH meters. If not, adjust the standards and samples to the same temperature.

Particulate matter or oily substances may coat the electrode surface and affect its response. Detergent washing followed by distilled water rinse will usually clean the surface. If stronger cleaning is required, a dilute hydrochloric acid solution (10% v/v) is recommended.

Reagents

Standard Buffer Solutions: Buffer solutions of pH 4, 7, and 10 are purchased commercially.

Procedure

1. Turn the pH meter on and connect the electrode to the meter according to manufacturer's recommendations.

2. Let the pH meter warm up for a minimum of 15 minutes.

3. For normal environmental samples calibrate daily with pH 7 buffer and pH 4 buffer and check the pH 10 buffer as the first sample. If the pH is requested on more basic samples, use pH 10 buffer and pH 7 buffer to calibrate and check the pH 4 buffer as the first sample. For meter pH1 use the following instructions to calibrate:

   a. Place electrode in pH 7 buffer. Press CAL button. The light for CAL 1 will turn on.

   b. Wait for the system to equilibrate.

   c. If needed, adjust the up(Λ) of down(V) arrows until 7.00 is displayed on the meter. The READY light should automatically be lit.

   d. Press the ENTER button. This accepts the value for pH 7 and it automatically switches the instrument to calibrate the second buffer. The CAL 2 light should be lit. Clean the electrode.

   e. Place the clean electrode into pH 4 buffer. Again, wait for the system to equilibrate.

   f. Adjust (if needed) the arrows until 4.00 is displayed on the meter. The READY light should be automatically on.

   g. Press the ENTER button. This accepts the value for pH 4 and it automatically switches the instrument to analyze samples. The SAMPLE light will be on.

   h. Check and record the pH 10 buffer as the first sample. The pH of this buffer solution should be within 0.05 pH units.

4. Liquid Samples:

   a. Place the electrode into the sample.

   b. Allow the system to equilibrate.

   c. Record the pH on the bench sheet shown in Figure 1.

5. Solid Samples:

   a. Place 3 grams of solid material into a 100 ml beaker.

   b. Add approximately 50 ml of distilled water. Enough water so that a majority of the solid is exposed.

   c. Allow the solution to stand for 10-15 minutes with occasional stirring.

   d. Place the electrode into the sample.

   e. Allow the system to equilibrate.

   f. Record the pH on the bench sheet shown in Figure 1.

Quality Control

1. The calibration of the pH meter is completed in the beginning of each analysis day. The calibration is maintained until the check standard is not within 0.05 pH units of the buffer or the pH meter is turned off.

2. Check standards are to be completed in the beginning, end, and every 20th sample as minimum. If there are less than 20 samples analyzed, a check standard should be completed at the beginning and at the end. The check standard must be within 0.05 pH units of the buffer or the meter should be recalibrated. All samples completed from the last good check standard to the one which was out of control must be repeated.

3. Duplicates of sample are to be completed every tenth sample. If there is less than 10 samples analyzed, a minimum of one duplicate must be completed. The duplicate result must be within 0.10 pH units to be acceptable.

Operating Notes and Routine Maintenance

1. The electrode must be thoroughly rinsed with distilled water between samples.

2. If the electrode becomes coated with oily or particulate matter, clean with detergent and rinse thoroughly with distilled water. If this does not remove the matter, clean with a dilute HCl solution (a stronger acid cleaning may be required (10% v/v)). Rinse thoroughly with distilled water prior to using again. If continuing with the analysis of more samples, complete a check standard to confirm that the electrode is working properly.

3. The electrode should be checked each day for scratches, deterioration, or accumulation of debris on the glass surface. Periodically, the electrode should be rejuvenated by completing the following procedure:

   a. Alternately immersing the electrode three time each in 0.1 N HCl and 0.1 N NaOH or if a stronger solution is needed immerse the tip in KF solution for 30 seconds. Rinse.
   b. Soak in pH 7.0 buffer overnight.
   c. Rinse and store in pH buffer 7.0.
   d. Rinse again with distilled water before use.

4. If the pH meter is not working properly check the reference electrode, glass electrode, and potentiometer to determine the problem.

   a. Check the reference electrode against another one of the same type that is known to be good. Using an adapter, plug good reference electrode into glass electrode jack of the potentiometer; then plug questioned electrode into the reference electrode jack. Set the meter to read millivolt and take readings with both electrodes immersed in the same KCl solution and then in the same buffer solution. The millivolt readings should be 0 ± 5mV for both solutions.
   b. Check the glass electrode by replacing it with one of the same type that is known to be good. Check each electrode individually in two different buffers which are about 3 pH units apart. A deviation of 0.1 pH units indicates a faulty electrode.
   c. To determine if the problem is with the potentiometer, disconnect electrodes and, using a short circuit strap, connect reference electrode terminal to the glass electrode terminal. Observe change in pH when instrument calibration knob is adjusted. If the potentiometer is functioning properly, it will respond rapidly and evenly to changes in calibration over a wide scale range. A faulty potentiometer will fail to respond, will react erratically, or will show a drift upon adjustment. Switch to the millivolt scale on which the meter should read zero.

In all cases, if the pH meter is not functioning properly, use one of the other pH meters located in the laboratory or replace the nonfunctioning part.

ENVIROSCAN BENCH SHEET - ANALYSIS OF PH

Method: EPA 150.1 (liquids)
EPA 9040 (solids)
Instrument: PH1
Date: ___/___/___
Analyst: _____

Calibration:

Buffer #	Vendor	Lot #	pH
4	_____	_____	_____
7	_____	_____	_____
10	_____	_____	_____

QC Limit for Buffers is +/-0.05

Analytical #	pH	Analytical #	pH
1_____	_____	21_____	_____
1_____dup	_____	21_____dup	_____
2_____	_____	22_____	_____
3_____	_____	23_____	_____
4_____	_____	24_____	_____
5_____	_____	25_____	_____
6_____	_____	26_____	_____
7_____	_____	27_____	_____
8_____	_____	28_____	_____
9_____	_____	29_____	_____
10_____	_____	30_____	_____
11_____	_____	31_____	_____
11_____dup	_____	31_____dup	_____
12_____	_____	32_____	_____
13_____	_____	33_____	_____
14_____	_____	34_____	_____
15_____	_____	35_____	_____
16_____	_____	36_____	_____
17_____	_____	37_____	_____
18_____	_____	38_____	_____
19_____	_____	39_____	_____
20_____	_____	40_____	_____
pH Buffer ____	_____ QC Limit +/- 0.05	pH Buffer ____	_____

Determination of volatile organic compounds by gas chromatography mass spectrometry (GC-MS) [Off site VOC analysis]

Scope / Purpose

To provide a standard method for the analysis of samples for the volatile organic compounds found in the EPA method 624, SW-846 methods 8240 and 8260 and Federal Register TCLP methodologies.

Reagents / Special Equipment

GC-MS System: ITS40 GC-ITMS-DS

Gas chromatography system includes a Varian 3400 gas chromatograph equipped with an on-column injector, a 75 meter long by 0.53 mm inside diameter DB-624 capillary chromatography column from J & W Scientific (or equivalent). The chromatography column runs up to a heated jet separator interface. A deactivated length of chromatography column is then used to interface the exit end of the jet separator through a heated transfer line directly into the ion trap mass spectrometer. The gas chromatograph is also equipped with a Tekmar LSC2000 purge and trap concentrator and an ALS2016 multiple position purging autosampler.

Mass spectrometer system includes a Finnigan ITS40 ion trap mass spectrometer operated in electron impact, positive ion mode directly interfaced to the Finnigan Magnum data system. The data system uses version 2.1 operating software, and also includes version 1.0 of the Turnkey software platform and version 1.0 of the Tracker quality control software package.

Standards:

Calibration standards are prepared from commercially available high concentration stock standards or manufacturer prepared custom stock standards. These stock standards are then diluted volumetrically to provide for a range of calibration standards. The stock standards are normally supplied at a level of 200 µg/ml in each component, although some mixes are received at higher concentrations to increase their stability.

Spiking standards are prepared from commercially available high concentration stock standards, as above.

Continuing calibration standards (CCS) are prepared from commercially available high concentration stock standards, as

above, with the exception being that the CCS is prepared from either a different lot of standards from the same manufacturer, or (preferably) prepared from stock standards purchased from another supplier.

Internal standards and surrogate standards are received from commercial suppliers (Accustandard CLP-PIPS or equivalent). A volumetric dilution of these stock standard(s) is taken to produce a working standard at a concentration of 25 µg/ml. The internal standards used for the compounds in the method 624, 8240, 8260, and Federal Register TCLP compound lists are chlorobenzene-d5 and 1,4-dichlorobenzene-d4. The surrogate standards used for the same lists of compounds are dibromofluoromethane, toluene-d8, and 4-bromofluorobenzene. Using this particular set of internal standards and surrogates allows the laboratory to use a constant working standard for the analysis of all volatile samples.

The tuning standard is prepared either in house from pure (97 % +) compound available from commercial suppliers, or from a commercially purchased standard mixture containing the tuning compound. The tuning compound is 4-bromofluorobenzene, and is prepared from either source to produce a solution with a concentration of 25 µg/ml.

For some compounds, additional standards must be prepared in house from pure (97 % +) compounds available from commercial suppliers. These standards are prepared separately due to their unavailability to be found in commercial mixes.

Other supplies:

Volumetric flasks - various sizes (1, 2, 5, 10, 50, 100, 200 ml)
Syringes - various sizes (10, 25, 50, 100, 500, 1000 µl capacity)
5 ml glass with teflon plunger on barrel

Other reagents:

Methanol - pesticide quality or equivalent.
Water - organic free by carbon trap filtration and constant nitrogen purge.

References

Test Methods for Evaluating Solid Waste, SW-846, United States Environmental Protection Agency, 3rd edition, 1986.

Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA 600/4-82-057, United States Environmental Protection Agency, 1982.

Magnum Software Operation Manuals, Finnigan publications, 1989-1993.

Tracker Software Operation Manuals, Finnigan publications, 1992.

Issued: 02/12/93
Revised: 07/22/93
11/01/93

Analysis of samples for volatile organic compounds by GC-MS can be broken down into the following steps:

1. Tuning the mass spectrometer
2. Calibration of the system
3. Method validation
4. Initial QA/QC Evaluation
5. Analysis of liquid samples
6. Analysis of solid samples
7. Data validation and quantitation
8. Ongoing QA/QC evaluation
9. Routine maintenance

Tuning the mass spectrometer

At the beginning of each day that analyses are to be performed, the GC-MS system must be checked to see that acceptable mass spectrometer performance criteria are achieved for the volatile tuning compound BFB. A brief overview will be given here; for more background and methodology, refer to SOP #127, which is the in-depth standard operating procedure for tuning the volatile GC-MS system.

The analysis parameters for both the GC and the mass spectrometer can be found in SOP #127.

At the beginning of each day, inject 2 µl of the tuning standard; this 2 µl standard injection of the 25 µg/ml tuning standard will be 50 ng of BFB on column. Obtain a background subtracted mass spectrum of BFB and check that all the key ion criteria listed in Table 1 are achieved. If any of the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. No samples can be analyzed until the mass spectrometer meets the specified criteria.

Again, refer to SOP #127 for a more in-depth discussion.

Calibration of the system

The GC-MS system must be calibrated in such a way that a sample's compound levels analyzed will fall between any two calibrated levels, except in the case of a low concentration analysis in which case the detected level may be below the lowest concentration standard.

Calibration standards are prepared by volumetric dilution of high concentration stock standards. Solutions are prepared at a final volume of at least 50 ml by adding the stock standards (in methanol) at appropriate amounts into organic free water. Solutions are prepared at levels of 1, 5, 10, 20, 50, 100, and

150 µg/l for each of the compounds to be determined. After addition of the proper stock standards, the volumetric flask containing the standard is inverted three times (no more than three times, as excessive inversion may cause a loss of analyte), and transferred (with rinsing) to a 5 ml glass syringe. After overfilling the syringe to prevent the addition of air to the standard, excess solution is pushed out with the plunger/barrel, to yield a syringe containing exactly 5 ml of standard with no air present. To this syringe is injected 10 µl of internal standard and surrogate standard working solution(s). The syringe will now contain the analytes at their specified concentration and the internal standards and surrogate standards at a concentration of 50 µg/l. The contents of the syringe are placed into one of the purging tubes on the autosampler and the valve sealed.

Each of the calibration standards is then analyzed using methods which meet the following specifications:

GC temperature program - Start at -10 degrees C
Hold isothermal for 5 minutes
Ramp to 200 degrees C
Ramp rate 8 degrees C / minute
End at 200 degrees C
Hold isothermal for 8.75 minutes
Total run time 40 minutes
Column head pressure approx. 10 psi

GC injector temperature - 220 degrees C

Autosampler parameters - Trap stdby/purge temp 35 degrees C
Purge for 11 minutes
Purge flow 40 cc/minute nitrogen
Moisture control module (MCM)
cooldown 0 degrees C
Desorb preheat 200 degrees C
Desorb at 220 degrees C 4 minutes
Bakeout at 260 degrees C 8 minutes
All valves and lines 100 degrees C
MCM bakeout 60 degrees C

GC to jet separator interface - 220 degrees C

Jet separator to MS interface - 220 degrees C

MS manifold temperature - 220 degrees C

MS scan range - 36 amu to 260 amu

MS scan time - full mass range scanned in 1 second
(including settling and pre-scan)

MS scan sequence - Filament/multiplier on for 35 minutes

MS mass defect - 30 mmu per 100 amu

Following analysis of each of the calibration standards, the quantitation software is employed to locate (by retention time) and identify (by mass spectrum) each compound in the standard by a mass spectral library search against compounds in the

appropriate cali file (see references for methods to be used in creating cali files). The program will locate and identify the compounds and tabulate the area of the primary characteristic ions of the internal standards, surrogate standards, and calibration standards. It is these primary characteristic ions that all subsequent calculations are based upon. Prior to running the quantitation software, the multiplier factor is entered which reflects the actual concentration of the standards. For example, if the cali file contains a default value for each compound at 20 µg/l, and the standard that is being quantitated is a 10 µg/l standard, a factor of 0.5 is entered so the system knows to use 0.5 x 20 µg/l for the actual concentration of the standard. Using the auto calibration function of the software, the area of the primary ion of each calibration compound, its correct standard amount, the area of that compound's appropriate internal standard primary ion, and the internal standard amount are all placed into a table for that compound in that cali file, along with the compounds calculated response factor for that calibration level. The response factor is calculated using equation 1:

Eq. 1 $$RF = (Ac * Cis) / (Ais * Cc)$$

where

RF = Response factor
Ac = Area of the calibration compound's primary ion
Cis = Concentration of the internal standard
Ais = Area of the internal standards's primary ion
Cc = Concentration of the calibration compound.

A listing of each compound commonly analyzed by these method can be found in Table 2, along with a listing of their appropriate internal standard and primary (quantitation) characteristic ion and secondary (qualification/identification) characteristic ions.

Following these steps on each calibration standard, response lists are prepared that contain all of the above information used to calculate the response factor, as well as the calculated response factor. This is accomplished using the auto calibration function of the software. These response lists are in tabular format and there exists one for each individual compound. Each response list should have at least five response factors (one from each standard), the nominal amount being seven.

To evaluate the performance of the system for the initial calibration, the Tracker software is used. This program will re-tabulate all the individual response factors for each compound on one page, and will also calculate the average and %RSD for each compound. In order for the initial calibration to be accepted for a compound, the %RSD for that compound's response factors

must be less than 30%. If it is over 30%, that compound cannot be quantitated and reported without a qualification of the data as estimated. It is recommended that any compounds that fail the initial calibration 30% RSD limit be recalibrated as soon as possible. An alternate approach to recalibration involves the editing of the response lists and the removal of one or more response factors, if a valid reason can be established as to why that particular response factor is unusable. An example of this is background contamination of ketones in the reagent water; the presence of this low level contamination prevents the use of the 1 (and sometimes 5) µg/l standard in the response list of some ketones. In no case should this editing process leave less than a minimum of five response factors in a particular compound's response list. The average response factor is to be used for all calculations of continuing calibration standard (CCS) standard evaluation and data quantitation.

Once calibration has been completed and all the response lists prepared and evaluated, a new calibration need not be performed until unsatisfactory results are observed with analysis of the continuing calibration standard, described in following sections, or until a significant change to the system, such as a new column, is installed or made.

Method Validation

To ensure accurate, reproducible data, the entire analysis method must be evaluated. This is to be done after any significant change to the system,. such as a new detector, is installed or made.

For information on method validation, refer to EPA method 624 or SW-846 method 8240 (documents listed in References section).

Initial QA/QC Evaluation

Before proceeding with any sample analysis, several QA/QC steps must be performed. This starts with acceptable mass spectrometer tuning, described in a previous section.

Once acceptable tuning is achieved, a continuing calibration standard (CCS) and a system blank are evaluated. The CCS is prepared by volumetric dilution of similar mixes to the ones used for initial calibration; however, they must be from a different lot (if from the same manufacturer) or a different supplier. The CCS is prepared at a mid-level concentration for the instrument's calibrated range, i.e. 20 to 50 µg/l for a calibrated range of 1 to 150 µg/l.

After the appropriate mixes are added to the volumetric flask

containing organic free water, the flask is inverted three times to mix the solution and the standard is transferred (with rinsing) to a 5 ml glass syringe. The syringe is overfilled to prevent air from entering the standard and the plunger/barrel is then pushed in and the excess solution is ejected. To the exactly 5 ml of CCS is added 10 µl of the internal standard and surrogate standard mix(es), and the solution is injected into one of the purge tubes on the autosampler. The preparation procedure is to be consistent with the procedure used to prepare the calibration standards.

Analyze the CCS using identical instrument parameters to those used for calibration, and process the data using the quantitation software, the difference being that auto calibration was used for the calibration standards and auto integration is used for the CCS.

Following auto integration of the CCS analysis, the Tracker software is used to evaluate the performance of the instrument. The Tracker software will calculate the observed response factor for each compound in the CCS using Equation 1. The software will then compare this observed response factor for each compound in the CCS to the average of all response factors in each compound's response list for the appropriate cali file, prepared during initial calibration. A ratio is calculated of average response factor for a compound versus the observe response factor for that compound in the CCS - this ratio must be within 0.75 and 1.25, that is, the relative difference between the two compared response factors must be 25 percent or less. If the relative difference is greater than 25 percent, then an examination of the system and its calibration should be done. The system must afford 25 percent or less relative difference of the compared response factors of any compound that has a value reported. If the response factor is greater than 25 percent for any compound, the quantitated value of that compound in any sample that is reported must be qualified as estimated. These acceptance limits are for the analysis of samples using the EPA SW-846 methods 8240 and 8260; when analyzing under EPA method 625, the acceptance limit is tightened to 20 percent relative difference.

Following CCS analysis and evaluation, a system blank must be analyzed. A sample of organic free water is taken and placed in a 5 ml glass syringe, using the same rinsing and overfilling techniques as used for the initial and continuing calibration standards; internal standards and surrogates standards are also added to this aliquot of water similar to standards. This system blank is analyzed using identical conditions as were used for the standard analyses.

Following analysis, the quantitation (auto integration and quantitation) are performed on the system blank run and the quantitation report is examined to check the calculated concentrations of any compounds found during the search. any compounds found must be at levels below their method quantitation limits. If any compounds are found at higher levels. the system should be baked out. If this does not remove the contamination, a more thorough cleaning of the system should be performed. The system blank should show no contamination above the method quantitation limits for compounds to be determined before proceeding with sample analysis. If any compounds are observed

above limits, and values are reported for those compounds, the values should be qualified on the final report.

Following acceptable tuning, acceptable CCS performance, and acceptable system blank performance, the analysis of samples may begin. These QA/QC checks should be done every 12 hour shift.

Analysis of liquid samples

The analysis of liquid samples by this method is to be done in an identical fashion to which the initial and continuing standards were analyzed. A 5 ml glass syringe is overfilled, with rinsing, and the plunger/barrel is inserted, ejecting excess sample and leaving the syringe containing exactly 5 ml of the sample to be analyzed with no air bubbles. If the sample is expected to have significant amounts of contamination, a dilution may be necessary to move the compounds into the analytical working range of the instrument or to prevent dirtying the instrument excessively. If a dilution is made, use the organic free water used in the system blank evaluation. Fill the appropriate size volumetric flask approximately halfway and add the appropriate aliquot of sample to be diluted. Then fill the volumetric flask to the mark and invert three times for mixing. Again, use the overfill with rinsing technique to result in a syringe that contains exactly 5 ml of the sample dilution with no air bubbles. To the glass syringe containing sample or sample dilution, add 10 μl of internal standard and surrogate standard mix(es) and inject the sample into one of the purge tubes on the auto sampler. This procedure is to be consistent with the methods used to prepare the standards for analysis.

Analyze the sample or sample dilution using identical conditions to those used for calibration.

Analysis of solid samples

Analysis of solid samples by this method requires additional steps not used in the calibration of the system. A purge tube is

removed from the autosampler and placed on an analytical balance. After taring the balance, approximately 0.5 grams to 5.0 grams of solid sample are added to the tube and weighted exactly. The variance in sample size is used to move the concentration of the compounds present into the analytical working range of the instrument or to prevent excessive dirtying of the instrument. The largest mass of sample that can be used should be, to provide the best representation of the sample and the lowest quantitation limits. The tube containing sample is then re-installed onto the autosampler, taking care not to plug the liquid sampling line that descends into the purge tube.

An aliquot of organic free water is placed in a 5 ml glass syringe using the same overfill with rinsing technique as used to prepare the system blank. Also similar, add 10 µl of the internal standard and surrogate standard mix(es) to the water, and inject this water into the tube containing the solid sample to be analyzed. The sample is now ready for analysis.

Analyze the sample or sample dilution using identical conditions to those used for calibration.

Data validation and quantitation

After the analysis for a sample is complete, the quantitation software is employed to locate and identify the compounds of interest, tabulate their primary ion areas and their appropriate internal standard primary ion areas, and use the response lists prepared during calibration to quantitate the compounds. The concentration of the compounds is determined using equation 2:

$$\text{Eq. 2} \qquad Ctc = (Atc * Cis) / (Ais * RF)$$

where

Ctc = Concentration of the target compound
Atc = Area of the target compound's primary ion
Cis = Concentration of the internal standard
Ais = Area of the internal standards's primary ion
RF = Response factor

The response factor to be used (at least five were calculated during calibration) is determined as the average of all in the appropriate response list.

The reports generated by the quantitation programs should be examined closely before further calculations are done or before reporting any value. First, the integration report is examined to see that any compound identified as a "hit" was located at its appropriate scan number (retention time). A compound fund more than 5 scans away from its predicted position should be

questioned and examined.

Next, the RIC trace of the analysis is examined, and the mass spectrum of any "hit" is called up and compared to its appropriate library entry. A visual comparison, as well as the data system's search algorithms, is used to confirm identification. Additionally, the primary and secondary ions of any compound "hit" should co-elute within 2 scans of one another. If all these criteria are met, the compound is considered a positive "hit" and the quantitation values provided by the software should be further examined by manually cling up the quantitation ion on screen and confirming the peak integration.

If this is in agreement with the report value, then the quantitated value provided by the program may be used. If there is some over or under integration, the value may have to be manually calculated.

Following confirmation, the concentration of the compound in the original sample is determined using any conditional information recorded during the sample preparation and analysis steps, such as initial sample volume or weight, and any special analysis conditions, such as dilutions taken or total solids conversion to a dry weight basis for solid samples.

Ongoing QA/QC evaluation

In addition to the initial QA/QC evaluations of tuning, continuing calibration standard and system blank, several ongoing steps in quality control must be taken to ensure acceptable accuracy and precision. These steps begin with evaluation of the internal standards and surrogates added to each sample.

The location of each of the three internal standards in each sample should be compared to the location of internal standards in the continuing calibration standard. The position of each sample internal standard must not be more than 30 seconds from the position of the corresponding CCS internal standard. If any are shifted more than that, re-analysis is required following examination of possible causes for the shifting.

Along with the retention time check, the area of each internal standard in each sample should be compared with the area of the internal standards in the CCS. The area of each of the sample internal standards cannot be less than 50 % of the corresponding CCS internal standard area, and cannot be more than 200 % of the corresponding area. Areas less than 50 % are typically due to matrix effects overloading the column, and the sample may require dilution to move the internal standard area ratio into an acceptable range. Areas greater than 200 % are typically due to a differential matrix effect observed when a particularly clean

sample is analyzed and compared to relatively complicated CCS sample. In either case, since all quantitations are internal standard based, a problem in the internal standard ratios is directly propagated into any values quantitated. Any values quantitated and reported using an internal standard which fails its area test should be qualified as estimated.

Following the internal standard retention time and area evaluations, the surrogate standards must next be examined. Each sample extract analyzed has surrogates added prior to analysis, so that a measure of overall system performance is available with each analysis. These surrogates should be examined to be sure that their recoveries are within established allowable recovery ranges. The surrogates for each fraction, and their allowable recovery ranges, can be found in Table 3.

If a surrogate or surrogates show unacceptable recoveries, the sample must be re-analyzed to check for an isolated GC-MS system error. If the same or similar results are observed, the sample should be re-analyzed, possibly at another sample aliquot size if interferences in the sample matrix are suspect. If this re-extraction and re-analysis yield the same or similar results, or if there is insufficient sample to repeat these steps, the results for the fraction or fractions with unacceptable surrogate recoveries must be identified as such on any report.

In addition to the above evaluation steps, which are performed on every sample analyzed, there is also a requirement for matrix spike and matrix spike duplicate analysis. The MS/MSD analyses are performed at a frequency of 5%, that is, every 20th sample, on average, must be analyzed as a matrix spike and a matrix spike duplicate. This frequency of 5% applies to each of the three main matrices: aqueous samples, solid samples, and TCLP samples.

A matrix spike is prepared by taking a sample aliquot identical to the one used for data generation and adding, along with the surrogate standards, a known amount of either a specific spike mixture or one of the standards used for calibration purposes. The spiked sample is then analyzed identically to the one used for data generation, and the spike recoveries are evaluated on a basis similar to the one used for surrogate recoveries. The matrix spike duplicate is merely a second spiked aliquot, again, treated identically to the sample used for data generation. For additional information of the MS/MSD analyses, and corresponding QA/QC limits, refer to the Enviroscan QA/QC Manual.

In the event of a recovery or duplicate precision data that is outside the acceptable ranges, any data reported on that sample for the affected compounds must be qualified as estimated.

Routine maintenance

The following procedures are done on the indicated timetable for preventive maintenance:

Weekly: Extended bake-out of volatile trap and moisture control module. Purge and trap system set to 260 degrees C (MCM set to 90 degrees C) for at least 1 hour.

Monthly: Removal of approximately 1 foot of chromatography column from the injector end. Also, removal of all glass sampling tubes from purge and trap unit for acid clean-up.

Every two to three months: Complete cleaning of the ion trap source and analyzer assemblies. Also, all mechanical pump oils are changed.

Once yearly: Preventive maintenance visit by the Finnigan technical support staff.

In the even of analyzing one or more particularly contaminated samples, any of the first three procedures may be completed on an as needed basis to maintain acceptable instrument performance.

Table 1
Volatile Organic Compound Analysis
4-Bromofluorobenzene Tuning Criteria

Mass/Charge	Ion Abundance Criteria
50	15 to 40 % of m/z 95
75	30 to 60 % of m/z 95
95	base peak, 100 % rel. abundance
96	5 to 9 % of m/z 95
173	less than 2 % of m/z 174
174	greater than 50 % of m/z 95
175	5 to 9 % of m/z 174
176	between 95 and 101 % of m/z 174
177	5 to 9 % of m/z 176

TABLE 2

Legend:
SURR Surrogate Standard
IS Internal Standard

SCAN NUMBER		COMPOUND NAME	CHARACT. MASSES PRIMARY	SECONDARY	INT STD	QUANTITATION LIMITS Water	Low Level Soil
1347	IS 1	Chlorobenzene-d5	117	82 119	1	1.0 ug/l	1.0 ug/kg
1593	IS 2	1,4-Dichlorobenzene-d5	152	150	2	1.0 ug/l	1.0 ug/kg
989	SURR	Dibromofluoromethane	113		1	1.0 ug/l	1.0 ug/kg
1202	SURR	Toluene-d8	98	70 100	1	1.0 ug/l	1.0 ug/kg
1465	SURR	4-Bromofluorobenzene	95	174 176	2	1.0 ug/l	1.0 ug/kg
229		Dichlorodifluoromethane	85	87 101	1	1.0 ug/l	1.0 ug/kg
313		Chloromethane	50	52 49	1	1.0 ug/l	1.0 ug/kg
368		Vinyl chloride	62	64 61	1	1.0 ug/l	1.0 ug/kg
492		Bromomethane	94	96 79	1	1.0 ug/l	1.0 ug/kg
533		Chloroethane	45-49	50 52	1	2.0 ug/l	2.0 ug/kg
604		Trichlorofluoromethane	101	103 66	1	1.0 ug/l	1.0 ug/kg
706		1,1-Dichloroethene	96	61 98	1	1.0 ug/l	1.0 ug/kg
788		Dichloromethane	84	51 86	1	1.0 ug/l	1.0 ug/kg
823		t-1,2-Dichloroethene	96	61 98	1	1.0 ug/l	1.0 ug/kg
874		1,1-Dichloroethane	63	65 83	1	1.0 ug/l	1.0 ug/kg
937		c-1,2-Dichloroethene	96	61 98	1	1.0 ug/l	1.0 ug/kg
972		Chloroform	83	85 47	1	1.0 ug/l	1.0 ug/kg
987		1,1,1-Trichloroethane	97	99 117	1	1.0 ug/l	1.0 ug/kg
1003		Carbon tetrachloride	117	119 121	1	1.0 ug/l	1.0 ug/kg
1024		Benzene	78	52 77	1	1.0 ug/l	1.0 ug/kg
1026		1,2-Dichloroethane	62	64 98	1	1.0 ug/l	1.0 ug/kg
1086		Trichloroethene	130	95 97	1	1.0 ug/l	1.0 ug/kg
1107		1,2-Dichloropropane	63	62 41	1	1.0 ug/l	1.0 ug/kg
1134		Bromodichloromethane	83	85 129	1	1.0 ug/l	1.0 ug/kg
1162		2-Chloroethylvinylether	63+106	65	1	1.0 ug/l	1.0 ug/kg
1176		c-1,3-Dichloropropene	75	77 39	1	1.0 ug/l	1.0 ug/kg
1208		Toluene	91	92 65	1	1.0 ug/l	1.0 ug/kg
1230		t-1,3-Dichloropropene	75	77 39	1	1.0 ug/l	1.0 ug/kg
1248		1,1,2-Trichloroethane	97	83 85	1	1.0 ug/l	1.0 ug/kg
1262		Tetrachloroethene	166	164 129	1	1.0 ug/l	1.0 ug/kg
1287		Dibromochloromethane	129	208 206	1	1.0 ug/l	1.0 ug/kg
1347		Chlorobenzene	112	114 77	1	1.0 ug/l	1.0 ug/kg
1358		Ethylbenzene	91	106	1	1.0 ug/l	1.0 ug/kg
1370		m- & p-Xylene	106	91	1	1.0 ug/l	1.0 ug/kg
1411		o-Xylene	106	91	1	1.0 ug/l	1.0 ug/kg
1432		Bromoform	173	171 175	1	1.0 ug/l	1.0 ug/kg
1480		1,1,2,2-Tetrachloroethane	83	85 131	2	1.0 ug/l	1.0 ug/kg
1582		1,3-Dichlorobenzene	146	148 111	2	1.0 ug/l	1.0 ug/kg
1592		1,4-Dichlorobenzene	146	148 111	2	1.0 ug/l	1.0 ug/kg
1632		1,2-Dichlorobenzene	146	148 111	2	1.0 ug/l	1.0 ug/kg
725		Carbon Disulfide	76	78 44	1	5.0 ug/l	5.0 ug/kg
730		Acetone	43	58	1	10.0 ug/l	10.0 ug/kg
782		Vinyl Acetate	43	86	1	10.0 ug/l	10.0 ug/kg
942		2-Butanone (MEK)	43	57 72	1	10.0 ug/l	10.0 ug/kg
1191		4-Methyl-2-pentanone (MIBK)	43	58 100	1	5.0 ug/l	5.0 ug/kg
1272		2-Hexanone	43	58 57	1	5.0 ug/l	5.0 ug/kg
412		Styrene	104	78 103	1	1.0 ug/l	1.0 ug/kg
720		Freon-113	101		1	1.0 ug/l	1.0 ug/kg

Quantitation limit notes: Water values based on 5 ml purged analysis of undiluted sample
Soil values based on a 5 gram aliquot of sample on an as received basis
(conversion to dry weight basis will increase these values)
For medium level soils, approximately 1 gram of sample will be used
(this will increase the quantitation limits listed here by a factor of five)

Table 3
Volatile Organic Compound Analysis
Surrogate Standard Recovery Limits

Surrogate	Allowable Recovery Range Aqueous Sample	Solid Sample
Dibromofluoroemethane	86 % - 118 %	80 % - 120 %
Toluene-d8	88 % - 110 %	81 % - 117 %
4-Bromofluorobenzene	86 % - 115 %	74 % - 121 %

SOP # 127

Standard Operating Procedure for:

Tuning the ITS 40 GC-ITMS-DS system.

Scope / Purpose

To provide a standard method for the tuning of the ITS 40 GC-ITMS-DS prior to volatile organic compound analysis work, as is required by all EPA methods for this type of work. Also, to provide a basic "plan of attack" for troubleshooting tuning problems.

Reagents / Special Equipment

The tuning standard solution is prepared in house from pure (97 % +) compound available from commercial suppliers, or from a commercially purchased standard mixture containing the tuning compound. The tuning compound is 4-bromofluorobenzene (abbreviated BFB), and is prepared from either source to produce a solution with a concentration of 25 μg/ml.

References

Test Methods for Evaluating Solid Waste, SW-846, United States Environmental Protection Agency, 3rd edition, 1986.

Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA 600/4-82-057, United States Environmental Protection Agency, 1982.

Magnum Software Operation Manuals, Finnigan publications, 1989-1993.

Issued: 07/27/93
Revised:

Prior to the analysis of any sample using US EPA approved methods, the mass spectrometer of a GC-MS system must be "tuned" to US EPA specified criteria. Tuning consists of adjusting mass spectrometer hardware parameters so that the ion ratios of US EPA approved tuning compounds fall within specified values. The tuning compound for volatile organic compound analysis is 4-bromofluorobenzene, or BFB. The key ion abundance criteria that must be achieved when 50 ng of the tuning compound is injected is given in Table 1.

When the GC-MS system is operated in electron ionization/ positive ion detection mode (EI/POS), as required for US EPA analyses, perfluorotributylamine (PFTBA or FC43) is used to adjust mass spectral parameters prior to injection and analysis of BFB. When FC43 is bled into the mass spectrometer ion source, the relative abundances of ions characteristic of FC43 are monitored and adjusted to target values so that when BFB is injected and analyzed, its ion abundances will fall within the criteria specified by the US EPA. Also, the initial evaluation of FC43 provides for mass calibration of the mass spectrometer, to ensure to proper mass/charge assignment of positive ion fragments produced during ionization. Figure 1 shows the mass spectrum of BFB when hardware parameters are adjusted correctly and would pass the BFB key ion criteria.

To begin tuning, several initial adjustments/instrument checks must be performed. Enter the instrument control program (I) and enter the **ADJUSTMENTS** menu using the mouse. First, examine the **RF voltage ramp** for linearity; second, examine the **electrometer zero** for proper instrument noise suppression; and third, examine the **calibration gas pressure** to be sure that there is sufficient FC43 entering the ion source for mass spectral evaluation. In each of these adjustment options, the system will provide pass/fail messages, and if there is a failure, the system will provide recommended hardware solutions.

Following initial evaluation, the proper instrument tuning parameters are loaded into the system either manually or by selecting a instrument parameter file from the **FILE** menu. For the sake of completeness, the manual approach will be discussed here.

Enter the **CONTROL** menu and set the **scan rate** to 1 second per scan (this will also be set in the acquisition method, discussed later). Next, the **instrument parameters** are set as follows: **axial modulation** is set to 3.5 volts, **emission current** is set to 10 μA, and the **manifold** heater is set to 220 degrees C. Also in the **CONTROL** menu, set the display to **profile**, set ionization mode to **EI**, and select a working filament (1 or 2). The values discussed in this paragraph are for the most part fixed, and once

set, will remain in the instrument without further data entry on a different analysis shift. Also, these values are fixed in the sense that they will not be adjusted to meet mass spectral tuning criteria.

Following these entries, the individual segments of mass analysis will be set (for a more in-depth discussion of mass analysis segments, refer to documents in the References section). As a starting default point, set the segments as follows:

Segment No.	Mass Range	Segment time	DAC counts
1	10 - 60	100	210
2	61 - 80	60	210
3	81 - 170	110	210
4	171 - 650	85	210

These segment parameters are set in the **SET-UP** menu, except for the mass range, which is set using the ^B command.

While in the **SET-UP** menu, several other parameters will be examined and/or set. First, select the **check air/water** option; this will have the system evaluate the amount of system leakage, and provide a pass/fail message. Following that, the **electron multiplier voltage** must be set; this is done automatically and will determine the recommended operating voltage for the multiplier to provide sufficient sensitivity for analysis. When the recommended voltage is determined, manually edit this value to add 100 volts for increased sensitivity (this will also change some ionization parameters, see References for discussion). Next, the **target** value is set; this is done automatically to determine the proper number of ions that should be stored in the trap for proper mass resolution.

Still in the **SET-UP** menu, enter the **AGC prescan** option and keep all values as their default values except for the **background mass** value, which is set to 35 amu. As the last step in this menu, select the **EI/AGC parameters** option; again, keep all values as their defaults except for **background mass**, which is set to 35 amu and the **AGC storage level**, which is set to 210 DAC counts (same value as set for the mass segments).

This completes the mass spectrometer hardware set-up. As with the **CONTROL** menu, the **SET-UP** values will not change unless specifically programmed to different values. Most of the values entered in the **SET-UP** menu will not be altered to affect specific tuning requirements.

Following complete instrument set-up, the instrument is mass calibrated using FC43. This is done by selecting the **MASS CALIB** option and performing the mass calibration against known **FC43**

mass assignments. This is done automatically after selecting these options, and when the mass calibration is complete, manually examine the mass calibration curve. The important points to note are first, that the slope of the mass calibration line should be approximately 6.3 DAC/amu (plus or minus 1.0 %), and second, that the relative error should be less than 1.0 %.

After completing the mass spectrometer adjustments steps described above, it is time to evaluate the instrument for compliance with US EPA tuning criteria by analyzing the tuning compound. The GC and MS system parameters for testing are:

GC temperature program - Start at 130 degrees C
Hold isothermal for 10 minutes
GC injector temperature - 220 degrees C
GC to jet separator interface - 220 degrees C
Jet separator to MS interface - 220 degrees C
MS manifold temperature - 220 degrees C
MS scan range - 36 amu to 260 amu
MS scan time - full mass range scanned in 1 second
(including settling and pre-scan)
MS scan sequence - Filament/multiplier off for 200 seconds
Filament/multiplier on for 400 seconds
(total sequence time 10 minutes)
MS mass defect - 30 mmu per 100 amu

Inject 2 µl of the tuning standard solution. Once the acquisition is complete, the GC peak for the tuning compound must be checked using the chromatographic display program **C.** Obtain a background correct mass spectrum of BFB and check that all the key ion abundance criteria of Table 1 are achieved. This can best be accomplished by running the procedure **BFB** from the initial software screen, provided the tuning datafile is selected as the default file. This procedure will prepare a pass/fail table based of BFB criteria. An example output of this procedure is provided as Figure 2.

If the table shows all PASS criteria, work for the day may continue, a tune is only valid for 12 hours, and the instrument must be rechecked for passing tune ion criteria on that timetable.

If the tune was unsuccessful, the following table may help solve some of the simple, often observed problems:

Problem	Adjustable Parameter	Technique to try
m/z 50 too low	Mass Segment Time	Increase
m/z 174 base peak	Mass Segment Time	Decrease
m/z 173 too high	Peak Threshold	Increase

Problem	Adjustable Parameter	Technique to try
m/z 176 too high	Target	Decrease
	Electron Multiplier	Increase
m/z 174/176	Target	Decrease
isotopes bad	Electron Multiplier	Increase

As seen here, the only parameters which will be adjusted (most of the time) are the target value and the electron multiplier voltage; these are the parameters which are most likely to change as the source gets dirty or the multiplier ages. All other parameters, including mass segment time and peak threshold, once set, will remain constant, for the most part. In the event of several tuning failures, the first items to check are the target value and the multiplier voltage, which can be quickly evaluated using the **SET-UP** procedures described above.

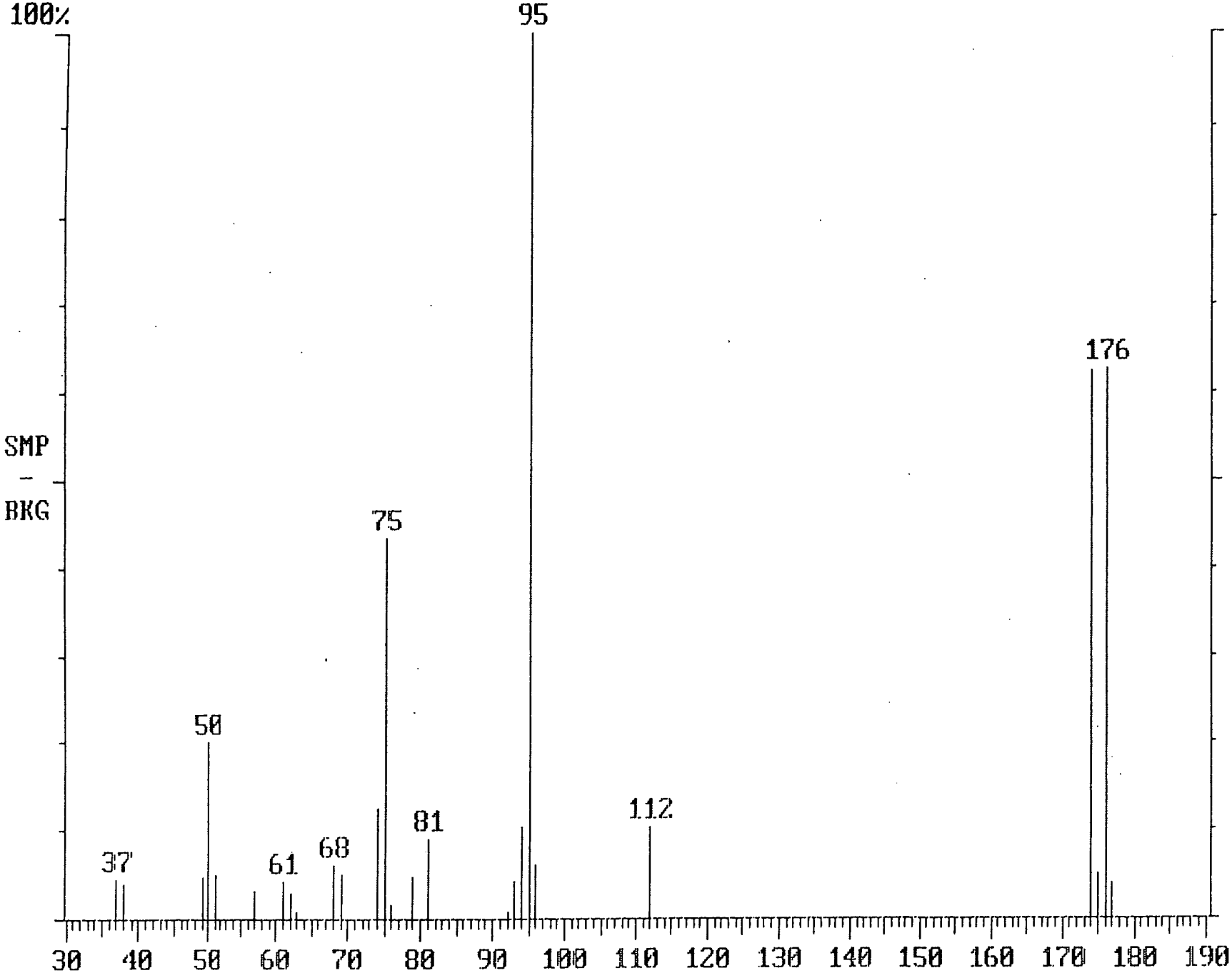
A tune should not vary that much from day to day, provided no significant change to the system was made during that interval. Therefore, avoid a complete system set-up as a starting point to tune. Check for air/water leaks, proper electrometer zero set, and sufficient calibration gas first, then perform a mass calibration (these can be quickly done using the **AUTO SET-UP** program). Other set-up procedures should be examined on a weekly basis. Following those steps, inject and analyze the tuning compound and if there is a failure, try the above steps before doing a complete system set-up. Excessive use of FC43 will prematurely dirty the source, causing difficulty in tuning and necessitating cleaning at more frequent intervals.

For a more complete discussion of the menus and options in this SOP, and hardware/software operating information, refer to documents in the References section.

Table 1
BFB Key Ions and Ion Abundance Criteria

Mass/Charge	Ion Abundance Criteria
50	15 - 40 % of m/z 95
75	30 - 60 % of m/z 95
95	Base peak, 100 % relative abundance
96	5 - 9 % of m/z 95
173	< 2 % of m/z 174
174	> 50 % of m/z 95
175	5 - 9 % of m/z 174
176	> 95 % but < 101 % of m/z 174
177	5 - 9 % of m/z 176

Background Subtract C:\MAGNUM\TUNE_\07199311 Date: 07/19/93 09:26:13
Comment: 4-BROMOFLUOROBENZENE - GC-MS TUNE (50 NG ON COLUMN)
Average of: 389 to 393 Minus: 361 to 365 100% = 31354



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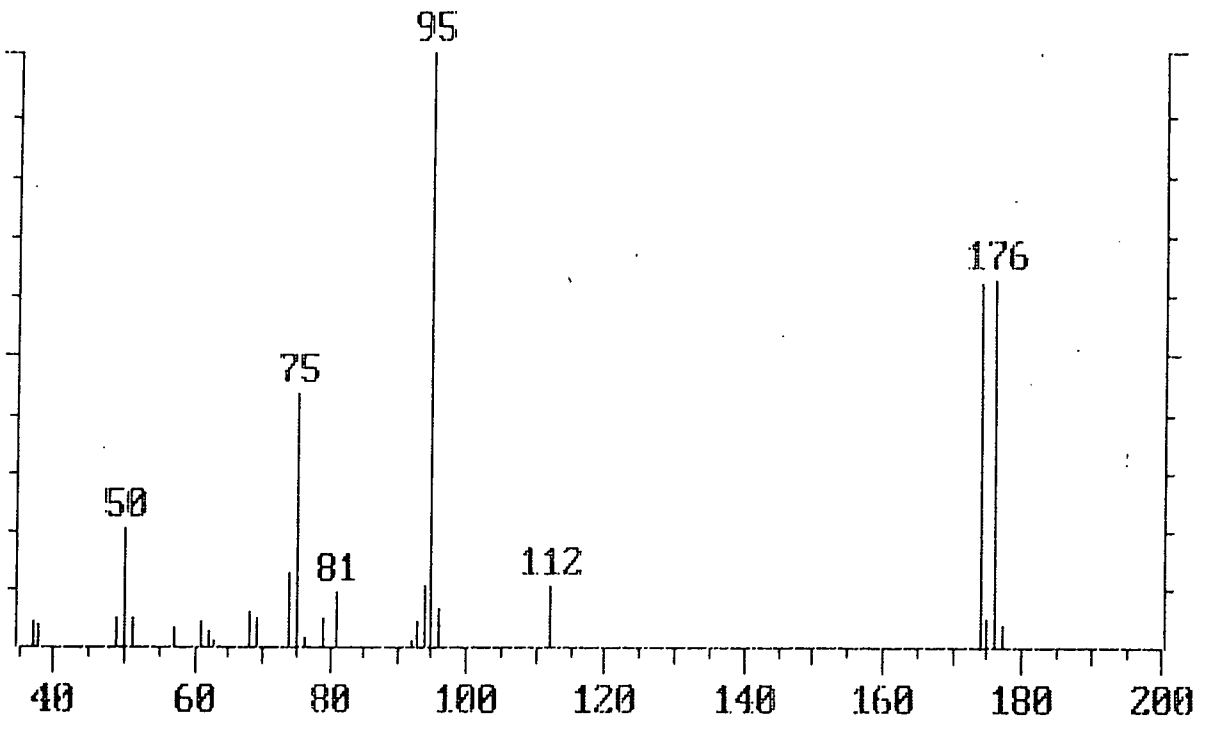
BFB Spectral Quality Report

Background Subtracted Spectrum



Data File: 071993T1
Cali File: BFB

Acqu Date: 07/19/93
Acqu Time: 09:26

Mass	Acceptance Criterion	Value	Pass/Fail
50	15 to 40% of Mass 95	20.13	Pass
75	30 to 60% of Mass 95	43.36	Pass
95	Base Peak, 100% Rel. Abund.	100.00	Pass
96	5 to 9% of Mass 95	6.09	Pass
173	< 2% of Mass 174	0.00	Pass
174	> 50% of Mass 95	62.38	Pass
175	5 to 9% of Mass 174	7.80	Pass
176	> 95% but < 101% of mass 174	100.55	Pass
177	5 to 9% of Mass 176	6.06	Pass

Press 'C' to continue

Determination of semi-volatile organic compounds by gas chromatography - mass spectrometry (GC-MS)

Scope / Purpose

To provide a standard method for the analysis of samples for the semi-volatile organic compounds found in the EPA method 625, SW-846 method 8270 and Federal Register TCLP methodologies.

Reagents / Special Equipment

GC-MS System: INCOS 50B GC-MS-DS

Gas chromatography system includes a Varian 3400 gas chromatograph equipped with a split/splitless injector, a thirty meter long by 0.25 mm inside diameter DB-5.625 capillary chromatography column from J&W Scientific (or equivalent). The chromatography column runs through a heated transfer line directly into the ion source of the mass spectrometer. The gas chromatograph is also equipped with a CTC-A200S autosampler.

Mass spectrometer system includes a Finnigan MAT INCOS 50B mass spectrometer operated in electron impact, positive ion mode directly interfaced to the Finnigan MAT INCOS data system. The data system uses version 11.0 operating software, and also includes version 11.0 Autoquan software, version 11.0 QA Report software, and version 11.0 NIST mass spectral library software.

Standards:

Calibration standards are prepared from commercially available high concentration stock standards (Supelco HC or TCL series or equivalent). These stock standards are then diluted volumetrically to provide for a range of calibration standards. The stock standards are normally supplied at a level of 2000 µg/ml in each component.

Spiking standards are prepared from commercially available high concentration stock standards, as above.

Continuing calibration standards (CCS) are prepared from commercially available high concentration stock standards, as above, with the exception being that the CCS is prepared from either a different lot of standards from the same manufacturer, or (preferably) prepared from stock standards purchased from another supplier.

Internal standards are received from commercial suppliers (Supelco HC or TCLP internal standard mix or equivalent) at a concentration of 2000 µg/ml in each component and used without further preparation. The internal standards used are 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12.

Surrogate fortification standards are prepared in house from pure (97 % +) compounds available from commercial sources. The three base/neutral and three acid compounds are prepared in individual solutions (base/neutrals in methylene chloride; acids in methanol) at a concentration of approximately 20 mg/ml (known exactly) and then combined to yield a surrogate fortification standard mix of 2000 µg/ml in each of the six components. The surrogates used are nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14 for the base/neutral fraction, and 2-fluorophenol, phenol-d6, and 2,4,6-tribromophenol for the acid fraction.

The tuning standard is prepared in house from pure (97 % +) compound available from commercial sources. The decafluorotriphenylphosphine (DFTPP) is prepared at a stock standard concentration of approximately 10 mg/ml (known exactly) and each day is volumetrically diluted to a concentration of 25 µg/ml for use during the tuning of the system.

Additional standards are prepared in house from pure (97 % +) compounds available from commercial sources. These standards are prepared separately due to their instability in lower concentration mixes, and their unavailability in commercial supplied mixes. These include, but are not limited to, benzidine, 3,3'-dichlorobenzidine, and pyridine, for example. These standards are added to the commercial supplied mixes in the preparation of calibration and continuing calibration standards.

Other reagents:

Methanol - pesticide quality or equivalent.
Methylene chloride (dichloromethane) - pesticide quality or equivalent.

References

Test Methods for Evaluating Solid Waste, SW-846, United States Environmental Protection Agency, 3rd edition, 1986.

Test Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA 600/4-82-057, United States Environmental Protection Agency, 1982.

Autoquan Operation Manuals, Finnigan Mat publications, 1988.

QA Report Operators Manual, Finnigan MAT publications, 1990.

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Revised: 07/22/93

Analysis of samples for semi-volatile organic compounds by GC-MS can be broken down into the following steps:

1. Tuning the mass spectrometer
2. Calibration of the system
3. Method validation
4. Initial QA/QC evaluation
5. Analysis of sample extracts
6. Data validation and quantitation
7. Ongoing QA/QC evaluation

Tuning the mass spectrometer

At the beginning of each day that analyses are to be performed, the GC-MS system must be checked to see that acceptable mass spectrometer performance criteria are achieved for the semi-volatile tuning compound DFTPP. A brief overview will be given here; for more background and methodology, refer to SOP #120, which is the in-depth standard operating procedure for tuning the semi-volatile GC-MS system.

The proper analysis parameters for both the GC and the mass spectrometer will be automatically loaded by running the procedure TUNSET.pr from the data system. These parameters can be found in SOP #120.

At the beginning of each day, inject 2 µl of the tuning standard solution, either by autosampler or manually. This 2 µl standard injection will be 50 ng of DFTPP on column. Obtain a background subtracted mass spectrum of DFTPP and check that all the key ion criteria listed in Table 1 are achieved. If any of the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. No samples can be analyzed until the mass spectrometer meets the specified criteria.

Again, refer to SOP #120 for a more in-depth discussion.

Calibration of the system

The GC-MS system must be calibrated in such a way that a sample's compound levels analyzed will fall between any two calibrated levels, except in the case of a low concentration analysis in which case the detected level may be below the lowest calibrated level.

Calibration standards are prepared by volumetric dilution of high concentration stock standards. Solutions are prepared at a final volume of 1 ml at levels of 5, 10, 20, 50, 80, and 120 µg/ml for each of the compounds to be determined. To each of these

solutions is added 20 µl of the internal standards mix so that each calibration standard is 40 µg/ml in internal standard concentration. The lowest concentration standard represents the quantitation limit for the majority of compounds analyzed using this method. Some of the compounds use a higher quantitation limit to due their inherent insensitivity for analysis by this method. In those instances, a sufficient number of additional standards are analyzed to provide six concentration levels for calibration.

Either using manual or autosampler injection, analyze 1 µl of each of the calibration standards using methods which meet the following specifications:

GC temperature program - Start at 35 degrees C
Hold isothermal for 4 minutes
Ramp to 300 degrees C
Ramp rate 10 degrees C / minute
End at 300 degrees C
Hold isothermal for 14.5 minutes
Total run time 45 minutes
Column head pressure approx. 10 psi

GC splitter valve - Open at 0.75 minutes
Splitter flow approx. 50 ml/minute

GC injector temperature - 300 degrees C

GC to MS transfer line temperature - 300 degrees C

MS ion source temperature - 180 degrees C

MS electron energy - 70 electron volts (nominal)

MS scan range - 35 amu to 500 amu

MS scan time - Full mass range scanned in 1 second (including settling time)

MS scan sequence - Filament/Multiplier off for 4 minutes
Filament/Multiplier on for 41 minutes

Autosampler - Rinse with sample 5 times x 5 µl
Syringe fill count of 5
Injection volume 1 µl
Air gap volume 2 µl
Pre-injection delay in injector port 2 seconds
Fast autosampler injection
No post-injection delay in injector port
Clean syringe after injection 5 times x 10 µl

The analysis parameters for the autosampler, gas chromatograph, and mass spectrometer can be automatically loaded by running the procedure BNASET.pr from the data system.

Following the analysis of the calibration standards, the Autoquan software is employed to locate (by retention time) and identify (by mass spectrum) each compound in the standard by a mass spectral library search against compounds in the appropriate quantitation library (see references for methods to be used in

creating quantitation libraries). The procedure will locate and identify the compounds, and also tabulate the area of the primary characteristic ions of the internal standards, surrogate standards, and calibration standards. It is these primary characteristic ions that all subsequent calculations are based upon. After tabulation of the areas, the quantitation list of

each standard is edited by adding the appropriate concentration for each of the components that were determined. After editing, the software will calculate and store with the quantitation list the response factor for each of the compounds. The response factor is calculated using the area and amount of the calibration compounds and its internal standard's area and amount using equation 1:

Eq. 1 $$RF = (Ac * Cis) / (Ais * Cc)$$

where

RF = Response factor
Ac = Area of the calibration compound's primary ion
Cis = Concentration of the internal standard
Ais = Area of the internal standard's primary ion
Cc = Concentration of the calibration compound

A listing of each compound commonly analyzed by this method can be found in Table 2, along with a listing of their appropriate internal standard and primary (quantitation) characteristic ion and secondary (qualification/identification) characteristic ions.

Following these steps on each calibration standard, response lists are prepared that contain all of the above information used to calculate the response factor, as well as the calculated response factor. This is done through the QUAN program of the INCOS software. These response lists are in tabular format and there exists one for each individual compound. Each response list should have six response factors (one from each standard).

To evaluate the performance of the system for the initial calibration, the REFC program of the QA Report software is used. This procedure will re-tabulate all the individual response factors for each compound on one page, and will also calculate the average and %RSD of the six response factors for each compound. In order for the initial calibration to be accepted for a compound, the %RSD for that compound's response factors must be less than 30%. If it is over 30%, that compound cannot be quantitated and reported without of a qualification of the data as estimated. It is recommended that any compounds that fail the initial calibration 30% RSD limit be recalibrated as soon as possible. An alternative approach to recalibration involves the editing of the response lists and the removal of

one or more response factors, if a valid reason can be established as to why that particular response factor is unusable. An example of this is the inherent insensitivity of several of the nitro group phenols; the lowest concentration standard is below a level which provides enough analytical signal to properly calculate the response factor. In instances such as this, additional calibration standards are prepared and analyzed, such that every compound has six response factors to be used in future calculations. The average response factor is to be used for all calculations of continuing calibration standard evaluation and data quantitation.

Once calibration has been completed and all the response lists prepared and evaluated, a new calibration need not be performed until unsatisfactory results are observed with analysis of the continuing calibration standard, described in following sections,

or until a significant change to the system, such as a new column, is installed or made.

Method Validation

To ensure accurate, reproducible data, the entire analysis method must be evaluated. This is to be done after any significant change to the system, such as a new detector or new extraction method, is installed or made.

For information on method validation, refer to EPA method 625 or SW-846 method 8270 (documents listed in References section).

Initial QA/QC Evaluation

Before proceeding with any sample analysis, several QA/QC steps must be performed. This starts with acceptable mass spectrometer tuning, described in a previous section.

Once acceptable tuning is achieved, a continuing calibration standard (CCS) and a system blank or evaluated. The CCS is prepared by volumetric dilution of similar mixes to the ones used for initial calibration; however, they must be from a different lot (if from the same manufacturer) or a different supplier. The CCS is prepared at a mid-level concentration for the instrument's calibrated range, i.e. 50 to 80 µg/ml for a calibration range of 5 to 120 µg/ml, and at a final volume of 1 ml.

Pipet or transfer 1 ml of the CCS into an autosampler vial and cap immediately. Add 20 µl of the internal standard mix to the 1 ml aliquot, giving a check standard that is 40 µg/ml in each of the internal standards. This procedure is to be consistent with the method used to analyze the calibration standards.

Inject a 1 µl aliquot of the CCS by either the manual or autosampler modes and analyze, using the same analysis parameters as used for both calibration and sample analysis, and process the data using the Autoquan procedure as used for quantitation.

Examination of the quantitation list prepared by the Autoquan procedure will have a listing of the response factor used to calculate the concentration value reported for each compound. This is the average of all the response factors in each compounds' response list, prepared earlier during the calibration phase of analysis. The values reported on the quantitation report have used this average response factor for calculation of the observed value in the CCS. Obviously, this should closely match the concentration at which the CCS was prepared. To evaluate this match, the quantitation report is edited and he actual prepared concentration of the standard is added. Now the response factors reported on the quantitation report reflect any variance in the curve, i.e. if the reported value for a known and prepared 80 ng standard is 70 ng, the response factor for this compound has decreased by a factor of 70/80. A ratio is then calculated of average response factor versus observed response factor for each compound - this ratio must be within 0.75 and 1.25, that is, the relative difference between the two response factor values must be 25 percent or less. If the relative difference is greater than 25 percent, then an examination of the system and its calibration should be done. The system must afford less than 25 percent relative difference of the response factors of any compound that has a value reported. If the response factor difference is greater than 25 percent for any compound, the quantitated value of that compound in any sample that is reported must be qualified as estimated.

The evaluation of the CCS can best be accomplished using the REFC program of the QA Report software that is resident in the data system. This is the same procedure that is used for the evaluation of the initial calibration. Operational details can be found in documents listed in the References section.

Following acceptable CCS performance, a system blank must be analyzed. Pipet 1 ml of methylene chloride into an autosampler vial and cap immediately. Add 20 µl of the internal standard mix to the vial, giving a blank that is 40 µg/ml in each of the internal standards. Inject a 1 µl aliquot of the blank using either manual or autosampler modes, and analyze using the same GC and MS parameters that were employed during system calibration.

After analysis, run the Autoquan procedure and check the calculated concentrations of any compounds found during its search. Any compounds found must be at levels below their method quantitation limits. If any compounds are found at higher

levels, the system should be baked out. If this does not remove the contamination, a more thorough cleaning of the system should be performed. The system blank should show no contamination above the method quantitation limits for compounds to be determined before proceeding with any sample analysis. If any compounds are observed above limits, and values are reported for those compounds, the values should be qualified on the final report.

Following acceptable tuning, acceptable CCS performance, and system blank performance, the analysis of sample extracts may begin. These QA/QC checks should be done every 12 hour shift.

Analysis of sample extracts

Once the sample has been received and extracted (refer to ES-404 for soil samples and ES-408 for liquid samples for information on sample extraction for semi-volatile analysis), it is prepared and analyzed by the GC-MS system. Prior to extraction, the sample aliquot should receive 100 µl of the surrogate standard solution - this will yield a sample than is 200 µg in each of the six surrogate standards. Assuming a normal concentration to 2 ml, the concentration of each surrogate standard in the extract should be 100 µg/ml.

Pipet a 1 ml aliquot of the extract into an autosampler vial and cap immediately. If the sample is expected to have significant amounts of contamination, a dilution may be necessary to move the compounds into the analytical working range of the instrument or to prevent dirtying the instrument excessively; use 1 ml of the dilution in these cases. Add 20 µl of the internal standard mix to each 1 ml aliquot, giving a sample extract that is 40 µg/ml in each of the internal standards. This procedure is to be consistent with the method used to analyze the calibration standards.

Inject and analyze 1 µl of the sample extract, using identical conditions to those used for calibration.

Data Validation and Quantitation

After the run is complete, the Autoquan procedure of the data system is employed to locate and identify the compounds of interest, tabulate their primary ion areas and their appropriate internal standard primary ion areas, and use the response lists prepared during calibration to quantify the compounds. The concentration of the compounds is determined using equation 2:

Eq. 2 $Ctc = (Atc * Cis) / (Ais * RF)$

where

Ctc = Concentration of the target compound
Atc = Area of the target compound's primary ion
Cis = Concentration of the internal standard
Ais = Area of the internal standard's primary ion
RF = Response factor

The response factor to be used (six were calculated during calibration) is determined as the average of all six determined earlier.

The report generated by the Autoquan procedure should be examined closely before further calculations are done or before reporting any value. The Autoquan report contains two tables, a diagnostic report and a quantitation report. The first table is examined to see that any compound identified as a "hit" was located at its appropriate scan number (retention time). A compound found more than 5 scans away from its predicted position should be questioned and examined. Next, the diagnostic report is examined again to see that any compound found during the retention time/mass spectral search was also found in the primary ion quantitation search, and that the peak locations for these two searches are within 1-3 scans of one another. If the two locations vary by more than this positional difference, the "hit" should be questioned and examined.

Next, the RIC trace of the analysis is examined, and the mass spectrum of any "hit" is called up and compared to its appropriate library entry. A visual comparison, as well as the data system's search algorithms, is used to confirm identification. Additionally, the primary and secondary ions of any compound "hit" should co-elute within 2 scans of one another. If all these criteria are met, the compound is considered a positive "hit" and the quantitation values provided by Autoquan should be further examined by manually calling up the quantitation ion on screen and confirming the peak integration. If this is in agreement with the Autoquan value, then the quantitated value provided by the program may be used. If there is some over or under integration, the value may have to manually calculated.

Following confirmation, the concentration of the compound in the original sample is determined using the information recorded during the extraction and concentration procedures, and any dilutions taken prior to sample extract analysis.

Ongoing QA/QC Evaluation

In addition to the initial QA/QC evaluations of tuning, continuing calibration standard and system blank, several ongoing

steps in quality control must be taken to ensure acceptable accuracy and precision. These steps begin with evaluation of the internal standards and surrogates added to each sample.

The location of each of the six internal standards in each sample should be compared to the location of internal standards in the continuing calibration standard. The position of each sample internal standard must not be more than 30 seconds from the position of the corresponding CCS internal standard. If any are shifted more than that, re-analysis is required following examination of possible causes for the shifting.

Along with the retention time check, the area of each internal standard in each sample should be compared with the area of the internal standards in the CCS. The area of each of the sample internal standards cannot be less than 50 % of the corresponding CCS internal standard area, and cannot be more than 200 % of the corresponding area. Areas less than 50 % are typically due to matrix effects overloading the column, and the sample may require dilution to move the internal standard area ratio into an acceptable range. Areas greater than 200 % are typically due to a differential matrix effect observed when a particularly clean sample is analyzed and compared to relatively complicated CCS sample. In either case, since all quantitations are internal standard based, a problem in the internal standard ratios is directly propagated into any values quantitated. Any values quantitated and reported using an internal standard which fails its area test should be qualified as estimated.

Following the internal standard retention time and area evaluations, the surrogate standards must next be examined. Each sample extract analyzed has surrogates added prior to extraction, so that a measure of overall system performance is available with each analysis. These surrogates should be examined to be sure that their recoveries are within established allowable recovery ranges. The surrogates for each fraction, and their allowable recovery ranges, can be found in Table 3.

If a surrogate or surrogates show unacceptable recoveries, the extract must be re-analyzed to check for an isolated GC-MS system error. If the same or similar results are observed, the sample should be re-extracted and re-analyzed, possibly at another sample aliquot size if interferences in the sample matrix are suspect. If this re-extraction and re-analysis yield the same or similar results, or if there is insufficient sample to repeat these steps, the results for the fraction or fractions with unacceptable surrogate recoveries must be identified as such on any report.

In addition to the above evaluation steps, which are performed on

every sample analyzed, there is also a requirement for matrix spike and matrix spike duplicate analysis. The MS/MSD analyses are performed at a frequency of 5%, that is, every 20th sample, on average, must be extracted as a matrix spike and a matrix spike duplicate.

A matrix spike is prepared by taking a sample aliquot identical to the one used for data generation and adding, along with the surrogate standards, a known amount of either a specific spike mixture or one of the standards used for calibration purposes. The spiked sample is then extracted and analyzed identically to the one used for data generation, and the spike recoveries are

evaluated on a basis similar to the one used for surrogate recoveries. The matrix spike duplicate is merely a second spiked aliquot, again, treated identically to the sample used for data generation. For additional information of the MS/MSD analyses, and corresponding QA/QC limits, refer to the Enviroscan QA/QC Manual.

In the event of a recovery or duplicate precision data that is outside the acceptable ranges, any data reported on that sample for the affected compounds must be qualified as estimated.

Routine Preventive Maintenance Procedures

The following procedures are done on the indicated timetable for preventive maintenance:

Weekly: Clean and/or replace glass injector liner.
Biweekly or monthly: Removal of approximately 1 foot of chromatography column.
Every two to three months: Complete cleaning of the ion source and quadropole rods of the mass spectrometer. Also, all mechanical pump oils are changed.
Every six months: Preventive maintenance visit by the Finnigan technical support staff.

In the event of analyzing one or more particularly contaminated samples, any of the first three procedures may be completed on an as needed basis to maintain acceptable instrument performance.

Table 1
DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60 % of mass 198
68	< 2 % of mass 69
70	< 2 % of mass 69
127	40 - 60 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5 - 9 % of mass 198
275	10 - 30 % of mass 198
365	> 1 % of mass 198
441	Present but less than mass 443
442	> 40 % of mass 198
443	17 - 23 % of mass 442

TABLE 2

Legend:
S-AC Acid Surrogate
S-BN Base/Neutral Surrogate
IS Internal Standard

APPROX. SCAN NUMBER		COMPOUND NAME	CHARACT. MASSES PRIMARY	SECONDARY	INT STD	QUANTITATION LIMITS Water	Low Level Soil
467		N-NITROSODIMETHYLAMINE	42	74 44	1	10. ug/l	0.34 ug/g
741	S-AC	2-FLUOROPHENOL	112	64	1		
943	S-AC	PHENOL-D6	99	42 71	1		
947		PHENOL	94	65 66	1	10. ug/l	0.34 ug/g
962		2-CHLOROPHENOL	128	64 130	1	10. ug/l	0.34 ug/g
962		BIS(2-CHLOROETHYL)ETHER	93	63 95	1	10. ug/l	0.34 ug/g
994		1,3-DICHLOROBENZENE	146	148 113	1	10. ug/l	0.34 ug/g
1006	IS 1	1,4-DICHLOROBENZENE-D4	152	150 115			
1010		1,4-DICHLOROBENZENE	146	148 113	1	10. ug/l	0.34 ug/g
1041		1,2-DICHLOROBENZENE	146	148 113	1	10. ug/l	0.34 ug/g
1075		BIS(2-CHLOROISOPROPYL)ETHER	45	77 79	1	10. ug/l	0.34 ug/g
1112		N-NITROSODI-N-PROPYLAMINE	130	42 101	1	10. ug/l	0.34 ug/g
1112		HEXACHLOROETHANE	117	201 199	1	10. ug/l	0.34 ug/g
1130	S-BN	NITROBENZENE-D5	82	128 54	2		
1135		NITROBENZENE	77	123 65	2	10. ug/l	0.34 ug/g
1195		ISOPHORONE	82	95 138	2	10. ug/l	0.34 ug/g
1203		2-NITROPHENOL	139	65 109	2	10. ug/l	0.34 ug/g
1223		2,4-DIMETHYLPHENOL	122	107 121	2	10. ug/l	0.34 ug/g
1244		BIS(2-CHLOROETHOXY)METHANE	93	95 123	2	10. ug/l	0.34 ug/g
1259		2,4-DICHLOROPHENOL	162	164 98	2	10. ug/l	0.34 ug/g
1273		1,2,4-TRICHLOROBENZENE	180	182 145	2	10. ug/l	0.34 ug/g
1285	IS 2	NAPHTHALENE-D8	136	68			
1290		NAPHTHALENE	128	129 127	2	10. ug/l	0.34 ug/g
1320		HEXACHLOROBUTADIENE	225	223 227	2	10. ug/l	0.34 ug/g
1420		4-CHLORO-3-METHYLPHENOL	142	107 144	2	20. ug/l	0.67 ug/g
1483		HEXACHLOROCYCLOPENTADIENE	237	235 272	3	10. ug/l	0.34 ug/g
1513		2,4,6-TRICHLOROPHENOL	196	198 200	3	10. ug/l	0.34 ug/g
1520	S-BN	2-FLUOROBIPHENYL	172	171	3		
1557		2-CHLORONAPHTHALENE	162	164 127	3	10. ug/l	0.34 ug/g
1634		DIMETHYLPHTHALATE	163	194 164	3	10. ug/l	0.34 ug/g
1648		2,6-DINITROTOLUENE	165	89 121	3	10. ug/l	0.34 ug/g
1651		ACENAPHTHYLENE	152	151 153	3	10. ug/l	0.34 ug/g
1683	IS 3	ACENAPHTHENE-D10	164	162 160			
1693		ACENAPHTHENE	154	153 152	3	10. ug/l	0.34 ug/g
1706		2,4-DINITROPHENOL	184	63 154	3	50. ug/l	1.67 ug/g
1726		4-NITROPHENOL	65	139 109	3	50. ug/l	1.67 ug/g
1733		2,4-DINITROTOLUENE	165	63 182	3	10. ug/l	0.34 ug/g
1799		DIETHYLPHTHALATE	149	177 150	3	10. ug/l	0.34 ug/g
1811		FLUORENE	166	165 167	3	10. ug/l	0.34 ug/g
1815		4-CHLOROPHENYLPHENYLETHER	204	206 141	3	10. ug/l	0.34 ug/g
1832		2-METHYL-4,6-DINITROPHENOL	198	182 77	4	50. ug/l	1.67 ug/g
1846		N-NITROSODIPHENYLAMINE	169	168 167	4	10. ug/l	0.34 ug/g
1866	S-AC	2,4,6-TRIBROMOPHENOL	330	332 141	3		
1927		4-BROMOPHENYLPHENYLETHER	248	250 141	4	10. ug/l	0.34 ug/g
1935		HEXACHLOROBENZENE	284	142 249	4	10. ug/l	0.34 ug/g
1981		PENTACHLOROPHENOL	266	264 268	4	50. ug/l	1.67 ug/g
2023	IS 4	PHENANTHRENE-D10	188	94 80			
2030		PHENANTHRENE	178	179 176	4	10. ug/l	0.34 ug/g
2042		ANTHRACENE	178	179 176	4	10. ug/l	0.34 ug/g
2172		DI-N-BUTYLPHTHALATE	149	150 104	4	10. ug/l	0.34 ug/g
2301		FLUORANTHENE	202	101 100	4	10. ug/l	0.34 ug/g
2336		BENZIDINE	184	92 185	5	50. ug/l	1.67 ug/g
2352		PYRENE	202	101 100	5	10. ug/l	0.34 ug/g

TABLE 2

Legend:
S-AC Acid Surrogate
S-BN Base/Neutral Surrogate
IS Internal Standard

APPROX. SCAN NUMBER		COMPOUND NAME	CHARACT. MASSES PRIMARY	SECONDARY	INT STD	QUANTITATION LIMITS Water	Low Level Soil
2395	S-BN	4-TERPHENYL-D14	244	122 202	5		
2513		BENZYLBUTYLPHTHALATE	149	91 206	5	10. ug/l	0.34 ug/g
2627		3,3'-DICHLOROBENZIDINE	252	254 126	5	20. ug/l	0.67 ug/g
2627		BENZO(A)ANTHRACENE	228	229 226	5	10. ug/l	0.34 ug/g
2630	IS 5	CHRYSENE-D12	240	120 236			
2637		CHRYSENE	228	226 229	5	10. ug/l	0.34 ug/g
2649		BIS(2-ETHYLHEXYL)PHTHALATE	149	167 279	5	10. ug/l	0.34 ug/g
2793		DI-N-OCTYLPHTHALATE	149	167 43	6	10. ug/l	0.34 ug/g
2870		BENZO(B)FLUORANTHENE	252	253 125	6	10. ug/l	0.34 ug/g
2878		BENZO(K)FLUORANTHENE	252	253 125	6	10. ug/l	0.34 ug/g
2952		BENZO(A)PYRENE	252	253 125	6	10. ug/l	0.34 ug/g
2966	IS 6	PERYLENE-D12	264	260 265			
3307		INDENO(1,2,3-CD)PYRENE	276	138 277	6	10. ug/l	0.34 ug/g
3319		DIBENZO(A,H)ANTHRACENE	278	139 279	6	10. ug/l	0.34 ug/g
3410		BENZO(GHI)PERYLENE	276	138 277	6	10. ug/l	0.34 ug/g
942		ANILINE	93	66 65	1	10. ug/l	0.34 ug/g
1041		BENZYL ALCOHOL	108	79 77	1	20. ug/l	0.67 ug/g
1071		2-METHYLPHENOL	108	107 79	1	10. ug/l	0.34 ug/g
1108		4-METHYLPHENOL	108	107 79	1	10. ug/l	0.34 ug/g
1253		BENZOIC ACID	122	105 77	2	50. ug/l	1.67 ug/g
1307		4-CHLOROANILINE	127	129	2	20. ug/l	0.67 ug/g
1447		2-METHYLNAPHTHALENE	142	141	2	10. ug/l	0.34 ug/g
1520		2,4,5-TRICHLOROPHENOL	196	198 200	3	10. ug/l	0.34 ug/g
1586		2-NITROANILINE	65	92 138	3	50. ug/l	1.67 ug/g
1683		3-NITROANILINE	65	108 92	3	50. ug/l	1.67 ug/g
1733		DIBENZOFURAN	168	139	3	10. ug/l	0.34 ug/g
1829		4-NITROANILINE	65	108 92	3	50. ug/l	1.67 ug/g
1852		1,2-DIPHENYLHYDRAZINE	77	105 182	4	10. ug/l	0.34 ug/g
2039		CARBAZOLE	167	166 139	4	10. ug/l	0.34 ug/g

Quantitation limit notes: Water values based on 1000 ml sample extracted to a final volume of 2 ml (extract analyzed without dilution)
Soil values based on a 30 gram sample extracted to a final volume of 2 ml (values are as received basis; conversion to dry weight will increase these values)
For medium level soils, less initial sample will be used, increasing quantitation limits.

Table 3
Surrogate Recovery Limits (%)

Surrogate Compound	Water Sample	Soil Sample
Nitrobenzene - d5	35 - 114	23 - 120
2-Fluorobiphenyl	43 - 116	30 - 115
p-Terphenyl - d14	33 - 141	18 - 137
Phenol - d6	10 - 94	40 - 111
2-Fluorophenol	21 - 100	26 - 112
2,4,6-Tribromophenol	10 - 123	19 - 122

Standard Operating Procedure for:

Tuning the INCOS 50B GC/MS/DS system.

Scope / Purpose

To provide a standard method for the tuning of the INCOS 50B GC/MS/DS prior to semi-volatile analysis work, as is required by all EPA methods for this type of work. Also, to provide a basic "plan of attack" for troubleshooting tuning problems.

Reagents / Special Equipment

The tuning standard solution is prepared in house using pure (97 % +) compounds available from commercial suppliers. The decafluorotriphenylphosphine (DFTPP) is prepared at a stock standard concentration of approximately 10 mg/ml (known exactly) and each day is volumetrically diluted to a concentration of 25 µg/ml for use during the tuning of the system.

References

Meeting Mass Spectral Tuning Requirements for US EPA Analyses using Finnigan MAT Single Quadrupole GC/MS Instruments, Finnigan MAT Technical Report 607, Finnigan MAT, 1988.

INCOS 50B Operators Manual, Finnigan MAT, 1989.

INCOS 50 MSDS Applications Software Operators Manual, Finnigan MAT, 1987.

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Prior to the analysis of any sample using US EPA approved methods, the mass spectrometer of a GC/MS system must be "tuned" to US EPA specified criteria. Tuning consists of adjusting mass spectrometer hardware parameters so that the ion ratios of US EPA approved tuning compounds fall within specified values. The tuning compound for semi-volatile analysis is decafluorotriphenylphosphine, or DFTPP. The key ion abundance criteria that must be achieved when 50 ng of the tuning compound is injected is given in Table 1.

When the GC/MS system is operated in the electron ionization / positive ion detection mode (EI/POS), as required for US EPA analyses, perfluorotributylamine (PFTBA or FC43) is used to adjust mass spectral parameters prior to injection and analysis of DFTPP. When FC43 is bled into the mass spectrometer ion source, the relative abundances of ions characteristic of FC43 are adjusted to target values so that when DFTPP is injected, its ion abundances will fall within the criteria specified by the US EPA. Figures 1 and 2 show mass spectra for FC43 and DFTPP, respectively, when hardware parameters are adjusted correctly and would pass the DFTPP key ion criteria.

Table 2 lists the target values for FC43, so that injection of DFTPP will give a successful tune. To begin tuning, enter the MTUN program of the system from the computer and check the electrometer zero:

&MT;EM1;SE;<cr>

The **&MT** command will bring up the scan descriptor MT, which is set up to monitor the five masses found in Table 2 that are characteristic of FC43. The **EM1** will turn on the electron multiplier, and the **SE** command will enable the scan, and begin scanning after typing return, **<cr>**. Adjust the electrometer zero setting **(EZ)** up or down to give only a few noise spikes for the displayed characteristic masses of FC43. Failure to adjust this setting correctly will either allow too many noise spikes to be interpreted as significant masses, which will distort the mass ratios, if the setting is too low, or it will subtract significant masses from the spectra, also distorting the mass ratios, but possible also altering the mass spectra generated to the point of misidentification later.

Once the electrometer zero is set correctly, turn on the filament (FI2) and FC43 gas valve **(CG1)**:

FI2;CG1;<cr>

Allow about thirty seconds for the calibration gas to come to an equilibrium in the system, and display the spectra by typing

D;<cr>. Compare the ratios observed on the screen to the ones found in Table 2.

If the criteria are not met, begin adjusting the hardware parameters found on the MTUN screen to meet the criteria. A basic sequence for doing so follows. It is important to remember that the ease of tuning a mass spectrometer is directly related to its cleanliness, so if a successful tune is very difficult to achieve, it may be time to clean the ion source. This is normally done about once every 2 months, or more frequently if tuning becomes a problem sooner.

1. Adjust **EM VOLTS** such that m/z 69 on the MTUN display is approximately 10000 to 15000 counts (the saturation level is 16383 counts). The needle valve setting on the calibration gas assembly may also be adjusted.

2. Check for optimal rod polarity. A toggle between RF voltage as applied to either one pair of rods or the other allows evaluation of which polarity provides the best sensitivity and mass peak shape. This adjustment is coarse and is used at the initial installation and following cleaning of the rods. The applied resolution values may vary quite dramatically between **REV** and **NOR** polarity.

3. Adjust **RESOLUTION HI** and **RESOLUTION LO** for proper resolution across the mass range. These two adjustments are highly interactive. Adjusting both settings in opposite directions provides a coarse adjustment of the ion ratios between low and high masses. Ideally, near baseline resolution should be achieved for all masses observed (toggling between **normal** and **square root display** will allow for closer examination of the resolution valley).

4. Adjust **ION OFFSET** so that the ratio of m/z 131 to m/z 69 is between 35 and 55 percent of m/z 69. The **ION OFFSET** value should range from +2 to +5 V. Raising the ion offset value will increase the ratio of m/z 131 to m/z 69; lowering this value will decrease this ratio.

5. Adjust **LENS OFFSET** so that the ratio of m/z 219 to m/z 131 is between 95 and 105 percent of m/z 131. The **LENS OFFSET** value should range from -20 to - 90 V. Raising the absolute value of the lens offset will increase the ratio of m/z 219 to m/z 131; lowering this value will decrease this ratio.

6. Adjust **ION PROGRAM** so that the ratio of m/z 414 to m/z 219 is between 5 and 10 percent of m/z 69. The **ION PROGRAM** value should be 2 to 4 times the ion offset. Raising the ion program will increase the ratio of m/z 414 to m/z 219; lowering the ion

program will decrease this ratio. Also check that the ratio of m/z 502 to m/z 414 is at least 75 percent of m/z 414.

7. Repeat steps 4 to 6 as needed to achieve the ratios given in Table 2 (adjusting the **EM VOLTS** as needed).

Once the FC43 ion ratios have been established, check that a good mass calibration exists. Calibration of the instrument need only be carried out once in this cycle, since tuning does not affect calibration. Only a change to the rod polarity and / or significant resolution changes will impact the mass calibration.

If it is necessary to prepare a new mass calibration, this can best be done by using the procedure CA from the data system, or refer to the documentation found in the References section for more specific direction to perform the mass calibration manually.

After completing the mass spectrometer adjustment steps described above, it is time to evaluate the instrument for compliance with to US EPA tuning criteria by analyzing the tuning compound. The GC and MS system parameters for testing are:

GC temperature program - Start at 125 degrees C
Hold isothermal for 0.1 minutes
Ramp to 275 degrees C
Ramp rate 12 degrees C / minute
End at 275 degrees C
Hold isothermal for 2.4 minutes
Column head pressure approx. 10 psi

GC splitter valve - Open at 0.70 minutes
Splitter flow approx. 50 ml / minute

GC injector temperature - 300 degrees C

GC to MS transfer line temperature - 300 degrees C

MS ion source temperature - 180 degrees C

MS electron energy - 70 electron volts (nominal)

MS scan range - 35 amu to 500 amu

MS scan time - Full mass range scanned in 1 second (including settling time)

MS scan sequence - Filament/Multiplier off for 4 minutes
Filament/Multiplier on for 11 minutes

These parameters are automatically programmed into the system by running the procedure TUNSET from the data system.

Inject 2 µl of the tuning standard solution. Once the acquisition is complete, the GC peak for the tuning compound must be checked using the chromatographic display program CHRO. Obtain a background corrected mass spectrum of DFTPP and check that all the key ion abundance criteria of Table 1 are met. This is done manually from the SPEC program, followed by the LIST

program and the T subprogram, which will prepare a pass/fail table based on DFTPP criteria.

If the table shows all PASS criteria, work for the day may continue; a tune is only valid for 12 hours, and the instrument must be rechecked for passing tune ion criteria on that timetable.

If the tune was unsuccessful, the following table may help solve some of the simple, often observed problems:

Problem	Suggested course of action
m/z 51 too high	Increase absolute value of the lens offset
m/z 69 isotopes high	Raise electrometer zero
m/z 442 base peak	Lower ion program
m/z 442 isotopes bad	Adjust resolution high

If these quick fixes do not help, go back to adjusting using FC43 to get the proper ratios. The above fixes should be tried before adjusting using FC43, as they can often fix simple problems quickly, providing the failed criteria are not too far out of line. Significant failures will, of course, require adjustment using FC43.

A tune should not vary from day to day that much, provided no significant change to the system was made during that interval. Therefore, avoid using FC43 as a starting point to tune; inject and analyze the tuning standard first and evaluate the actual tune criteria, and if there is a fail, try and correct using the above table before going back to FC43. Excessive use of FC43 will prematurely dirty the sources, causing difficulty in tuning and necessitating cleaning at more frequent intervals.

The above tuning method is the most accepted way to tune, that is, using the ion offset and ion program voltages to achieve mass ratios. Alternatively, other hardware parameters may be used to achieve acceptable tuning. Refer to documents in the reference section for information on more creative tuning, if necessary.

Table 1
DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60 % of mass 198
68	< 2 % of mass 69
70	< 2 % of mass 69
127	40 - 60 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5 - 9 % of mass 198
275	10 - 30 % of mass 198
365	> 1 % of mass 198
441	Present but less than mass 443
442	> 40 % of mass 198
443	17 - 23 % of mass 442

Table 2
Target Values of FC43 for Tuning on DFTPP

Mass (m/z)	Target Abundance Values
69	Base peak, 100 % relative abundance
131	35 to 55 % of m/z 69
219	-5 % to 10 % of m/z 131
414	5 to 10 % of m/z 219
502	> 75 % of m/z 414

FIGURE 4 —>

FC-43 Mass Spectrum

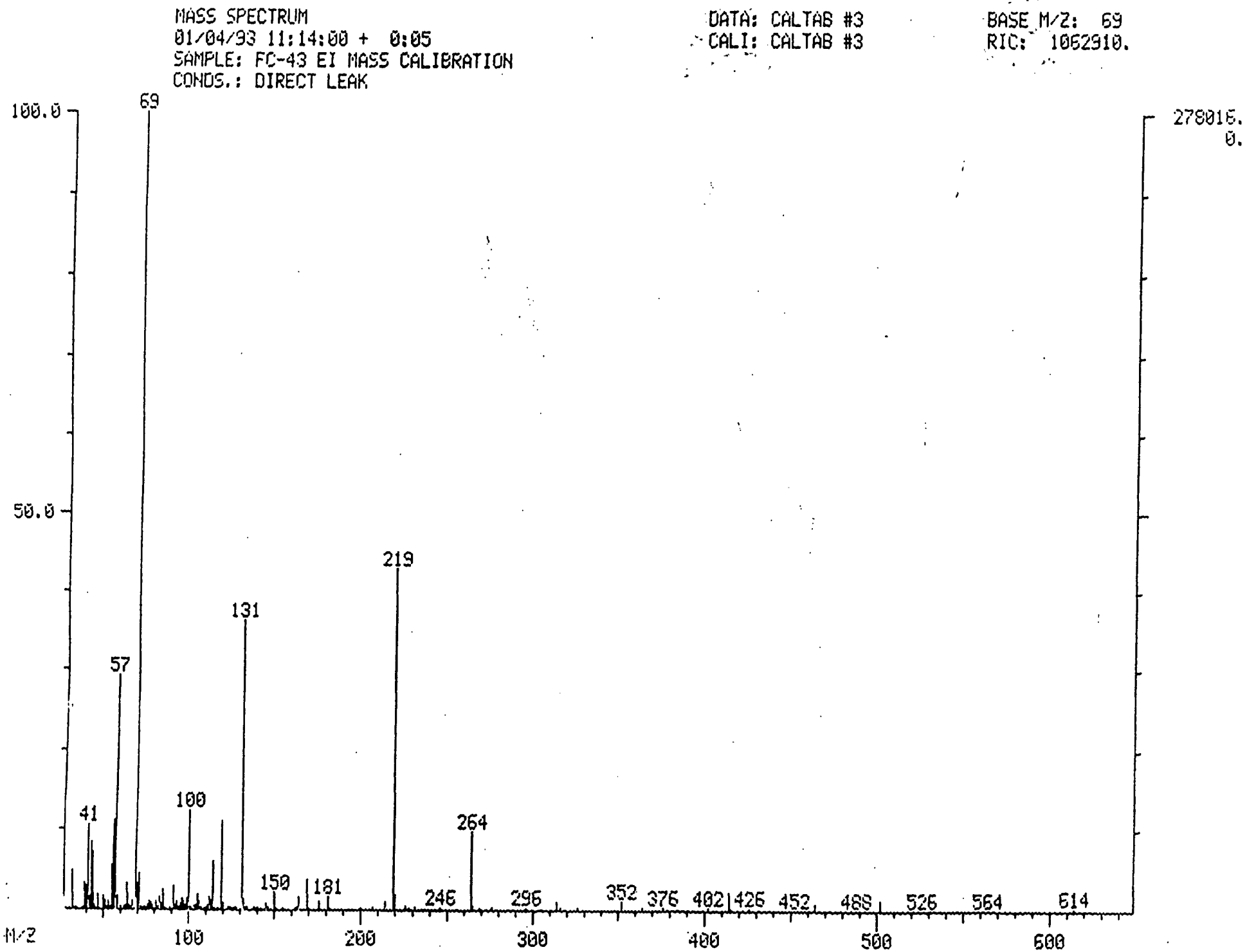
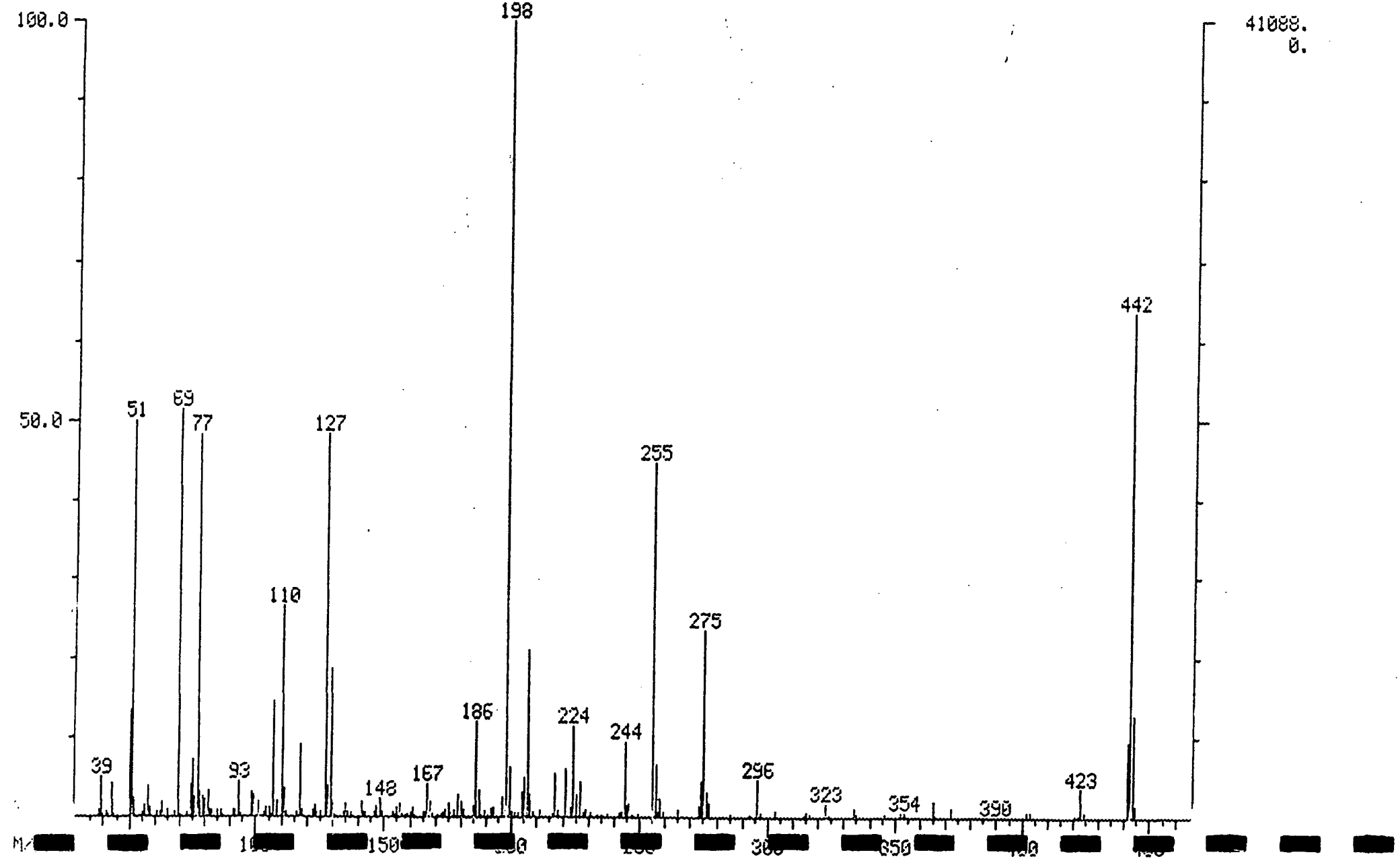


Figure 2 →
DFTPP Mass Spectrum

MASS SPECTRUM
03/02/93 9:50:00 +. 9:15
SAMPLE: EPA GC-MS SEMI-VOLATILE TUNE - DFTPP (25 PPM)
CONDS.: 30 M X 0.25 MM ID DB-5.625, 2.0 UL SPLITLESS MANUAL INJECTION
TEMP: 233 DEG. C
#1632 TO #1634 SUMMED

DATA: 030293TUNE #1633
CALI: CALTAB #3

BASE M/Z: 198
RIC: 332288.



Route 3

DECAFLUOROTRIPHENYLPHOSPHINE

SOP #120
page 10 of 1

Tuning Report
03/02/93 9:50:00 + 9:15
Instrument: FINN
#1632 to #1634 summed
Case Number:
Comments: METHOD 625 ION ABUNDANCE CRITERIA

Data: 030293TUNE #1633
Cali: CALTAB # 3
Analyst: JBE
Laboratory:

Base m/z: 198
RIC: 332288.
Acct. No.: QA/QC
Contract:

m/z	Intensity	% RA	Ion Abundance Criteria Min %	Max %	Mass	Actual	Status
51	20544.	50.00	30.00	60.00	198	50.00	PASS
68	184.	0.45	---	2.00	69	0.87	PASS
69	21120.	51.40	0.00	100.00	198	51.40	PASS
70	100.	0.24	---	2.00	69	0.47	PASS
127	19808.	48.21	40.00	60.00	198	48.21	PASS
197	0.	0.00	---	1.00	198	0.00	PASS
198	41088.	100.00	100.0	---	---	100.00	PASS
199	2592.	6.31	5.00	9.00	198	6.31	PASS
275	9648.	23.48	10.00	30.00	198	23.48	PASS
365	824.	2.01	1.00	---	198	2.01	PASS
441	3824.	9.31	---	100.00	443	73.88	PASS
442	26144.	63.63	40.00	---	198	63.63	PASS
443	5176.	12.60	17.00	23.00	442	19.80	PASS

ES-404

DETERMINATION OF: Extraction Method For EPA 525/625/8270 For Water/Wastewater

METHOD: Separatory Funnel Liquid/Liquid Extraction

REAGENTS: 6N Sulfuric Acid
Methylene Chloride
Anhydrous Sodium Sulfate
6N Sodium Hydroxide

EQUIPMENT: Separatory Funnels
Drying Column
Kuderna-Danish Apparatus
Water Bath
Nitrogen Blow Down Apparatus

REFERENCES: EPA Method 8270, Sept 1986. Test for Evaluating Solid Waste, SW-846, 3rd Edition. U.S. Environmental Protection Agency, Cincinnati, OH.

EPA Method 625, July 1982. Method for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057. U.S. Environmental Protection Agency, Cincinnati, OH.

EPA 525, December 1989. Method for the Determination of Organic Compounds in Drinking Water, EPA-600/4-039. U.S. Environmental Protection Agency, Cincinnati, OH.

ISSUED: July 26, 1993

EXTRACTION METHOD FOR EPA 525/625/8270 WATER/WASTEWATER

Scope/Purpose

To provide a procedure to extract semivolatile compounds out of water and wastewater samples.

Reagents/Special Equipment

Reagents

1) Reagent water - Nitrogen Purged distilled water

2) 6N Sulfuric Acid - Measure out 500 ml of reagent water and place in a 2000 ml reagent bottle. Add 165 ml of sulfuric acid (Mallinckrodt Sulfuric Acid AR, ACS grade) slowly to the 500 ml of reagent water. Let this mixture cool to room temperature. Add 335 ml of reagent water to the reagent bottle. CAUTION: HEAT IS GENERATED IN THIS PROCESS.

3) Methylene Chloride - Pesticide grade (Burdick & Jackson Methylene Chloride, B&J Brand

4) Surrogate - See chemist

5) Spike Mix - See chemist

6) Anhydrous Sodium Sulfate - Mallinckrodt Sodium Sulfate Anhydrous AR, ACS, Granular

7) 6N Sodium Hydroxide - Measure out 240 grams of sodium hydroxide pellets (Mallinckrodt Sodium Hydroxide AR, ACS, pellets) and place in a reagent bottle. Add slowly 500 ml of reagent water. Let this mixture cool to room temperature. Add 500 ml of reagent water to the reagent bottle. CAUTION: HEAT IS GENERATED IN THIS PROCESS.

Apparatus/Materials

1) Separatory Funnel - 2000 ml, with Teflon stopcock
125 ml, with Teflon stopcock
1000 ml, with Teflon stopcock

2) Drying Column - 20 mm ID - Fritted

3) Kuderna-Danish (K-D) apparatus
   a. Concentrator Tube - 10 ml Graduated - Pyrex
   b. Evaporation Flask - 500 ml - Pyrex
   c. Synder Column - Three-ball macro - Pyrex
   d. Plastic clip

4) Boiling Chips - Alltech - Hengar (Stock # 5785)

5) Water Bath - Operation of a temperature between 90 - 95 C

6) Vials - 2 ml capacity with teflon lined septa caps

7) pH indicator paper - Range of 0.0 - 6.0 pH
   Range of 7.0 - 14.0 pH

8) Erlenmeyer Flask - 500 ml

9) Graduate Cylinder - 1000 ml
   100 ml
   250 ml

10) Syringes - Volume to be added should be in the middle of the syringe capacity range

11) Nitrogen Blow Done Apparatus

Sample Extraction Procedure

NOTE: IF THE EXTRACTION APPEARS TO BE GOING INCORRECTLY OR IS DIFFICULT SEE THE CHEMIST. TWO DISTINCT PHASES SHOULD BE PRESENT.

1) Allow the sample to reach room temperature.

2) Mark the meniscus on the side of the bottle for later determination of sample volume used.

3) Invert the sample bottle three times to insure that the sample is homogeneous. NOTE: IF THE SAMPLE HAS SEDIMENT PRESENT OR TWO PHASES SHAKE VIGOROUSLY. SAMPLE BOTTLE MAY NEED TO BE VENTED.

4) Pour the sample into a 2000 ml separatory funnel.

5) Add surrogate to the 2000 ml separatory funnel making sure that the syringe needle hole is within the sample. Swirl the liquid in the separatory funnel.

6) Adjust the sample to a pH of 12 or greater with 6N sodium hydroxide. NOTE: ADD JUST ENOUGH SODIUM HYDROXIDE TO ACHIEVE THIS pH.

7) Add 60 ml of methylene chloride to sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the 2000 ml separatory funnel.

8) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

9) Allow the organic layer to separate from the water phase for 5 minutes.

10) Swirl the liquid in the 2000 ml separatory funnel.

11) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

12) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

13) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

14) Record the volume of methylene chloride recovered.

15) Transfer the methylene chloride to a 500 ml Erlenmeyer flask.

16) Transfer the water phase back to the 2000 ml separatory funnel.

17) Add a second 60 ml of methylene chloride to the 2000 ml separatory funnel.

18) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

19) Allow the organic layer to separate from the water phase for 5 minutes.

20) Swirl the liquid in the 2000 ml separatory funnel.

21) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

22) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

23) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

24) Record the volume of methylene chloride recovered.

25) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

26) Transfer the water phase back to the 2000 ml separatory funnel.

27) Add a third 60 ml of methylene chloride to the 2000 ml separatory funnel.

28) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

29) Allow the organic layer to separate from the water phase for 5 minutes.

30) Swirl the liquid in the 2000 ml separatory funnel.

31) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

32) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

33) Collect the methylene chloride layer in the a 100 ml graduate cylinder from the 125 ml separatory funnel.

34) Record the volume of methylene chloride recovered.

35) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

36) Transfer the water phase back to the 2000 ml separatory funnel.

37) Adjust the sample to a pH 2 or less with 6N sulfuric acid.
NOTE: ADD JUST ENOUGH SULFURIC ACID TO ACHIEVE THIS pH.

38) Add 60 ml of methylene chloride to the 2000 ml separatory funnel.

39) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

40) Allow the organic layer to separate from the water phase for 5 of minutes.

41) Swirl the liquid in the 2000 ml separatory funnel.

42) Allow the organic layer to separate from the water phase for a minimum 5 minutes.

43) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

44) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

45) Record the volume of methylene chloride recovered.

46) Transfer the methylene chloride to a 500 ml Erlenmeyer flask.

47) Transfer the water phase back to the 2000 ml separatory funnel.

48) Add a second 60 ml of methylene chloride to the 2000 ml separatory funnel.

49) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

50) Allow the organic layer to separate from the water phase for 5 minutes.

51) Swirl the liquid in the 2000 ml separatory funnel.

52) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

53) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

54) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

55) Record the volume of methylene chloride recovered.

56) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

57) Transfer the water phase back to the 2000 ml separatory funnel.

58) Add a third 60 ml of methylene chloride to the 2000 ml separatory funnel.

59) Shake the 2000 ml separatory funnel for 2 minutes with periodic venting to release excess pressure.

60) Allow the organic layer to separate from the water phase for 5 minutes.

61) Swirl the liquid in the 2000 ml separatory funnel.

62) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

63) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

64) Collect the methylene chloride layer in the a 100 ml graduate cylinder from the 125 ml separatory funnel.

65) Record the volume of methylene chloride recovered.

66) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

67) Dispose of the water layer into the acid waste container.

68) Add approximately 20 ml of methylene chloride to the 2000 ml separatory funnel and swirl. Add solvent to the 500 ml Erlenmeyer flask. This will allow for a complete transfer of any anlayte that maybe clinging to the glassware.

69) Assemble a K-D concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporation flask.

70) Place a methylene chloride rinsed drying column containing about 10 cm of anhydrous sodium sulfate on the 500 ml evaporation flask.

71) Pour the combined extract through the drying column.

72) Rinse the Erlenmeyer flask and column with 20 to 30 ml of methylene chloride. Rinse a total of three times.

73) Remove the drying column.

74) Add one or two clean boiling chips.

75) Place a Synder column on the 500 ml evaporation flask.

76) Wet the Synder column with 2 ml of methylene chloride.

77) Place the K-D apparatus on a hot water bath (90-95F) so that the concentrator tube is partially immersed in the hot water bath.

78) Take the K-D apparatus off the hot water bath when the volume of the liquid approximately is 1 ml.

79) Allow the K-D apparatus to drain and cool for at least 10 minutes.

80) Rinse the Synder column before disassembling the apparatus with methylene chloride.

81) Disassemble the K-D apparatus allowing for the concentrator tube to be placed on the nitrogen blow down apparatus. Rinse lower joint of the Synder column with methylene chloride over the evaporation flask. Rinse the evaporation flask with methylene chloride over the concentrator tube.

82) Place the concentrator tube on the nitrogen blow down. NOTE: THIS STEP NEEDS TO BE WATCHED CLOSELY.

83) Concentrate the sample to a volume of 0.5 ml.

84) Remove the sample from the blow down.

85) Bring the sample up to a final volume of 2 ml with methylene chloride.

86) Transfer the sample to 2 ml vial and mark the meniscus.

87) Store the extract vial in the freezer.

88) Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to 1000 ml graduate cylinder. Record the sample volume to the nearest 5 ml.

Matrix Spike/Matrix Spike Duplicate Sample

NOTE: IF THE EXTRACTION APPEARS TO BE GOING INCORRECTLY OR IS DIFFICULT SEE THE CHEMIST. TWO DISTINCT PHASES SHOULD BE PRESENT.

1) Allow the sample to reach room temperature.

2) Shake the sample bottle vigorously to insure that the sample is homogeneous. NOTE: SAMPLE BOTTLE MAY NEED TO BE VENTED.

3) Measure out 500 ml of sample and place in a 2000 ml separatory funnel labelled sample. Record volume in extraction log.

4) Add 500 ml of reagent water to the separatory funnel labelled sample. Invert the separatory funnel three times to insure that the sample is homogenous.

5) Split the remaining sample into two equal parts. Place each part into a 1000 ml separatory funnel labelled matrix spike and matrix spike duplicate. Record volume in extraction log.

6) Add appropriate volume of reagent water to bring the sample volume to 500 ml for the matrix spike and matrix spike duplicate. Invert the separatory funnel three times to insure that the sample is homogenous.

7) Add surrogate to the three labelled separatory funnels making sure that the syringe needle hole is within the sample. The syringe should be cleaned between samples to eliminate the possibility of cross contamination. Swirl the liquid in the separatory funnels.

8) Add the spike mix to the two 1000 liter separatory funnels making sure that the syringe needle hole is within the sample. The syringe should be cleaned between samples to eliminate the possibility of cross contamination. Swirl the liquid in the separatory funnels.

9) Adjust the liquid to a pH of 12 or greater with 6N sodium hydroxide in the three labelled separatory funnels. NOTE: ADD JUST ENOUGH SODIUM HYDROXIDE TO ACHIEVE THIS pH.

10) Add 60 ml of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel labelled sample.

11) Add 60 ml of methylene chloride to the two separatory funnels labelled matrix spike and matrix spike duplicate.

12) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

13) Allow the organic layer to separate from the water phase for 5 minutes.

14) Swirl the liquid in the labelled separatory funnels.

15) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

16) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

17) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

18) Record the volume of methylene chloride recovered.

19) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

20) Transfer the water phase back to the labelled separatory funnels.

21) Add a second 60 ml of methylene chloride to each of the three labelled separatory funnels.

22) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

23) Allow the organic layer to separate from the water phase for 5 minutes.

24) Swirl the liquid in the labelled separatory funnels.

25) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

26) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

27) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

28) Record the volume of methylene chloride recovered.

29) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

30) Transfer the water phase back to the labelled separatory funnels.

31) Add a third 60 ml of methylene chloride to each of the three labeled separatory funnels.

32) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

33) Allow the organic layer to separate from the water phase for 5 minutes.

34) Swirl the liquid in the labelled separatory funnels.

35) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

36) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

37) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

38) Record the volume of methylene chloride recovered.

39) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

40) Transfer the water phase back to the labelled separatory funnels.

41) Adjust the liquid to a pH of 2 or less with 6N sulfuric acid in the three labelled separatory funnels. NOTE: ADD JUST ENOUGH SULFURIC ACID TO ACHIEVE THIS pH.

42) Add 60 ml of methylene chloride to the to the labelled separatory funnels.

43) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

44) Allow the organic layer to separate from the water phase for 5 minutes.

45) Swirl the liquid in the labelled separatory funnels.

46) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

47) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

48) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

49) Record the volume of methylene chloride recovered.

50) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

51) Transfer the water phase back to the labelled separatory funnels.

52) Add a second 60 ml of methylene chloride to each of the three labelled separatory funnels.

53) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

54) Allow the organic layer to separate from the water phase for 5 minutes.

55) Swirl the liquid in the labelled separatory funnels.

56) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

57) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

58) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 250 ml separatory funnel.

59) Record the volume of methylene chloride recovered.

60) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

61) Transfer the water phase back to the labelled separatory funnels.

62) Add a third 60 ml of methylene chloride to each of the three labelled separatory funnels.

63) Shake the labelled separatory funnels for 2 minutes with periodic venting to release excess pressure.

64) Allow the organic layer to separate from the water phase for 5 minutes.

65) Swirl the liquid in the labeled separatory funnels.

66) Allow the organic layer to separate from the water phase for a minimum of 5 minutes.

67) Drain off the methylene chloride layer and a small amount of the water phase into a 125 ml separatory funnel.

68) Collect the methylene chloride layer into a 100 ml graduate cylinder from the 125 ml separatory funnel.

69) Record the volume of methylene chloride recovered.

70) Transfer the methylene chloride to 500 ml Erlenmeyer flask.

71) Dispose of the water layer into the acid waste container.

72) Add approximately 20 ml of methylene chloride to the labelled separatory funnels and swirl. Add solvent to the 500 ml Erlenmeyer flask. This will allow for a complete transfer of any anlayte that maybe clinging to the glassware.

73) Assemble a K-D concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporation flask.

74) Place a methylene chloride rinsed drying column containing about 10 cm of anhydrous sodium sulfate on the 500 ml evaporation flask.

75) Pour the combined extract through the drying column.

76) Rinse the Erlenmeyer flask and column with 20 to 30 ml of methylene chloride. Rinse a total of three times.

77) Remove the drying column.

78) Add one or two clean boiling chips.

79) Place a Synder column on the 500 ml evaporation flask.

80) Wet the Synder column with 2 ml of methylene chloride.

81) Place the K-D apparatus on a hot water bath (90-95F) so that the concentrator tube is partially immersed in the hot water bath.

82) Take the K-D apparatus off the hot water bath when the volume of the liquid is approximately 1 ml.

83) Allow the K-D apparatus to drain and cool for at least 10 minutes.

84) Rinse the Synder column before disassembling with methylene chloride.

85) Disassemble the K-D apparatus allowing for the concentrator tube to be placed on the nitrogen blow down apparatus. Rinse lower joint of the Synder column with methylene chloride over the evaporation flask. Rinse the evaporation flask with methylene chloride over the concentrator tube.

86) Place the concentrator tube on the nitrogen blow down. NOTE: THIS STEP NEED TO BE WATCHED CLOSELY.

87) Concentrated the sample to a volume of 0.5 ml.

88) Remove the sample from the blow down.

89) Bring the sample up to a final volume of 2 ml with methylene chloride.

90) Transfer the sample to a 2 ml vial and mark the meniscus.

91) Store the extract vial in the freezer.

ES-408

DETERMINATION OF: Extraction Method For EPA 8270 For Soil Samples

METHOD: Sonication Extraction

REAGENTS: Methylene Chloride
Anhydrous Sodium Sulfate
Acetone

EQUIPMENT: Drying Column
Kuderna-Danish Apparatus
Water Bath
Nitrogen Blow Down Apparatus
Vacuum Filtration Apparatus
Top Loading Balance
Sonicator

REFERENCES: EPA Method 8270, Sept 1986. Test for Evaluating Solid Waste, SW-846, 3rd Edition. U.S. Environmental Protection Agency, Cincinnati, OH.

ISSUED: July 26, 1993

EXTRACTION METHOD FOR EPA 8270
SOIL SAMPLES

Scope/Purpose

To provide a procedure to extract semivolatile compounds out of soil samples.

Reagents/Special Equipment

Reagents

1) Methylene Chloride:Acetone - Measure 1000 ml of methylene chloride (Pesticide grade, Burdick & Jackson Methylene Chloride, B&J Brand) and place into a 4 liter bottle. Measure 1000 ml of acetone (Pesticide grade, Burdick & Jackson Acetone, B&J Brand) and add to the 4 liter bottle. Invert the bottle three times to insure that the mixture is homogenous.

2) Surrogate - See chemist

3) Spike Mix - See chemist

4) Anhydrous Sodium Sulfate - Mallinckrodt Sodium Sulfate Anhydrous AR, ACS, Granular

Apparatus/Materials

1) Drying column - 20 mm ID - Fritted

2) Kuderna-Danish (K-D) apparatus
   a. Concentrator Tube - 10 ml Graduated - Pyrex
   b. Evaporation Flask - 500 ml - Pyrex
   c. Synder Column - Three-ball macro - Pyrex
   d. Plastic clip

3) Boiling Chips - Alltech - Hengar (Stock # 5785)

4) Water Bath - Operation of a temperature between 90 - 95 C

5) Vials - 2 ml capacity with teflon lined septa caps

6) Filtering Flask - 500 ml

7) Syringes - Volume to be added should be in the middle of the syringe capacity range

8) Nitrogen Blow Done Apparatus

9) Spatula - Stainless steel

10) Vacuum Filtration Apparatus
    a. Buchner funnel
    b. Filter paper - Whatman No. 41 - 11.0 cm

11) Beaker - 400 ml

12) Sonicator - Ultrasonic cell disrupter - Heat Systems-Ultrasoics, Model W-385 (475 watt) or equivalent

Sample Extraction Procedure

NOTE: IF THE EXTRACTION APPEARS TO BE GOING INCORRECTLY OR IS DIFFICULT SEE THE CHEMIST.

1) Allow the sample to reach room temperature.

2) Weigh out 30.0 ± 0.5 grams of soil into a 400 ml beaker.

3) Record the weight to the nearest 0.01 gram and record in the extraction log.

4) Add anhydrous sodium sulfate to the soil and mix. NOTE: ADD ENOUGH SODIUM SULFATE TO ACHIEVE A DRY TEXTURE.

5) Add surrogate to the soil.

6) Add 100 ml of methylene chloride:acetone to the 400 ml beaker.

7) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

8) Sonicate for 3 minutes.

9) Assemble the vacuum filtration apparatus by placing a Buchner funnel onto a 500 ml filtering flask. Place a Whatman No 41 filter paper in the Buchner funnel. Connect the 500 ml filtering flask to a vacuum line.

10) Decant and filter extract through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN ALL THE LIQUID IS DECANTED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

11) Add a second 100 ml of methylene chloride:acetone to the 400 ml beaker.

12) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

13) Sonicate for 3 minutes.

14) Decant and filter extract through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN ALL THE LIQUID IS DECANTED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

15) Add a third 100 ml of methylene chloride:acetone to the 400 ml beaker.

16) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

17) Sonicate for 3 minutes.

18) Transfer the entire sample into the Buchner funnel and filter the liquid through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN THE ENTIRE SAMPLE IS TRANSFERRED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

19) Rinse the 400 ml beaker with 10 ml of methylene chloride and filter the liquid through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN THE LIQUID IS TRANSFERRED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER. Rinse a total of three times.

20) Remove the filter paper from the Buchner funnel and place under a hood to dry. Once the filer paper is dry dispose into the garbage.

21) Assemble a K-D concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporation flask.

22) Place a methylene chloride rinsed drying column containing about 10 cm of anhydrous sodium sulfate on the 500 ml evaporation flask.

23) Pour the combined extract through the drying column.

24) Rinse the 500 ml filtrating flask and column with 20 to 30 ml of methylene chloride. Rinse a total of three times.

25) Remove the drying column.

26) Add one or two clean boiling chips.

27) Place a Synder column on the 500 ml evaporation flask.

28) Wet the Synder column with 2 ml of methylene chloride.

29) Place the K-D apparatus on a hot water bath (90-95F) so that the concentrator tube is partially immersed in the hot water bath.

30) Take the K-D apparatus off the hot water bath when the volume of the liquid is approximately 1 ml.

31) Allow the K-D apparatus to drain and cool for at least 10 minutes.

32) Rinse the Synder column before disassembling the apparatus with methylene chloride.

33) Disassemble the K-D apparatus allowing for the concentrator tube to be placed on the nitrogen blow down apparatus. Rinse lower joint of the Synder column with methylene chloride over the evaporation flask. Rinse the evaporation flask with methylene chloride over the concentrator tube.

34) Place the concentrator tube on the nitrogen blow down. NOTE: THIS STEP NEEDS TO BE WATCHED CLOSELY.

35) Concentrate the sample to a volume of 0.5 ml.

36) Remove the sample from the blow down.

37) Bring the sample up to a final volume of 2 ml with methylene chloride.

38) Transfer the sample to 2 ml vial and mark the meniscus.

39) Store the extract vial in the freezer.

Matrix Spike/Matrix Spike Duplicate Sample Extraction Procedure

NOTE: IF THE EXTRACTION APPEARS TO BE GOING INCORRECTLY OR IS DIFFICULT SEE THE CHEMIST.

1) Allow the sample to reach room temperature.

2) Weigh out 30.0 + 0.5 grams of soil into a 400 ml beaker labelled sample.

3) Record the weight to the nearest 0.01 gram and record in the extraction log.

4) Weigh out 30.0 + 0.5 grams of soil into a 400 ml beaker labelled matrix spike.

5) Record the weight to the nearest 0.01 gram and record in the extraction log.

6) Weigh out 30.0 + 0.5 grams of soil into a 400 ml beaker labelled matrix spike duplicate.

7) Record the weight to the nearest 0.01 gram and record in the extraction log.

8) Add anhydrous sodium sulfate to the three soils and mix. NOTE: ADD ENOUGH SODIUM SULFATE TO ACHIEVE A DRY TEXTURE.

9) Add surrogate to the three soil samples.

10) Add the matrix spike to the two 400 ml beakers labelled matrix spike and matrix spike duplicate.

11) Add 100 ml of methylene chloride:acetone to the three 400 ml beakers.

12) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

13) Sonicate for 3 minutes.

14) Assemble the vacuum filtration apparatus by placing a Buchner funnel onto a 500 ml filtering flask. Place a Whatman No 41 filter paper in the Buchner funnel. Connect the 500 ml filtering flask to a vacuum line.

15) Decant and filter extract through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN ALL THE LIQUID IS DECANTED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

16) Add a second 100 ml of methylene chloride:acetone to the 400 ml beakers.

17) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

18) Sonicate for 3 minutes.

19) Decant and filter extract through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN ALL THE LIQUID IS DECANTED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

20) Add a third 100 ml of methylene chloride:acetone to the 400 ml beakers.

21) Place the bottom surface of the tip of the disrupter horn about 1/2 inch above the soil. NOTE: THE TIP OF THE DISRUPTER HORN SHOULD BE AT LEAST 1/2 INCH BELOW THE SURFACE OF THE METHYLENE CHLORIDE.

22) Sonicate for 3 minutes.

23) Transfer the entire sample into the Buchner funnel and filter the liquid through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN THE ENTIRE SAMPLE IS TRANSFERRED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER.

24) Rinse the 400 ml beaker with 10 ml of methylene chloride and filter the liquid through the vacuum filtration apparatus. NOTE: TURN THE VACUUM ON WHEN THE LIQUID IS TRANSFERRED OVER. TURN OFF THE VACUUM WHEN ALL THE LIQUID HAS PAST THROUGH THE FILTER. Rinse a total of three times.

25) Remove the filter paper from the Buchner funnel and place under a hood to dry. Once the filer paper is dry dispose into the garbage.

26) Assemble a K-D concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporation flask.

27) Place a methylene chloride rinsed drying column containing about 10 cm of anhydrous sodium sulfate on the 500 ml evaporation flask.

28) Pour the combined extract through the drying column.

29) Rinse the 500 ml filtering flask and column with 20 to 30 ml of methylene chloride. Rinse a total of three times.

30) Remove the drying column.

31) Add one or two clean boiling chips.

32) Place a Synder column on the 500 ml evaporation flask.

33) Wet the Synder column with 2 ml of methylene chloride.

34) Place the K-D apparatus on a hot water bath (90-95F) so that the concentrator tube is partially immersed in the hot water bath.

35) Take the K-D apparatus off the hot water bath when the volume of the liquid is approximately 1 ml.

36) Allow the K-D apparatus to drain and cool for at least 10 minutes.

37) Rinse the Synder column before disassembling the apparatus with methylene chloride.

38) Disassemble the K-D apparatus allowing for the concentrator tube to be placed on the nitrogen blow down apparatus. Rinse lower joint of the Synder column with methylene chloride over the evaporation flask. Rinse the evaporation flask with methylene chloride over the concentrator tube.

39) Place the concentrator tube on the nitrogen blow down. NOTE: THIS STEP NEEDS TO BE WATCHED CLOSELY.

40) Concentrate the sample to a volume of 0.5 ml.

41) Remove the sample from the blow down.

42) Bring the sample up to a final volume of 2 ml with methylene chloride.

43) Transfer the sample to 2 ml vial and mark the meniscus.

44) Store the extract vial in the freezer.

Determination of: Total Cyanide

Method: Automated UV, Colorimetric

Reagents:
Phosphoric Acid
Potassium Dihydrogen Phosphate
Disodium Phosphate
Chloramine-T
Barbituric Acid
Pyridine
Hydrochloric Acid
Sodium Hydroxide
Sulfuric Acid
Magnesium Chloride

Interferences:
Thiocyanates
Sulfide
Nitrate and Nitrite
Oxidizing Agent

References:

Methods of Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268. Revised 1983, including EPA-600/4-84-017, March 1984. Method 335.3.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, EPA, Office of Solid Waste and Emergency Response, 401 M Street, S.W., Washington D.C. 20460, November 1986 including December 1987 and November 1990 updates. Method 9012.

Standard Methods for the Examination of Water and Wastewater, 17th Edition, American Public Health Association, 1015 Fifteenth Street NW, Washington D.C. 20005, 1989. Method 4500-CN C and E.

Issued: Unknown
Revised: 7/93

Discussion

The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry

In the colorimetic measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

Interferences

Thiocyanates are a positive interference. During the UV digestion thiocyanates are decomposed to cyanide.

Sulfides adversely affect the colorimetric procedure. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat by adding bismuth nitrate prior to distillation.

High results may be obtained for samples that contain nitrate and/or nitrite. During distillation, nitrate and nitrite from nitrous acid, which will react with some organic compounds to form oximines. These compounds will decompose under test conditions to generate HCN. The possible interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

Oxidizing Agents such as chlorine decompose most cyanide. To determine whether oxidizing agents are present, test a drop of sample with acidified potassium iodide (KI)-starch test paper at the time the sample is collected; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then add an additional 0.6 g of ascorbic acid for each liter of water.

Sample Preservation and Holding Time

Analysis	Sample Preservation	Holding Time	Quantitation Limit
Cyanide	NaOH to pH > 12, cool 4°C	14 days	0.01 mg/l

Reagents

If manually distilling, prepare the following reagents:

Sodium Hydroxide Solution, 0.1 N: Weigh 4.0 grams of NaOH pellets and dissolve in a 1000 ml volumetric containing approximately 900 ml of distilled water. Bring to volume and mix.

Bismuth Nitrate Solution: Weigh 30.0 g of bismuth nitrate, $Bi(NO_3)_3$ and dissolve in a 2 liter beaker containing 100 ml of distilled water. While stirring slowly add 250 ml of glacial acetic acid. Stir until dissolve. Dilute to 1000 ml with distilled water.

Sulfuric Acid, 1:1: Slowly add 500 ml of concentrated sulfuric acid, H_2SO_4, into 500 ml of distilled water. CAUTION: this is an exothermic reaction which will create a lot of heat.

Magnesium Chloride: Weigh 510.0 grams of magnesium chloride, $MgCl_2$ $6H_2O$, and dissolve in a 1000 ml volumetric flask containing approximately 700 ml of distilled water. Bring to volume using distilled water and mix.

Sulfamic Acid: Weigh 40.0 grams of sulfamic acid and dissolve in a 1000 ml volumetric flask containing 800 ml of distilled water. Bring to volume with distilled water and mix.

If using the automated distiller, prepare the following reagent:

Distillation Reagent: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water, mix, and dilute to one liter with distilled water.

Prepare the following reagents for the Auto Analyzer:

Phosphate Buffer, pH 5.2: Weigh 13.6 grams of potassium dihydrogen phosphate and 0.28 grams of disodium phosphate and dissolve in a 1000 ml volumetric containing 800 ml of distilled water. Dilute to volume with distilled water and mix.

Chloramine-T: Weigh 2.0 grams of chloramine-T and dissolve in a 500 ml volumetric flask containing 400 ml of distilled water. Bring to volume with distilled water and mix. Refrigerate until ready to use.

Pyridine Barbituric Acid Reagent: Weigh 15 grams of barbituric acid and place in a one liter beaker. Wash the sides of the beaker with about 100 ml of distilled water. Add 75 ml of pyridine and mix. Add 15 ml of concentration HCl and mix. Cool to room temperature. Dilute to about 900 ml with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to a one liter flask and dilute to the mark. Solution is good for six months if stored in a cool dark place.

Sodium Hydroxide, 1 N: Weigh 40 grams of NaOH and dissolve in a one liter flask containing approximately 700 ml of distilled water. Bring to volume with distilled water and mix.

Standards

Stock Cyanide Solution, 100 mg/l: Weigh 0.2510 grams of potassium cyanide, KCN, and 2 grams of NaOH and dissolve in a 1000 ml volumetric flask containing 800 ml of distilled water. Add 2 ml of 1 N NaOH to preserve. Bring to volume with distilled water and mix.

Intermediate Standard Solution, 10 mg/l: Pipet 10.0 ml of Stock Cyanide Solution into a 100 ml volumetric flask containing 70 ml of distilled water. Add 2 ml of 1 N NaOH to preserve. Bring to volume with distilled water and mix.

Intermediate Standard Solution, 1.0 mg/l: Pipet 10.0 ml of 10 mg/l Intermediate Standard Solution into a 100 ml volumetric flask containing 70 ml of distilled water. Add 2 ml of 1 N NaOH to preserve. Bring to volume with distilled water and mix.

Working Calibration Standards: Prepare the working calibration standards by adding the appropriate concentration and amount of the intermediate standard solution as indicated in table 1 to a 100 ml volumetric flask containing 2 ml of 1 N NaOH as a preservative.

Table 1. Working Calibration Standards

Intermediate Standard Concentration	Volume of Standard Added	Final Volume	Final Concentration
Blank	-	-	0.00 mg/l
1.0 mg/l	1.0 ml	100 ml	0.01 mg/l
1.0 mg/l	3.0 ml	100 ml	0.03 mg/l
1.0 mg/l	5.0 ml	100 ml	0.05 mg/l
1.0 mg/l	10.0 ml	100 ml	0.10 mg/l
10 mg/l	2.0 ml	100 ml	0.20 mg/l
10 mg/l	3.0 ml	100 ml	0.30 mg/l

Sample Preparation - Manual Distillation

1. Measure 250 ml of sample if liquid or 10 grams of sample if it is a solid. Place into the 500 ml round bottom flask.

2. Pipet 25.0 ml of 0.1 n NaOH into the impinger (absorbing tube).

3. Connect the round bottom, impinger and condenser as given in Figure 2.

4. Turn on the vacuum and water. Adjust the vacuum source so that approximately two bubbles of air per second enter the flask through the air inlet tube.

5. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample by adding 50 ml of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to the addition of sulfuric acid.

6. If samples are suspected to contain nitrate and/or nitrite, add 50 ml of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to the addition of sulfuric acid.

7. Slowly add 50 ml of 1:1 Sulfuric Acid through the air inlet tube.

8. Rinse tube with distilled water and allow the airflow to mix the flask contents for 3 minutes.

9. Pour 20 ml of magnesium chloride into the air inlet and wash down with a stream of distilled water.

10. Heat the solution to boiling.

11. Reflux for 1 hour.

12. After one hour, turn off the heat but continue the airflow for at least 15 minutes.

13. After the cooling the boiling flask, disconnect the impinger and close of the vacuum source.

14. Drain the solution from the impinger into 50 ml glass sample container and label.

Sample Analysis

1. Set up the manifold as shown in Figure 1 in a hood or a ventilated area.

2. If samples were not manually distilled, set the temperature of the heating bath at 150 °C.

3. Place the 570 nm filter and the 15 mm flow cell into the colorimeter.

4. Place all lines into the distilled water and turn on the ON/OFF switch located on the pump.

5. Turn on the strip chart recorder. The recorder settings should be:
   Rate: 1 cm/sec
   Volts: 0.1 V
   Switch set to VARIABLE

6. Allow the baseline to stabilize. With the distilled water pumping through all lines, adjust the baseline to zero using the BASELINE dial and set the STD CAL dial to 1.00.

7. If the sample was not prepared by manual distillation, check the temperature of the heating bath. It should be 150 °C.

8. Place all lines in the correct reagents. (If the sample was distilled manually, bypass the automated distillation unit). Allow baseline to stabilize (10 min) and record how many chart units the reagent raised the baseline. Enter this on "Reagent Blank Response:___" on the bench sheet. An example bench sheet is given in Figure 3.

9. Set baseline at 5 chart units using the BASELINE dial.

10. Set up auto sampler:
    a. The first position should be the highest standard followed by a blank or two.
    b. The working standards (calibration standards) are then placed on in increasing concentration.
    c. A blank or two is placed on between each sample and standard so that there is sufficient rinsing that the response returns to the baseline.
    d. Place all cups on the autosampler tray.

11. Press the red POWER button on the autosampler tray to begin analysis.

12. When the high standard in the first position is at its peak adjust the STD CAL so it reads approximately 95 chart units. (To increase units turn the STD CAL clockwise).

13. If no problems occur, allow the remainder of the analysis run to continue. If problems do occur, the red POWER switch will stop the autosampler.

14. After the run, identify each peak with the corresponding number on the bench sheet. Measure the peak height in chart units and record on the bench sheet.

15. Enter ATOAN in the LIMS computer system in order to calculate results and automatically transfer data. ATOAN plots peak height vs. concentration to obtain a linear or quadratic curve. The peak height from the sample and quality control is entered into the curve's equation in order to obtain concentration of cyanide in the sample. A print out of data from ATOAN is generated after the data is automatically transferred. This along with the bench sheet and strip chart recording are attached together and stored.

Quality Control

Check Standard: A check standard is run initially, after every twenty samples, and at the end of the analytical run. The percent recovery must be within the established limits or within the ± 10 % default limit, whichever is smaller.

Duplicates: Duplicates are completed at a minimum of 10% or at least once per analytical batch whichever is greater. The percent difference must be within the established limits. If no limits exist use 25% as a default control limit.

Matrix Spike: Matrix spikes are completed at a minimum of 5 % or at least once per analytical batch whichever is greater. The percent recovery must be within the established limits. If no limits exist, use 75-125% as a default limit.

Blanks: Blanks are completed at a 5% frequency.

Calibration: The calibration curve must contain a minimum of four standards and a blank for a linear curve and seven standards and a blank for a quadratic curve. The minimum correlation coefficient for a linear curve is 0.9995 and for a quadratic is 0.99995 to be acceptable. If the correlation coefficient is less than this value but each standard has a percent variance less than 10%, the curve is also acceptable. Two standards for the calibration curve should be manually distilled if the samples being analyzed are manually distilled.

Quantitation Limit: The quantitation limit used is low standard. An Method Detection Limit study is completed periodically to ensure that the quantitation limit is appropriate.

Corrective Action Reports (CAR): CARs are filed whenever quality control parameters have exceeded their acceptance limits and sample data is effected. Also CARs are filed if any instrument problems have effected data.

Routine Maintenance

Every Analysis Day:
- Preform general clean-up and inspection
- Check all tubing for loose connections and leaks
- Wash out the system as recommended in the applicable method

Every Seven Days or After 40 Hours of Operation:
- Thoroughly wipe clean all surfaces with a damp cloth
- Clean wash reservoir with mild detergent
- Check sample tubing and discard if dirty or clogged
- Change dialyzer membrane, if applicable
- Remove and lubricate the side-rails on the pump

Every Two Weeks or After 80 Hours of Operation:
- Flush recorder pen
- Clean pump rollers and platen using cloth moistened with solvent, if necessary.

Once a Month:
- Clean colorimeter optical system
- Clean colorimeter lamp and socket contacts, if necessary
- Clean sample probe with wire stylet
- Lubricate pump as per instructions on decal mounted on underside of platen cover.
- Change pump tubes

Every Three Months:	Replace sample tubing Clean and lubricate recorder slidewire, if necessary Grease drive gears
Every Six Months:	Replace CO2 absorbent cartridge, if applicable
Every Twelve Months:	Oil sampler motor Lubricate sampler gears

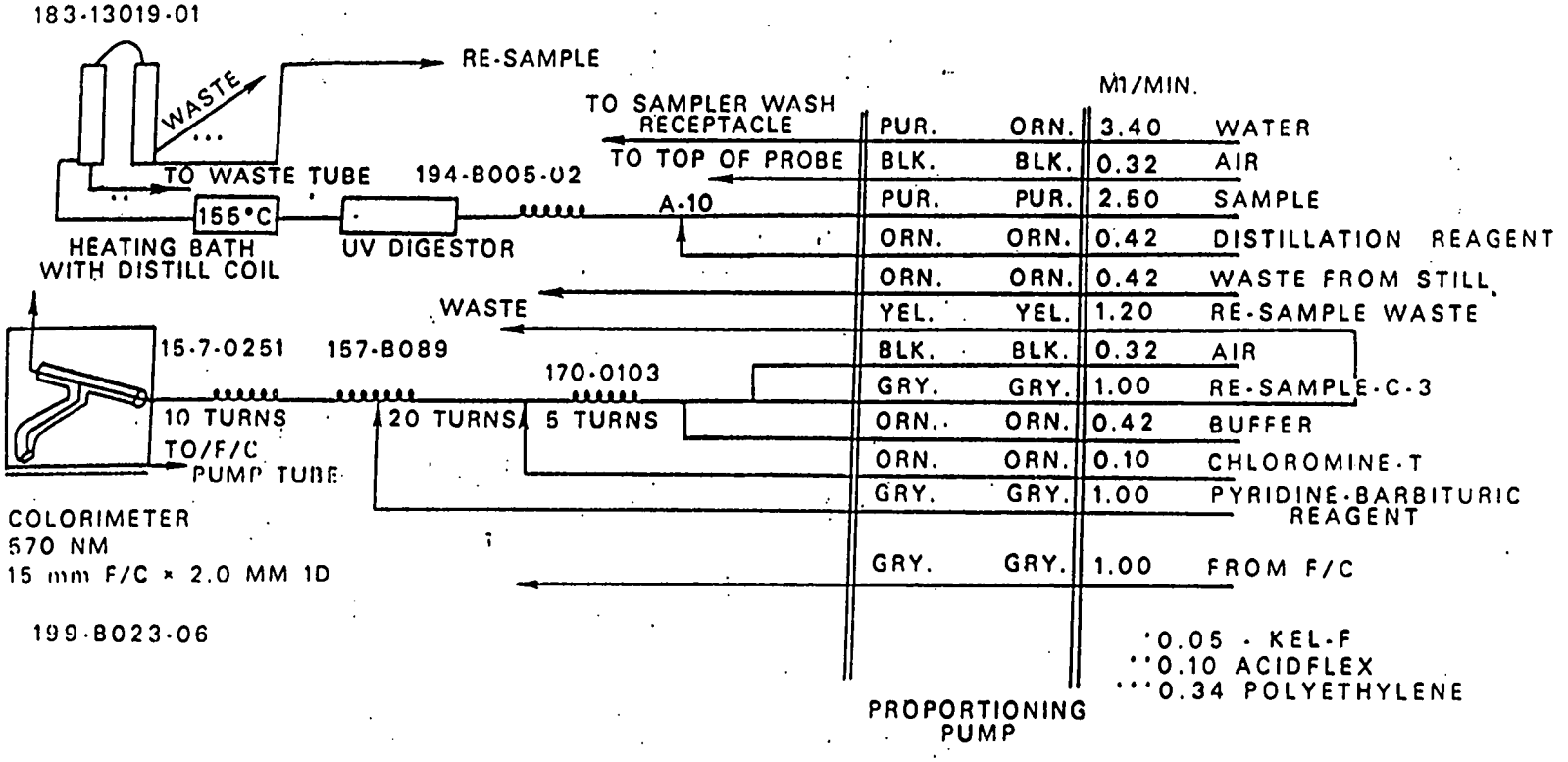


FIGURE 1. CYANIDE MANIFOLD AA11

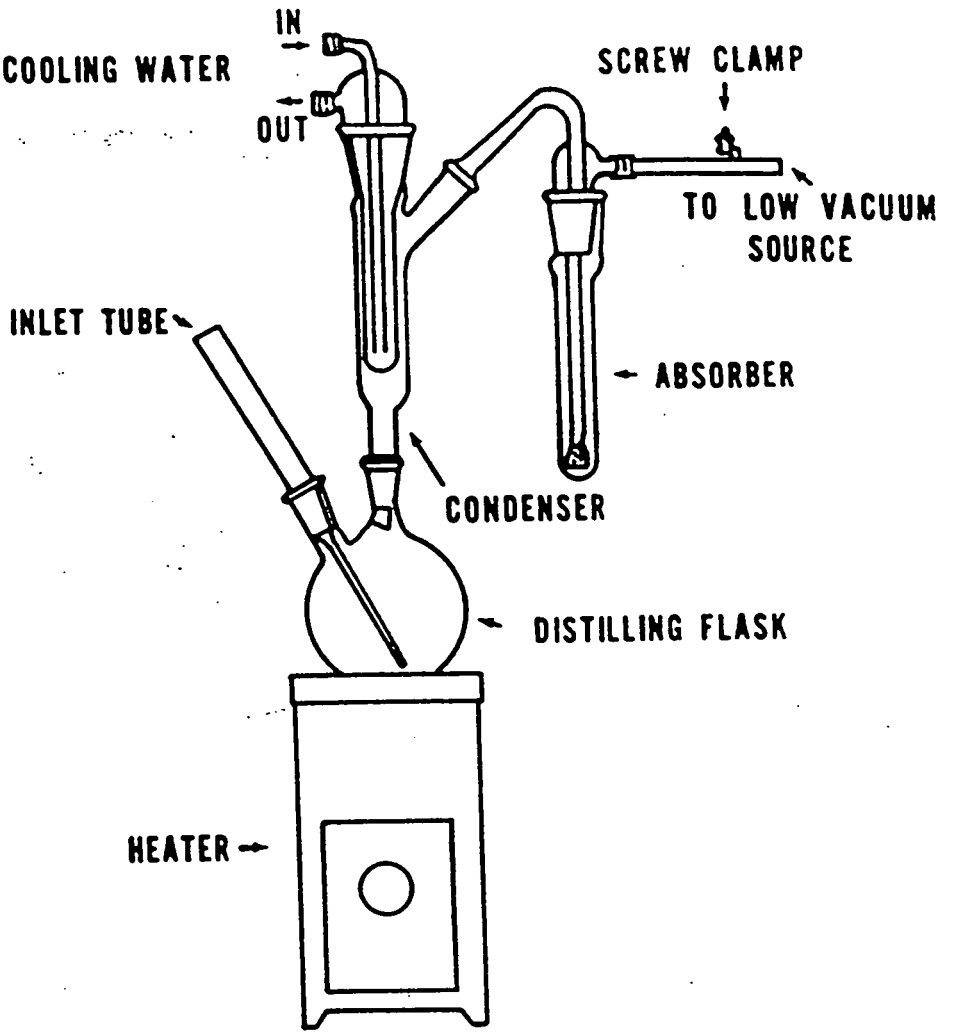


Figure 2. Cyanide distillation apparatus.

ENVIROSCAN CORP. BENCH SHEET
for
TOTAL CYANIDE & AMENABLE CYANIDE

Methods: Total CN EPA 335.3
Amenable CN EPA 335.1

Date: _____/_____/_____

Analyst:_____

Wavelength: 570 nm

Reagent Blank Response: _____

Flow Cell: 15 mm

Standard Cal.: _____

Regression Equation:
Linear: Conc. = [(Response - B)/A] x dilution factor
Quad.: Conc. = (A x Resp. + B x $Resp^2$ + C x $Resp^3$ + D) x dil. factor

STANDARD CURVE:

Concentration mg/l	Response Peak Height	Concentration mg/l	Response Peak Height
Blank			

QUALITY CONTROL

ECK STANDARDS

Analysis (circle)	Theor. Value mg/l	Observ. Value mg/l	% Recovery	Plot
CN / CN-A				
CN / CN-A				
CN / CN-A				
CN / CN-A				
CN / CN-A				

DUPLICATES

Analysis (circle)	Analytical #	Dup. 1 mg/l	Dup. 2 mg/l	% Difference	Plot
CN / CN-A					
CN / CN-A					
CN / CN-A					
CN / CN-A					

SPIKES

Analysis (circle)	Analytical #	Sample Result	Spike Conc., mg/l	Sample + Spike Conc., mg/l	% Rec
CN / CN-A					
CN / CN-A					

Analytical #	Conc. of Std. added	Volume of Std. added	Final Vol. of Sample + Spike

ENVIROSCAN CORP. BENCH SHEET
for
TOTAL CYANIDE BY AUTO-ANALYZER

RAY # _____ DATE: ____/____/____

PAGE ____ OF ____

NO.	SAMPLE #	DILUTION	DILUTION FACTOR	PEAK HEIGHT	PROJECT #
1	_____	_____	_____	_____	___-_____
	Blank				
2	_____	_____	_____	_____	___-_____
	Blank				
3	_____	_____	_____	_____	___-_____
	Blank				
4	_____	_____	_____	_____	___-_____
	Blank				
5	_____	_____	_____	_____	___-_____
	Blank				
6	_____	_____	_____	_____	___-_____
	Blank				
7	_____	_____	_____	_____	___-_____
	Blank				
8	_____	_____	_____	_____	___-_____
	Blank				
9	_____	_____	_____	_____	___-_____
	Blank				
10	_____	_____	_____	_____	___-_____
	Blank				
11	_____	_____	_____	_____	___-_____
	Blank				
12	_____	_____	_____	_____	___-_____
	Blank				
13	_____	_____	_____	_____	___-_____
	Blank				
14	_____	_____	_____	_____	___-_____
	Blank				
15	_____	_____	_____	_____	___-_____
	Blank				
16	_____	_____	_____	_____	___-_____
	Blank				
17	_____	_____	_____	_____	___-_____
	Blank				
18	_____	_____	_____	_____	___-_____
	Blank				
19	_____	_____	_____	_____	___-_____
	Blank				
20	_____	_____	_____	_____	___-_____

QC: Duplicate: completed at minimum frequency of 10%. One duplicate must be completed if less than ten samples are analyzed.
Spikes: completed at a minimum frequency of 5%. One spike must be completed if less than twenty samples are analyzed.
Check Standards: completed initially, after every 20 samples and at the end of the run.

On-site VOC Analysis of Soil Gas Samples

Method ES-521

Determination of: VOC's in soil gas samples using Envirosacn's Mobile Laboratory.

Method: Gas Chromatography (GC) method for rapid on-site analysis of VOC's in soil gas samples.

Reagents: None required

Instrument: HNU, Model 321 Gas Chromatograph with a 30 meter, wide-bore, capillary column and PID-FID or PID-ECD detectors operated in series (in Mobile Laboratory).

References: EPA Methods 601/602, 8000, 8010/8020, & 8021.

Issued: March 1993

Revised: July 1993

DISCUSSION

This method is intended for use in applications where rapid, on-site analyses of soil gas samples are required for the volatile organic contaminants most often encountered in soil gas surveys. The "standard" list of soil gas VOC's typically analyzed for and their respective detection limits are contained in the table at the end of this document.

INTERFERENCES

Although this GC method is capable of detecting a large number of volatile organic compounds, only those having relatively low water solubilities and relatively high vapor pressures are targeted for analysis. VOC's that do not have these characteristics, are generally not well suited for detection or quantitation by soil gas testing.

Additional method limitations are summarized below:

- Since soil gas samples typically contain high concentrations of water vapor, the PID response may be suppressed early in the chromatogram. This results in the loss of early eluting peaks such as vinyl chloride on the PID detector. If the concentration of these early eluters is sufficiently high, they may be detectable on the FID or ECD detectors.

- To accommodate rapid (approximately 15 minute) GC run times, a 30 meter wide bore capillary column and temperature programming above 45°C is specified. Although good chromatography is achieved for most VOC compounds, these GC operating conditions do not allow effective detection or quantitation of compounds eluting prior to 1,1-Dichloroethylene.

- Whenever possible, samples should be analyzed sequentially from those having low-level contamination to those having higher contamination to minimize sample syringe carry-over. The sample syringe should be rinsed with methanol followed by air flushing between samples if high soil gas contamination is encountered. A syringe blank should be considered if sample carry-over is suspected.

SAMPLE PRESERVATION AND HOLDING TIME

Soil gas samples collected in a sampling syringe should be analyzed as quickly as possible to minimize the potential loss of VOC's. Generally a soil gas syringe sample should be analyzed within 30 minutes of collection.

REAGENTS

Chemical reagents are not required for this method. Reagent grade water and purge & trap grade methanol, however, should be available to clean sample syringes if necessary.

STANDARDS

A GC calibration curve for each compound of interest should be prepared using a minimum of five standard concentrations. Gaseous calibration standards should be used as the matrix being analyzed (i.e. soil gas) is also a gas / vapor. Commonly used multi-compound standards prepared in methanol are not well suited for GC calibration for soil gas analysis as the methanol tends to suppress the PID detector and over-whelm the FID detector. To eliminate the problems associated with methanol standards, the desired compounds in the calibration mixture are prepared gravimetrically using pure (neat) compounds. This neat compound "cocktail" is then used to prepare in-house gas standards as described below. The concentration range of the gas standards should span the working range of the detector (i.e. about 0.2 to 200 ng for the PID and about 2.0 to 500 ng for the FID). Seven gaseous calibration standards (at approximately 0.4, 1.2, 4.4, 13.2, 48.4, 145, and 532 ppb) are prepared and a minimum of five are used for calibration.

The standards should be prepared as follows:

- Obtain an appropriate number of clean 1,000 ml. amber glass bottles with Teflon lined septa caps.

- To each bottle add one clean 3/8 inch diameter Teflon bead and purge the bottle with zero air or nitrogen.

- Using an appropriate size syringe, add the desired volume of liquid neat compound cocktail by opening one of the bottles, injecting the neat compound mixture and quickly closing the cap tightly. This bottle should be allowed to equilibrate in a warm place for at least 30 minutes with occasional mixing facilitated by the Teflon bead inside the bottle. After equilibration, the gas standard "stock solution" inside this bottle can be used full strength for the higher calibration concentrations or may be diluted in another glass bottle, as described below, to prepare standards of lower concentrations.

- To prepare a dilution from the "stock solution" bottle, the following procedure should be used:

    * All gas to be added or removed from the calibration gas preparation bottles must be done using an appropriately sized gas tight syringe through the septum in the cap. The calibration gas preparation bottle caps should remain firmly closed at all times during the calibration standard preparation process.

* Calculate the volume of "stock solution" needed to make the desired dilution.

* Using an appropriate sized syringe, remove a volume of gas from the bottle in which the dilution will be made equal to the volume of "stock solution" gas that will be added. For example; if 100 mls of "stock solution" will be diluted in a 1 liter bottle, exactly 100 mls. should be removed from the dilution bottle before the "stock solution" is added. This insures that the gas pressure inside the bottle remains constant.

* Before the desired volume of gas is removed from the "stock solution" bottle, an equal volume of zero air or nitrogen should be added and the new concentration calculated. For example; if 100 mls. of "stock solution" is needed to make the desired dilution, exactly 100 mls. of zero air or nitrogen should be injected into the "stock solution" bottle and the new concentration calculated by:

$$\frac{\mu g \text{ in "stock soln."}}{1.1 \text{ liters}} = \text{New Concentration } (\mu g/l)$$

This bottle should be thoroughly mixed before the desired volume of "stock solution" is removed.

* After the pressurized "stock solution" bottle is thoroughly mixed, the desired volume should be removed and immediately injected into the dilution bottle that was previously evacuated as described above.

* Upon completion of the above procedure, both the "stock solution" bottle and the dilution bottle should be at atmospheric pressure.

* The procedure described above is not necessary if less than 40 mls. of gas are removed. Volumes totaling less than 40 mls. will not have a significant effect on the pressure or concentration in the sealed one-liter calibration standard bottles.

- Gaseous calibration standards prepared in one-liter amber glass bottles should not be stored for periods exceeding 3 or 4 days.

- Standard injections are performed by simply drawing a 2.5 to 5 ml. volume from the calibration standard bottle using a gas tight syringe and injecting the entire syringe volume into the GC sample loop. The sample loop should then be injected immediately. Approximately eight 5 ml. injections can be made from a single calibration gas bottle without changing the concentration significantly.

SAMPLE PREPARATION

There are no special sample preparation procedures required for soil gas samples other than possibly direct injecting a smaller volume of soil gas if the sample is highly contaminated rather than using the sample loop. Direct injecting sample volumes of less than 10 μl. should not be attempted as it is very difficult to do this quantitatively.

Generally soil gas samples should be collected in 50 ml. glass syringes. Immediately after collection the syringe needle should be plugged using a GC septa (edge-wise). The soil gas sample should be analyzed as quickly as possible to minimize loss of VOC's.

ANALYSIS PROCEDURE

1. When arriving at a project site, it is desirable to run the GC at an elevated temperature for 1 or 2 hours before starting analysis. Set injector / detector temperature at 220°C and the oven at 200°C.
2. Enter the desired temperature program, turn on the PID lamp and ignite the FID. The detectors should be allowed to stabilize for about one hour prior to running analysis.
3. Run a system blank by cycling the sample loop and initiating data acquisition. If a clean base line is obtained, proceed to the next step. If the base line is not normal, run another system blank. If the second system blank base line is not acceptable, determine what is causing the problem and take corrective action.
4. Run a check standard containing at least one early eluter, one mid-range eluter, and one late eluter. All check standards should be run using the sample loop. If the check standard compounds are within $\pm$30% of the expected value, the GC may be considered in calibration. If the check standard compounds are not within $\pm$30%, run a second check standard. If the second check standard is still outside acceptable QA/QC limits, a new calibration may be necessary.
5. When a normal base line is established and check standard compounds are with acceptable limits, sample analysis may begin.
6. The (1 ml.) sample loop should be used as much as possible for normal sample analysis. If high soil gas contamination is encountered, direct injecting sample volumes of less than 1 ml. may be necessary. Direct injecting volumes of less than 10 μl., however, are not recommended.

QUALITY CONTROL

Minimum QA/QC requirements for on-site soil gas analysis in the Mobile Lab are as follows:

- GC calibration using at least five standards concentrations per target compound in accordance with EPA Method 8000. This calibration should be done prior to mobilizing to the project site. If on-site re-calibration is necessary, a minimum of three standards concentrations per target compound should be run.

- QA/QC control limits established in EPA Method 8000 are generally applicable to soil gas analysis in the Mobile Laboratory. However, since gas standards are being used for calibration, the acceptable range for check standards has been increased from ±15% (EPA Method 8000) to ±30%. This QA/QC limit increase is considered appropriate as compound concentrations in gas standards and gas samples tend to be more variable than in liquids.

- At least one system blank at the beginning of each field day to establish a normal / clean base line. A system blank at the end of each field day is also recommended.

- At least one check standard at the beginning of each field day to determine if the GC is in calibration. Another check standard at the end of each field day is highly recommended. Check standard compounds should be within ±30% of the predicted value based on the calibration curve being used.

- At least one duplicate soil gas sample per field day or 20 samples should be analyzed to determine if analytical results are reproducible.

- Sample syringe blanks should be run if high soil gas contamination is encountered. The syringe blank should be run after the syringe has been completely flushed or cleaned to determine if the decontamination procedure is sufficient to prevent carry-over from sample to sample.

- Field or equipment blanks are recommended if on-site decontamination of soil gas sampling equipment is required or if contaminated sampling equipment is suspected.

- The above QA/QC procedures are considered the minimum required, additional QA/QC may be required on a project specific bases.

LIST OF "STANDARD" SOIL GAS VOC'S AND DETECTION LIMITS

Compound	Det. Limi(μg/l)		IP (eV)	Chk Stnd Conc (μg/l)	Retention Time	Comments
	PID	FID				
1,1-Dichloroethylene	0.2	1.5	–	20	1:40	
Methylene Chloride	ND	~2.0	–	(20)	1:53	
trans 1,2- Dichloroethylene	0.1	~1.0	9.66	20	2:04	
1,1-Dichloroethane	ND	2.4	–	(20)	2:19	
cis 1,2-Dichloroethylene	0.1	1.0	9.65	20	2:47	
1,1,1-Trichloroethane	ND	2.5	–	20	3:22	
Carbon Tetrachloride	ND	TBD	–	20	–	low resp/co-elutes w/benzene
1,2-Dichloroethane	ND	~2.0	11.12	20	3:52	co-elutes w/benzene
Benzene	0.1	~1.0	9.25	20	3:52	co-elutes w/12DCA
Trichloroethylene	0.1	~2.0	9.45	20	4:45	
Bromodichloromethane	ND	~4.0	–	20	5:21	
Toluene	0.2	~1.0	8.82	20	6:48	
1,1,2-Trichloroethane	ND	~3.0	–	20	7:24	
Tetrachloroethylene	~0.6	~1.5	9.32	20	7:57	
Dibromochloromethane	ND	~4.0	–	20	8:15	
Chlorobenzene	~0.7	~1.0	9.07	20	9:41	
Ethylbenzene	~1.5	~2.0	8.76	20	9:59	
m-Xylene	~1.0	~2.0	8.56	20	10:14	
o-Xylene	~1.2	~2.0	8.56	20	11:18	
Bromoform	ND	~4.0	–	20	11:56	
1,1,2,2-Tetrachloroethane	ND	~2.0	–	20	12:29	
1,3-Dichlorobenzene	~3.6	~4.0	9.12	20	14:23	
1,4-Dichlorobenzene	~3.1	~4.0	8.94	20	14:37	
1,2-Dichlorobenzene	~3.0	~4.0	9.07	20	15:20	
Methyl-t-butyl ether	~1.0	~2.0	–	–	1:59	
1,2,4-Trimethylbenzene	~1.0	~2.0	–	–	13:36	
1,3,5-Trimethylbenzene	~1.0	~2.0	–	–	14:18	

ND = Not detected by this detector
TBD = To be determined, but greater than 2.0
( ) = Check Standard contains methanol which masks these compounds.

Soil Gas Sampling Procedure

SOP ES-524

Clean soil gas probes are used at each sample point. Before mobilizing to the project site, all probes and sampling equipment are decontaminated in the laboratory by washing thoroughly in a hot water/detergent solution followed by rinsing with hot tap water. When necessary, probes are also cleaned in the field by washing with a water/detergent solution and rinsing with tap water. Equipment is allowed to air dry prior to use in the field.

After driving the soil gas probe to the desired sampling depth, the probe is pulled back four to six inches, releasing the expendable probe tip and opening a cavity from which the soil gas is drawn. A sampling cap with a stainless steel ball valve is installed on the probe and a 12 VDC vacuum pump is connected to the valve port via silicone tubing. The vacuum pump is turned on and the probe is purged by removing five to six internal probe volumes of soil gas. Purge volume is measured at the discharge of the vacuum pump using a dry gas test meter. Vacuum developed during purging is monitored and recorded on field log sheets as an indication of relative gas/air permeability of the soil.

After the soil probe is purged, two 50-milliliter glass syringes is used to collect the soil gas samples. With the vacuum pump running, the syringe needle is inserted through the silicone tubing adjacent to the sampling valve. Three syringe volumes are drawn and wasted before the sample is collected for analysis. Collection of a representative soil gas sample is ensured by allowing the vacuum pump to run during sample collection. Heating the syringe after use, flushing at least 20 times in ambient air, and purging with soil gas helps prevent contaminant carryover between samples. If high VOC concentrations are encountered in the soil gas samples, the sampling syringes are flushed with reagent grade methanol to minimize carry-over from sample to sample.

If adsorption tube samples are being collected, a third syringe (100 milliliters) is also collected. The contents of the syringe are injected slowly into an adsorption tube. Immediately after sample injection, the adsorption tube is sealed using gas tight storage caps, recorded on the field log sheet and placed in a laboratory desiccator containing activated carbon. The gas tight storage caps are placed on the adsorption tubes in the laboratory immediately after they are baked out and are not removed until the soil gas sample is ready for injection in the field. Unexposed adsorption tubes are stored in a separate laboratory desiccator also containing activated carbon.

For a preliminary field determination of the degree of contamination, one syringe-volume of soil gas (50 milliliters) is injected into an HNU Photoionization Analyzer with an 10.2 eV lamp (calibrated on 10.1 ppm Benzene in air calibration gas). The results of field screening are used to determine the appropriate attenuation for GC analysis.

Soil Gas Sampling Procedure
(Continued)

Data collected while sampling are recorded on field log sheets provided by Enviroscan. The field log sheets also serve as a sample chain-of-custody record.

Prior to removing the probe after sampling, a thermocouple can be inserted to the bottom of the probe and a soil temperature taken, if requested. After probe removal, holes are filled with granular bentonite.

Trip blanks, syringe blanks, ambient air blanks, equipment blanks, and duplicate samples are taken and analyzed as appropriate to document effectiveness of field QA/QC procedures.

Although the above procedures are considered "standard", site and project specific factors may require sampling procedures other than those stated above.

Revised: July 1993

SOP #111

Standard Operating Procedure for:

Sample Receiving

Scope/Purpose

To provide a standard procedure for sample receiving and storage.

Reagent/Special Equipment

Bates Numbering Machine

Speciality Tapes: Refrigerate, Non-hazardous, Hazardous, Do in Hood, Limited Sample, Cancer Suspect Agent, Special Handling

References

N/A

Issued: February 1990
Revised:

SOP #111

Procedure for Sample Receiving

Samples are received in several areas such as the front desk, mailroom, and from the shipping and receiving department but the final destination is the log-in area in the inorganic lab. Once the packages or coolers reach log-in the following procedure is to be followed to insure that the customer receives the analyses requested from the correct samples and all paperwork is accurately and correctly filled out on all forms so that information can be transferred to the LIMS program.

Guidelines

1. When samples are received in a package or a cooler, the seals must be checked to make sure the container was not opened previously. (If samples are dropped off at the front desk they are usually not in sealed containers.)

2. The seals are then broken and the samples and paperwork are removed from the shipping container.

3. Make sure sample bottles are closely inspected for cracks, breakage or leakage. If broken, leaking or inappropriate bottles are found it should be noted on the chain of custody or analysis request form if a chain of custody was not included in the shipment.

4. Next check the paperwork with the chain of custody and with the samples to make sure everything agrees.

   a. If everything is in agreement proceed to step 5.

   b. If a discrepancy is found the client should be contacted and all decisions recorded on the chain of custody or whatever paperwork is provided. At this time if samples were broken in shipment the client is notified. The client may want to re-sample the broken samples or just continue with the remaining samples. If inappropriate bottles are used, for instance plastic versus glass, or insufficient sample to complete an analysis request, or wrong preservative, the client is told and they make the decision as to what should be done. This contact and any obtained information is noted on the paperwork.

c. Sometimes there isn't any accompanying paperwork. Clients may have just written on the sample label what they want analyzed. If this is not the case check to see if an in-house memo is on the log-in work bench. If no information can be obtained the client must be called.

d. At times some of the samples need to be held until clients decide what is needed. In that case the samples are put in refrigerator C and information about the samples is entered into a holding journal.

5. Sign the chain of custody and note the date and time of receipt. Complete any other information required on the chain of custody by the receiving lab.

6. Check for quote sheets or any in-house information on the samples or project.

7. If the samples were received in a cooler belonging to the client, fill out the proper shipping forms and labels returning the cooler to the client. If the cooler belongs to Enviroscan:

   a. Mark the returned date on our cooler check in and out list. Also look in the Sample-Kit book and pull the appropriate sheet. There may also be information about the samples on this form.

   b. Return the cooler to the storeroom

8. Fill out the Enviroscan, Inc. Analytical Request Form. See attachment. Make sure all information is complete and accurate. Check to make sure due dates are entered on this form if available.

9. After the Request Form is completed, a label(s) and the corresponding Analytical No. location on the bottom of the form is stamped with a number by using the Bates Numbering Machine for each sample. Apply the stamped label(s) to the corresonding sample(s).

   An example of the numbered label:

The first two numbers always refer to the shelf location number. The remaining five numbers are the unique sample number.

10. The sample numbers should be written on the paperwork (chain of custody or any correspondence sent to Enviroscan by the client). Place this paperwork in the appropriate file folder in the log-in desk. Set the Enviroscan Analytical Request Form in the brown basket on top of the log-in desk.

11. Once the numbers are on the bottles, they should be labeled with the specialty tapes for noting precautions. (Refrigerate, Non-hazardous, Hazardous, Limited Sample, Cancer Suspect Agent, Do in Hood, Special Handling).

12. The samples are then taken to the appropriate lab (organic or inorganic) for proper storage in refrigerators or on non-refrigerated shelves until work can be started. The samples are placed in these areas by using the shelf location number.

13. The sample information is then entered into the Laboratory Information Mangement System (LIMS). See LIMS Manual page 15-19.

ENVIROSCAN, INC. ANALYTICAL REQUEST FORM

ODE: _____
USTOMER: _____
REC'D DATE: ___/___/___
UST. PROJ. No.: _____
UE DATE: ___/___/___
NVIROSCAN PROJ. No.: _____
QUOTE: _____
OCATION: _____
RECAUTIONS: _____
Contact: _____ Phone: _____

Del'v: Hand Comm.
Ship. Cont. OK? Y N N/A
Rec'd Refrig.? Y N N/A
Ship. form OK? Y N N/A
Seals OK? Y N N/A
Samples leaking? Y N N/A
COC OK? Y N N/A
Comments: _____

Sample ID:							
Sample type:							
Sample date:							
Test	Est.	Test	Est.	Test	Est.	Test	Est.

ANALYTICAL No. _____

oject Chemist: _____

REQUEST FOR SERVICES

303 W. MILITARY RD. ROTHSCHILD, WI 54474 1-800-338-SCAN

CLIENT INFORMATION

Name:
Company:
Address:
Phone: ( )
P.O. # / Project #:
Quote / Reference #:
Note: Terms and conditions printed on back apply.

Turnaround Time
- ☐ Normal
- ☐ Rush

Date Needed
(Preapproved by Lab)

Sample Type *(Check all that apply)*
- ☐ Groundwater
- ☐ Wastewater
- ☐ Soil
- ☐ Solid Waste
- ☐ Oil
- ☐ Other

Sample Handling
- ☐ Nonhazardous
- ☐ Flammable
- ☐ Skin Irritant
- ☐ Highly Toxic
- ☐ Other *(specify)*
- ☐ Refrigerate
- ☐ Work In Hood
- ☐ Wear Gloves

ANALYTICAL REQUESTS
(use separate sheet if necessary)

LAB USE ONLY	DATE	TIME	No. of Containers COMP	No. of Containers GRAB	SAMPLE ID						REMARKS

CHAIN OF CUSTODY RECORD

SAMPLERS: *(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

Del'y: Hand Comm
Ship. Cont. OK? Y N N/A
Rec'd Refrig.? Y N N/A
Seals OK? Y N N/A
Samples leaking? Y N N/A
Comments:

MPLING INSTRUCTIONS

Date Rec'd___/___/___

SAMPLE RECEIPT REPORT

CLIENT: _____

Anal. No.: _____ to _____

Reference Code	Explanation
1.	Sample(s) received at_____°C which is above the EPA protocol of 4 °C.
2.	Samples received without appropriate paperwork. Explain _____
3.	VOC vial(s) received with headspace contrary to EPA protocol. Explain_____
4.	Sample(s) received in bottles not furnished by Enviroscan. Preservation method, if used, are unknown.
5.	Sample(s) not properly preserved per EPA protocol for the following: _____
6.	Sample(s) not field filtered. Lab filtered upon receipt.
7.	Sample(s) received beyond EPA holding time for: _____
8.	Sample date/time not supplied by client. Actual holding time unknown.
9.	Insufficient sample size to complete analysis or obtain required detection limit.
10	Other: _____

STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIPT AND CHAIN-OF-CUSTODY

1.0 PURPOSE

This document presents the procedures in use at ENCOTEC for identifying and maintaining control of sent to the company for analysis. The document covers sample receipt and custody.

2.0 SAMPLE RECEIPT

2.1 Delivery of Samples by Contract Courier

Samples are generally delivered to ENCOTEC by an overnight carrier (Federal Express, Airborne, or UPS). The Log-In Technician on duty signs for the shipment and is responsible for signing and dating the shipping receipt on the package. The Log-In Technician is also responsible for securing the unopened package in one of two walk-in coolers and notifying the Sample Custodian of its arrival. (Samples are never left unrefrigerated for more than the time required to actually log them in.) Upon notification, the Sample Custodian takes custody of the package. The package is opened under a hood and the Sample Custodian signs and dates the Chain-of-Custody contained within the package.

2.2 Delivery of Samples by Other Means

All samples which are not received by overnight courier are delivered by client or ENCOTEC field personnel. A properly completed Chain-of-Custody, signed and dated by the individual relinquishing custody of the samples, is required. ENCOTEC log-in personnel accept custody of the samples by signing, dating and indicating the time of receipt on the Chain-of-Custody form.

2.3 Chain-of-Custody

A Chain-of-Custody accompanies all delivered samples. The Sample Custodian ensures that the Chain-of-Custody contains the following information:

- Sample Collection Date/Time
- Field Sampler's Identification
- Requested Analyses
- Signature of the Delivery Individual
- Date of Delivery

- Preservation During Shipment
- Client Technical Contact

A copy of the Chain-of-Custody is provided to the person relinquishing the samples. The original chain-of-custody is retained by ENCOTEC and included if necessary as a part of the final data package. Occasionally, ENCOTEC Sample Support Group (SSG) personnel may retrieve samples directly from sampling crews on site. In this case, all procedures as discussed above are followed.

2.4 Sample Custodian

The designated Sample Custodian is notified whenever samples are delivered to the Log-In Technician on duty. The Sample Custodian will verify that the paperwork is in order and that the sample receipt date and times are correct. An ENCOTEC sample log-in sheet is then obtained and the sample log-in procedure is initiated. The following is a step by step chronology describing the sample log-in procedure. If any of the following conditions are not met, corrective measures are followed to rectify the problem in a timely manner.

3.0 SAMPLE LOG-IN PROCEDURE

3.1 The first step of the log-in procedure is to examine the shipping container(s) for the presence or absence of all custody seals, and note on the sample log-in form the condition of these seals. If the seals are not intact and legible, the result is duly noted on the form and the project manager is notified in writing. A copy of this notification is attached to the batch file.

3.2 Following the initial shipping container inspection, the sample shipping container(s) are moved to the hood area and opened by the custodian. The bottles contained within the shipping container are inspected for breakage.

3.2.1 If sample bottles have been broken in shipment, the shipping container(s) is(are) re-sealed immediately and placed under the log-in fume hood. The ENCOTEC Project Manager is notified. Further log-in activities will not occur until additional safety information is obtained from the shipper. After inspection of safety information, the Laboratory Support Group Leader will specify the appropriate safety requirements for further log-in activities. The contents of the shipping container(s) are removed, the

adsorbent is lab-packed (if considered hazardous) and the shipping container(s) is(are) decontaminated (if possible).

3.3 Enclosed sample documents are removed and information pertaining to these documents is recorded on the log-in sheet. Sample information includes:

- Presence/absence of Chain-of-Custody forms.
- Presence/absence of Request for Analysis forms.
- Presence/absence of bill of lading or other sample information documents.

The sample custodian signs the Chain-of-Custody document if all is present and the document agrees with the samples delivered. Before signing the Chain-of-Custody, the Sample Custodian will ensure that the information outlined in Section 2.3, above, is contained within the document.

3.4 The samples will be spread out on a bench and the bottles will be grouped by parameter. The samples are compared to the Chain-of-Custody to verify that the documentation is consistent. Discrepancies will be noted in detail on the Chain-of-Custody and on the various documentation forms. The Sample Custodian will check the physical condition of the samples. The following information will be noted on the Chain-of-Custody and/or the sample logbook:

- Cracked or broken container or cap
- Improper sample container
- Insufficient sample volume
- Improper bottle filling technique (headspace in volatiles, etc.)
- Improper preservation (no ice, improper preservative, etc.) - this will be verified by testing the sample with pH paper
- Missing, mis-marked, improper or unlabeled bottles
- Leaking bottles
- Custody seals broken or missing
- Chain-of-Custody or purchase order missing or illegible
- Disagreement of paperwork received with samples received
- Samples need to be divided for different analyses
- Samples need to be composited prior to analysis
- Samples contain hazardous substances or high concentrations of analytes

Discrepancies are noted in detail on the appropriate documentation forms by the Sample Custodian. This information is provided to the ENCOTEC Project Manager, who will discuss the problems with the client.

3.5 Once the assessment of the samples' condition has been completed and documented, a unique sequential ENCOTEC control number is assigned to each discreet sample. Each sample is entered in an interim database; all samples received from one client or site and assessed in one log-in session will be grouped in a batch and assigned a batch number.

3.5.1 The information entered as a part of each sample's record in the interim database includes the following:

- Client's identification for the sample
- Sampling date
- Sample matrix
- The ENCOTEC number assigned to the sample
- The analyses requested in the documentation arriving with the sample

3.5.2 The information entered for the batch of samples includes:

- Client identification and client job number
- Date of the sample receipt at ENCOTEC
- Batch number
- Sample Delivery Group (SDG) number

3.6 The sample information is also entered into the sample log-in book; this is a list, ordered by increasing ENCOTEC number, of all samples received with such general information for the samples as matrix, number of bottles, parameters to be tested, client identification and date received.

3.7 The ENCOTEC number is placed on all aliquots of a received sample for identification. Non-waste sample containers are stored in the appropriate (soil or water) walk-in cooler located in the log-in area. Waste samples are stored in the waste sample storage cabinets located in the waste storage room. The storage location is recorded in the sample log-in book.

3.8 A hard copy, called a project sheet, of the information entered in the interim database for a batch is issued and taken to the Project Manager assigned to the client from

which the batch of samples has been received. The Project Manager will review this sheet, making any necessary changes in the information provided. When the Project Manager is satisfied that the project sheet presents the client's needs for the batch, the Project Manager assigns a due date for the batch and initials the sheet. When the Project Manager returns the project sheet, a sample documentation package is made up, containing the Chain-of-Custody, the project sheet, and the assessment documentation; this package is stored in the document control file, located in the log-in area.

3.9 The final step in the sample log-in procedure is the authorization and distribution of the project sheet by the Sample Custodian. The samples are transferred from the interim database to the laboratory schedule system by entering the due date specified by the Project Manager for the project sheet. Copies of the project sheet are then distributed to the Group Leaders in charge of the laboratories responsible for the analyses requested, the ENCOTEC Project Manager, the Technical Director, the Quality Assurance Officer, the Inorganics Department Manager, and the Laboratory Manager.

4.0 SAMPLE CUSTODY PROCEDURE

4.1 In order to maintain custody of the samples, each of the following conditions will be observed at all times:

- Access to the laboratory will be through a monitored reception area.
- All visitors will sign-in at the reception area and be escorted while in the laboratory.
- Samples and sample extracts will be stored in secure areas; samples will remain in secure sample storage until removed for sample preparation or analysis.
- Samples designated for Volatile analysis will be stored separately from other samples.
- Analytical standards will not be stored in the same storage areas as samples.
- Only the designated Sample Custodian, sample librarian and supervisory personnel will have access to the sample storage area(s).
- When a sample has been removed from storage by the sample librarian and relinquished to an analyst, the analyst is responsible for the custody of the sample. Each analyst must return the samples to the storage area before the end of the working day or for any other time period during which the analyst cannot maintain custody.

- All transfers of samples into and out of storage will be documented on internal Chain-of-Custody records, maintained by the sample librarian.
- Internal custody documentation will be maintained in sample documentation files.
- Samples, digestates and extracts will be disposed of in an appropriate manner and this disposal will be documented.

4.2 Sample Retrieval

After the samples have been received by the Sample Custodian and placed in a secure storage area, they are removed only for analysis or disposal. To obtain samples for laboratory analysis, a completed sample request form is submitted to the Sample Librarian. The Sample Librarian locates the storage area for a sample by reviewing sample information documented in the sample log book. Once the storage area is known, the Sample Librarian retrieves the sample, noting date and time of sample removal on the sample request form and initialling the notation. When the analyst returns the sample to the Sample Librarian, the date and time of return is recorded on the sample request form along with the analyst's initials. The Sample Librarian returns the sample to its original storage location and files the completed request form for future reference. It is the responsibility of the Sample Custodian to verify that the sample control information has been completed on the form and that the storage areas are secure.

5.0 QUALITY CONTROL

5.1 Sample Bottle Specifications

5.1.1 All sample kits prepared at ENCOTEC will contain a Chain-of-Custody signed and dated by the ENCOTEC log-in technician responsible for filling a bottle order. This will formally relinquish custody of the bottles to the client.

5.1.2 When bottle kits are prepared by ENCOTEC, the bottles are certified as being of integrity sufficient for the analysis to be completed. As a result of this requirement, ENCOTEC uses only certified pre-cleaned sample bottles and does not re-use any sample bottles. ENCOTEC suppliers are required to meet the minimum specifications contained in the USEPA Document "Specification and Guidance for Obtaining Contaminant-Free Sample Containers".

5.2 Trip Blanks - A trip blank is a sample container filled with water and transported with a bottle kit to a sampling site and returned in the same transport container with the collected samples. The trip blank provides useful information about possible bottle and atmospheric contamination. ENCOTEC bottle kits contain one trip blank for every 20 samples or one for every batch, whichever generates the greater number of trip blanks.

5.3 Refrigerator Blanks - A refrigerator blank is kept in each refrigerator dedicated to storage of samples for volatiles analysis. Refrigerator blanks are analyzed on an ongoing basis to give indication of possible cross-contamination from sample to sample. (All samples are segregated based on the probable concentration of volatile organics. However, it is possible that cross contamination could occur.) The refrigerator blank serves as an early warning system for the laboratory analyst.

6.0 PERSONNEL/RESPONSIBILITIES

6.1 Sample Custodian

Once the Laboratory Support Group Technician on duty notifies the Sample Custodian that a shipment of samples is on site, the Sample Custodian is responsible for ensuring that all the procedures detailed in Sections **2.0** through **4.0** are performed as described in a timely manner. In addition, the Sample Custodian is responsible for maintaining all generated sample documentation under control, accessible only to authorized personnel and readily accessible to them. In the event that the Sample Custodian is not available when samples arrive, the following person(s) will assume responsibility:

- Laboratory Support Group Leader
- Designated Support Group Technician

6.2 Sample Librarian

It is the responsibility of the Sample Librarian to maintain custody records for each sample stored in the walk-in coolers. In addition, the sample librarian or his/her designate is responsible for the following:

- Maintaining all sample request records
- When sample custody is relinquished to an analyst, recording on the sample request record

the date, time, and ENCOTEC numbers for the samples released
- When samples are returned by an analyst, recording on the sample request record the date, time, and ENCOTEC numbers for the samples returned
- Maintaining daily temperature logs and corrective action logs for all sample storage areas

12.0 REFERENCES

13.0 PROVENANCE

This method was written by

C.M. O'[illegible] Laboratory Manager

[illegible] Senior Chemist/Technical

It has been reviewed and accepted by

[illegible] Quality Assurance Officer

C.M. O'[illegible] Laboratory Manager

[illegible] Technical Director

PRE-LOGIN CHECKLIST

Login Technician: _____

Project name _____ Receipt date/time _____

Project # _____ Submission # _____

Courier _____ Airbill number _____

SHIPPING CONTAINER(S)

YES NO N/ • Were shipping container seals intact on arrival?

YES NO N/ • Were shipping containers packed with ice or icepacks?

YES NO N/A • If containers were packed with icepacks, are the icepacks still frozen?

YES NO • Were containers and sample bottles subjected to radiologic scan on arrival?

CHAIN OF CUSTODY SHEET (COC)

YES NO • Is COC present? **If COC is not present, do not proceed before contacting Project Manager.**
Project Manager was contacted _____ (date/time)

YES NO • Is COC signed and dated?

YES NO N/A Is COC an ENCOTEC form?

YES NO • Were all requests for analysis listed on the COC sheet (and/or other included documents) matched with sample bottles found in the shipping container(s)?

YES NO • Is all preservation information on the COC in agreement with the preservation specified on the sample bottles?

SAMPLE BOTTLES

YES NO • Are all sample bottles intact and undamaged?

YES NO Were ENCOTEC (pre-preserved) sample bottles used?

YES NO • Are the sample bottles labeled?

YES NO Were ENCOTEC labels used?

YES NO N/ • Were those samples preserved in the field marked SP (site-preserved)?

YES NO • Is each sample bottle the correct type for the analyses specified on it?

YES NO N/ • Are those sample bottles scheduled for POC, POX, VOA, or TOX without air bubbles?

YES NO • Does each bottle contain sufficient sample for the analyses specified on its label?

YES NO • Is the preservation specified on each bottle label the proper one for the analyses specified

If a question marked with * has not been answered "YES" please describe the deviation here.
If necessary, continue the description on the reverse of this sheet.

DEVIATION(S): _____

_____

OTHER OBSERVATION(S): _____

_____

PROJECT MANAGER
RESOLUTION(S): _____

_____

Enter Laboratory Support Group and Project Management authorizing signatures on the reverse of this sheet.

SAMPLE LOG-IN FORM

PAGE____

DATE/TIME RECEIVED (INITIAL)	PROJ. NAME PROJ.#/BATCH # CofC/INV.#	CLIENT SAMPLE ID SAMPLING DATE	ENCOTEC #	MATRIX	PARAMETER LIST	CONTAINER TYPES	STORAGE LOC.	REMARKS	pH

REVIEWED BY _____ DATE _____

LSOLOIN.FOR 08/1997

SAMPLE FILTERING REQUEST FORM DATE & TIME REQUESTED: BY: PAGE #:

BATCH #: CLIENT: TOTAL NUMBER OF BOTTLES:

SAMPLE ID	UNFILTERED #	FILTERED #	BOTTLE TYPE & QUANTITY	PARAMETERS	DATE & TIME FILTERED	DATE & TIME PRESERVED	INITIA

SAMPLE COMPOSITING REQUEST LOG DATE & TIME REQUESTED: BY: PAGE #:

BATCH #: CLIENT: TOTAL NUMBER OF BOTTLES:

COMPOSITE ID	COMPOSITE #	BOTTLE SIZE & QUANT.	COMPOSITE OF: (LIST #'S)	PRESERVE WITH:	DATE & TIME COMPOSITED	INITIAL

SAMPLE REQUEST FORM

ENCOTEC

DATE/TIME REQUESTED: _____

ANALYST: _____ LABORATORY: _____

CLIENT	ENCOTEC NUMBER	MATRIX	PARAMETER	PRESER-VATION	BOTTLE TYPE	LOC.	DATE/TIME REMOVED	INTLS	DATE/TIME RETURNED	INTLS

SMP_RQST.FOR 07/09/92

DC-8a

SAMPLE DISCREPANCY REPORT

DATE: / /

Client: _____ Date Sampled: _____

Project #: _____ Submission #: _____

Date Rec'd: _____

Sample ID: _____

Analysis: _____
analysis for which results cannot be submitted under present conditions.

ENCOTEC #: _____ Matrix: _____

CIRCUMSTANCES MAKING SAMPLE UNAVAILABLE FOR ANALYSIS

☐ Sample was broken in shipment. See PRELOGIN CHECKLIST, copy attached.

☐ Sample was broken on site.

Comment: _____

☐ Client provided insufficient properly preserved sample for analysis requested.
Mark the required preservation with "R" and the provided preservation with "P".

___Nonpreserved	___Zero Head Space	___Sulfuric Acid
___Nitric Acid	___Hydrochloric Acid	___Sodium Hydroxide
___Ascorbic Acid	___Sodium Thiosulfate	___Zinc Acetate

Other Required: _____ Other Provided: _____
Describe volume/mass and other preservation required as well as volume/mass and other preservation provided.

Comment: _____

☐ Sample used in analysis left insufficient amount for other analyses.

Comment: _____
Describe volume/mass and preservation of remaining sample.

☐ Sample used for other analyses left insufficient amount for the analysis requested.

Comment: _____
Describe volume/mass and preservation required as well as vol/mass/pres. found.

☐ Unable to locate sample. See SAMPLE LIBRARIAN DISCREPANCY REPORT, copy attached.

☐ Sample was dumped on _____/_____/_____, per _____

☐ Other: _____

Comment: _____

PM/PC Response: _____

_____

_____

NOTIFICATION RECORD

Analyst/
Technician: _____ Date: _____
Signature of person initiating form.

LSG: _____ Date: _____
Signature of Laboratory Support Group Leader, or designate.

Project
Manager: _____ Date: _____
Signature of Project Manager or designate.

SAMPLE LIBRARIAN DISCREPENCY REPORT

DATE: / /

SAMPLE IDENTIFICATION

Client: _____ Date Sampled: _____

Project #: _____ Submission #: _____

Sample ID: _____ Date Received: _____

ENCOTEC #: _____ Matrix: _____

Analyst requesting search: _____

Date of Request: _____ Analysis for which sample is requested: _____

A search for the sample described above was performed on _____/_____/_____.

The following narrative represents my findings.

_____

_____

_____

Sample Librarian: _____

NOTIFICATION RECORD

LSG _____ Date: _____

Signature of Laboratory Support Group Leader, or designate.

Project Manager _____ Date: _____

Signature of Project Manager, or designate.

SAMPLES THAT HAVE BEEN
USED FOR ANALYSIS

DATE	CLIENT	ENCOTEC NO.	CONTAINER SIZE/TYPE	LAST ANALYSIS PERFORMED	INITIALS

3978

ENVIRONMENTAL
CONTROL
TECHNOLOGY
CORPORATION

3985 RESEARCH PARK DRIVE
ANN ARBOR, MICHIGAN 48108
313/761-1389

July 28, 1993

RECEIVED
JUL 30 1993
CRA, INC.

Ms. Ruth Lewis
Conestoga-Rovers & Associates Limited
1801 Old Highway 8
Suite 114
St. Paul, MN 55112

RE: Amendments for TO14 Standard Operating Procedure
Wausau Superfund Site - Wausau Wisconsin

Dear Ms. Lewis:

As per your fax forwarded on July 16, please find attached an Appendix for ENCOTEC's Standard Operating Procedure (SOP) for TO14 analysis which amends the SOP according to the comments received. As I previously indicated, the requested modification in Section 6.c of your fax is not possible, as the standards provided for this method are only available at nominal concentrations. This is indicated in Section 7.3.2 of the SOP as originally forwarded to your attention.

Following review of this Appendix, please contact me if you have any questions or require further information.

Very truly yours,

ENVIRONMENTAL CONTROL TECHNOLOGY CORPORATION

Timothy J. Schenk
Program Manager

Attachment

#10000

APPENDIX TO METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING SUMMA PASSIVATED CANISTERS AND ANALYSIS BY GAS CHROMATOGRAPHY/ION TRAP MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 No change from TO14LL.SOP.

1.2 Table 1 indicates compounds and lists the limit of quantification (LOQ) in parts per billion by volume (ppbv).

2.0 SUMMARY OF METHOD

2.1 No change from TO14LL.SOP.sop.

2.2 No change from TO14LL.SOP.sop.

2.3 No change from TO14LL.SOP.sop.

2.4 Quantification is by the internal standard technique with multiple three-point internal standard calibration curves providing response factors for most of the compounds of interest. Those compounds identified for which no analytical standard is available are estimated.

2.5 No change from TO14LL.SOP.sop.

3.0 INTERFERENCES

No change from TO14LL.sop.

4.0 APPARATUS AND MATERIALS

No change from TO14LL.sop.

5.0 REAGENTS

No change from TO14LL.sop.

6.0 SAMPLE COLLECTION , PRESERVATION, AND HANDLING

No change from TO14LL.sop.

7.0 PROCEDURE

7.1 Standard Preparation - No change from TO14LL.sop.

7.2 Analysis- No change from TO14LL.sop.

7.3 Calibration-

7.3.1 Prior to the analysis of standards, blanks and any samples, the GC/MS system must meet the mass spectral ion abundance criteria for a 25 ng injection for the instrument performance check solution, bromofluorobenzene(BFB). The ion abundance criteria that must be met are given in Table 2.

TABLE 2
BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criterion
50	8.0 - 40.0% of mass 95
75	30.0 - 66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120.0 % of mass 95
175	4.0 - 9.0% of mass 174
176	Greater than 93.0% but less than 101.0% of mass 174
177	5.0 - 9.0% of mass 176

The instrument performance check solution must be analyzed initially and once per 12 hours of operation. The 12-hour time period for GC/MS instrument performance check begins at the injection of the BFB which is to be submitted as documentation of a compliant tune. The mass spectral ion abundance criteria for *p*-bromofluorobenzene must be met before any calibration standards, blanks, or samples are analyzed.

7.3.2 No change from TO14LL.sop.

7.3.3 No change from TO14LL.sop.

7.3.4 No change from TO14LL.sop.

7.3.5 No change from TO14LL.sop.

7.3.6 If time remains in the 12 hour period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. If there is no time remaining, an instrument performance check solution (see 7.3.1) must be analyzed. If the BFB meets the ion abundance criteria, a continuing calibration standard containing approximately 5.0 ppbv will be analyzed in lieu of the initial three-way calibration (see 7.3.4 and Table 4). Calculate the response factors for the continuing calibration and the percent differences of the response factors from the mean response factors in the initial calibration. The percent difference for each compound must be less than or equal to 30.0 percent. If this criterion is not met, an initial three-way calibration must be analyzed.

7.4 No change from TO14ll.sop.

7.5 No change from TO14LL.sop.

7.6 No change from TO14LL.sop.

8.0 QUALITY CONTROL

8.1 Instrumentation and Sample Canisters

8.1.1 No change from TO14LL.sop.

8.1.2 There must be an initial three point calibration or a continuing calibration meeting the criteria specified in 7.3.

8.1.3 No change from TO14LL.sop.

8.1.4 No change from TO14LL.sop.

8.1.5 No change from TO14LL.sop.

8.2 No change from TO14LL.sop.

8.3 No change from TO14LL.sop.

8.4 No change from TO14LL.sop.

8.5 No change from TO14LL.sop.

8.6 No change from TO14LL.sop.

8.7 No change from TO14LL.sop.

9.0 METHOD PERFORMANCE

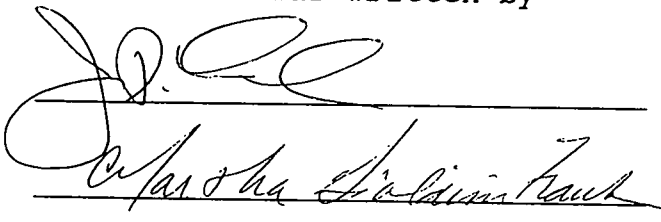
No change from TO14LL.sop

10.0 REFERENCES

No change from TO14LL.sop.

11.0 PROVENANCE

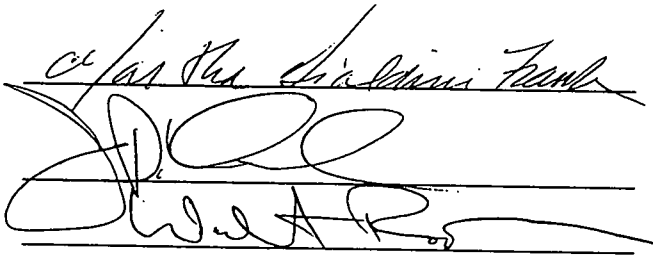
This method was written by



Organics Department Manager

Technical Documentation Officer

It has been reviewed and accepted by



Technical Documentation Officer

Organics Department Manager

Technical Director

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING SUMMA PASSIVATED CANISTERS AND ANALYSIS BY GAS CHROMATOGRAPHY/ION TRAP MASS SPECTROMETRY

1.0 Scope and Application

1.1 This method describes a procedure for the analysis of volatile organic compounds (VOCs) in ambient air using SUMMA passivated canisters and is based on procedures defined in EPA method TO14. This method is applicable to the analysis of canisters with final pressures both above and below atmospheric pressure.

1.2 Table 1 indicates compounds that may be determined by this method and lists the limit of quantification (LOQ) in parts per billion by volume (ppbv).

1.3 This method is applicable to VOCs which are stable when stored in pressurized and sub-atmospheric canisters. Long term stability in pressurized canisters has been demonstrated for numerous compounds; however, minimal documentation is available for sub-atmospheric sampling and caution must be exercised in the evaluation of such data. The sampling procedures used in conjunction with this method utilize a pressurized sampling protocol.

TABLE 1

VOLATILE COMPOUNDS

TO-14 COMPOUND LIST	CAS #	LOQ[1] (ppbv)
Benzene	71-43-2	1.0
Benzyl chloride	100-44-7	1.0
Bromomethane	74-83-9	1.0
Carbon tetra-chloride	56-23-5	1.0
Chloroethane	75-00-3	1.0
Chloroform	67-66-3	1.0
Chloromethane	74-87-3	1.0
3-Chloropropene (Allyl chloride)	107-05-1	1.0
1,2-Dibromoethane	106-93-4	1.0
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	106-46-7	1.0
Dichlorodifluoro-methane	75-71-8	1.0
1,1-Dichloroethane	75-34-3	1.0
1,2-Dichloroethane	107-06-2	1.0
1,1-Dichloroethene	75-35-4	1.0
cis-1,2-Dichloro-ethene	156-60-5	1.0
1,2-Dichloropropane	78-87-5	1.0
1,2-Dichlorotetra-fluoromethane	76-14-2	1.0
cis-1,3-Dichloro-propene	10061-01-5	1.0
trans-1,3-Dichloro-propene	10006-02-6	1.0
Ethylbenzene	100-41-4	1.0
4-Ethyltoluene	622-96-8	1.0
Hexachlorobuta-diene	87-68-3	1.0
Methylene chloride	75-09-2	1.0
Styrene	100-42-5	1.0
1,1,2,2-Tetra-chloroethane	79-34-5	1.0
Tetrachloroethene	127-18-4	1.0
Toluene	108-88-3	1.0
1,2,4-Trichloro-benzene	120-82-1	1.0

[1] LOQ = Limit of Quantification

TABLE 1 (con't.)

TO-14 COMPOUND LIST	CAS #	LOQ[1] (ppbv)
1,1,1-Trichloro-ethane	71-55-6	1.0
1,1,2-Trichloro-ethane	79-00-5	1.0
Trichloroethene	75-69-4	1.0
Trichlorofluoro-methane	75-69-4	1.0
1,1,2-Trichloro-1,2,2-trifluoro-ethane	76-13-1	1.0
1,2,4-Trimethyl-benzene	95-63-6	1.0
1,3,5-Trimethyl-benzene	108-67-8	1.0
Vinyl chloride	75-01-4	1.0
total-Xylenes	1330-20-7	1.0

[1] LOQ = Limit of Quantification

2.0 Summary of Method

2.1 This method provides for automated subsampling of a canister sample, cryogenic concentration, gas chromatographic focusing/separation, detection, and identification of VOCs by Ion Trap mass spectrometry.

2.2 Prior to the use of this method, appropriate sampling techniques must be used.

2.3 The sensitivity of this method is highly dependent upon minimization of background VOC levels, subsample volume, humidity levels in the samples, and instrumental response.

2.4 Quantification is by the internal standard technique with multiple three-point external standard calibration curves providing response factors for most of the compounds of interest. Those compounds identified for which no analytical standard is available are estimated.

2.5 A 500 cm^3 (nominal) sample is withdrawn from the canister, passed through a Nafion dryer for reduction of water content, and cryogenically concentrated with liquid nitrogen in a two-stage concentration sequence. Transfer to a chromatographic column follows with subsequent separation of individual target compounds by temperature programming. Detection by Ion Trap mass spectrometry follows with identification by both retention time and spectral match. Most of the above procedures are automated.

3.0 Interferences

3.1 The most significant interference is that of water vapor present in the sample. The relative humidity of the sample may have a significant effect on recovery efficiencies. This method incorporates a Nafion dryer for removal of most of this water. Without removal, mechanical obstruction due to freezing of the cryogenic traps in the canister sample concentrator may occur. Additionally, degradation in chromatographic performance may occur along with excessive fragmentation and/ or protonation of some polar VOCs in the EI mode, making spectral interpretation difficult. Polar, water-miscible compounds in the vapor state may also be reduced in concentration due to condensation of the water vapor in the canister if it is pressurized. However, some water

vapor needs to be present (estimated at 10-30% relative humidity) in order to minimize surface adsorption effects on the interior walls of the canister.

3.2 Interferences can occur if moisture accumulates in the Nafion dryer. An automated cleanup procedure involving the heating of the dryer assembly along with a system purge is a feature of the concentrator used in this SOP.

3.3 Residual water eluting from the GC column has been found to interfere with chloroethane determination.

3.4 Polar compounds such as methanol, ethanol, butanol, acetonitrile, and 2-butanone have been found to be less stable than the more nonpolar VOCs when stored in canisters over seven day periods.

3.5 Contamination may occur if the canisters are not properly cleaned before use. This process must be capable of reducing each of the target volatile compounds to less than Limit of Quantitation (LOQ). Improperly cleaned canisters may also be a source of non-target compounds which may interfere, through co-elution, with the identification and quantification of the analytes of interest. Reduced analyte recoveries and mis-quantification may also occur due to irreversible adsorption on the interior surface of the canister if it is not clean.

3.6 Common laboratory solvents such as methylene chloride and acetone may be introduced into the analytical system through the standard generation manifold humidifier. Due to the high sensitivity of this method, caution must be exercised in order to minimize or eliminate these contaminants.

3.7 Contamination may also arise from any point in the system exposed to the sample and/or standard air streams. The use of clean, high quality components and the adherence to consistent, thorough cleaning procedures is a necessity.

3.8 Impurities in carrier gases and/or dilution air, outgassing from fitting seals, contamination from the laboratory air if leaks are present in the system, etc. may all contribute to the presence of unacceptable background levels.

3.9 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This, in turn, can result in carryover contamination in subsequent analyses. This method is intended for analysis of ambient air samples and, due to its high sensitivity, is not intended for source or stack sampling.

3.10 Canisters should be stored in a contaminant free location and should be capped tightly during shipment and when not in use to prevent leakage of ambient air into or out of the canister in the event that a leak develops in the valve.

4.0 Apparatus and Materials

Standard Preparation

4.1 Standard Dilution Manifold - A system designed to accurately dilute certified stock standard gases (ppmv level) with ultrapure air to ppbv levels, humidify, and transfer them to SUMMA canisters. The system is comprised of a number of discrete components described in 4.2-4.13. Figure 1 which follows this section provides a general schematic (Waltomatic Model 1, ENCOTEC, Ann Arbor, MI).

4.2 Sample Canister - Leak free, stainless steel, SUMMA passivated spherical pressure vessel with a volume of 6 liters and fitted with a stainless steel Nupro bellows valve. These canisters are used both in collection and storage of samples and in preparation and storage of working standards (Biospherics, Portland, OR or equivalent).

4.3 Electronic Mass Flow Control Console - An eight channel micro-processor-based console that can operate up to eight mass flow control modules simultaneously (Model FM 4660 Operator Console, Union Carbide, Linde Division, Cleveland, OH or equivalent).

4.4 Mass Flow Control Modules - Modules which accurately control and measure the flow of gas streams. For this procedure, eight modules are required; six for the inlet gas streams and one to control the outlet gas stream of diluted gas standard. One, to be used with the dilution air, has a range of 2-1000 cm^3/min and six, to be used with the certified standard gases, have a range of 0.2-10

cm³/min. The outlet mass flow control module has a range of 2-1000 cm³/min (Models 2C and 10C "Standard Mass Flow Control Modules," Union Carbide, Linde Division, Cleveland, OH or equivalent).

4.5 Chromatographic grade stainless steel, type 316, tubing and fittings - To be used in all connections from the standard cylinders to the sample canisters. Tubing used in the dilution manifold is composed of fused silica lined tubing and/or micro-polished tubing (Restek, Bellefont, PA; Biospherics, Portland, OR; Supelco, Bellefont, PA or equivalent).

4.6 Stainless steel mixing chamber - 850cm³ volume cylindrical SUMMA-treated chamber with dip tube for mixing of dilution air and certified stock standards (Biospherics, Portland, OR or equivalent).

4.7 Humidification Bubbler - 6-Liter SUMMA-treated canister with two Nupro bellows valves and dip tube. Used to contain boiled and purged, volatile-free reagent water for use in supplying approximately 10-30% relative humidity to standards (Biospherics, Portland, OR or equivalent).

4.8 Toggle valves, shut-off valves, 30" Hg-30 psi gauge, miscellaneous fittings - for dilution manifold (Swagelock, Nupro, or equivalent).

4.9 Gas regulators - Single stage, ultra-high purity, low flow regulators for use with certified stock standards (Model 19, Scott Specialty Gases, Troy, MI or equivalent) with 0-15 psi stainless steel pressure gauges (Scott Specialty Gases, Troy, MI or equivalent), mounted directly downstream of each regulator.

4.10 Gas regulators - Two stage, ultra-high purity, medium flow regulators (Scott Specialty Gases, Troy, MI or equivalent).

4.11 Vacuum pump - Pump capable of maintaining a vacuum of 27-30" Hg (Model Alcatel 2004A or equivalent) equipped with in-line backstream diffusion fitting to prevent backstreaming of oil into lines.

4.12 Charcoal Filter- Used to remove organic impurities from deionized water which is used in humidifying the dilution air (Tekmar, Cinncinati, OH or equivalent).

4.13 Heat tape and varistat controller - Used to wrap lines, fittings, and mixing chamber in order to maintain this section of dilution manifold at approximately 50-60°C (Cole-Parmer, Chicago, IL or equivalent).

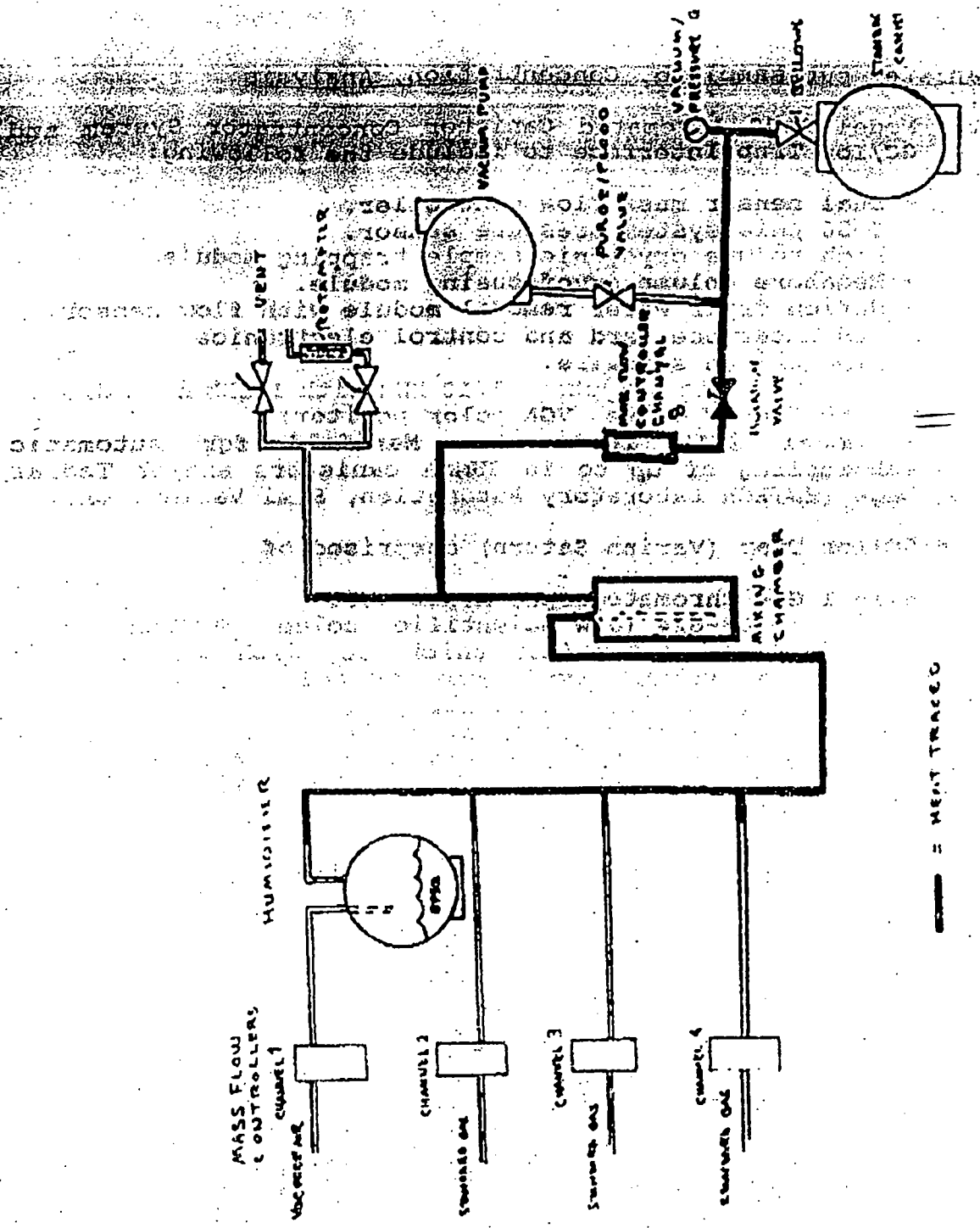


Figure 1: Diagrammatic representation of the Standard Dilution Manifold.

4.14 Model 2000 Automated Canister Concentrator System and GC/Ion Trap Interface to include the following:

- Dual sensor mass flow controller.
- 0-50 psia system pressure sensor.
- high volume cryogenic sample trapping module.
- Megabore column cryofocusing module.
- Nafion dryer water removal module with flow sensor.
- IBM interface card and control electronics.
- Menu driven software.
- AT Compatible computer (8/12 MHz with 1.2Mb hard drive, 1.2 Mb floppy drive, VGA color monitor).
- Model 2010, 16-Canister Manifold for automatic subsampling of up to 16 SUMMA canisters and/or Tedlar bags (ENTECH Laboratory Automation, Simi Valley, CA).

4.15 GC/Ion Trap (Varian Saturn) comprised of

4.15.1 Gas Chromatograph, Model 3400
- DB-624 (J&W Scientific) column, 0.32mm i.d. X 30m X 1.8um film thickness, with direct zero-dead volume connection to heated transfer line from canister concentrator.
- oven cryogenics (optional).
- an open split interface or jet separator is not needed if used with a 0.32mm i.d. capillary column.

4.15.2 Ion Trap Mass Spectrometer with
- Axial Modulation.
- Automatic Gain Control.
- capability to meet BFB tuning criteria.
- capable of acquiring 1 scan per second with a mass range of 35-300 amu.

4.15.3 Data system consisting of
- a computer/instrument interface, personal computer, monitor, printer.
- software programs for control of the instrument, automatic setting of system parameters, scan control and acquisition, data processing, library search, editing, and diagnostics for system hardware.

Canister Cleaning

4.16 Canisters may be cleaned and certified in-house (see 8.6) or cleaned and certified by an approved external laboratory.

5.0 Reagents

5.1 VOC-free Air - ultra high purity air, 99.999% volatile organic compound-free, which is to be used as dilution gas in the working standards.

5.2 Certified Calibration Standard Gases - Cylinders which contain a combination of the following compounds at approximately 2 ppmv each (parts per million by volume). Mixtures are based, in part, on stability and compound compatibility. (AlphaGaz, Walnut Creek, CA or equivalent)

Compound

Dichlorodifluoromethane
1,2-Dichlorotetrafluoroethane
Chloromethane
Vinyl chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
1,1-Dichloroethene
Methylene chloride
3-Chloropropene
1,1,2-Trichloro-1,2,2-trifluoroethane
1,1-Dichloroethane
cis-1,2-Dichloroethene
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon tetrachloride
1,2-Dichloropropane
Trichloroethene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,2-Trichloroethane
Toluene
1,2-Dibromoethane
Tetrachloroethene
Chlorobenzene
Ethylbenzene
m-Xylene
p-Xylene
Styrene
o-Xylene
1,1,2,2-Tetrachloroethane
4-Ethyltoluene
1,3,5-Trimethylbenzene

Compound (cont.)

1,2,4-Trimethylbenzene
Benzyl chloride
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
1,2,4-Trichlorobenzene
Hexachlorobutadiene

The cylinder(s) should be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM) if such a standard exists. If such a standard does not exist, the supplier will certify the accuracy of the cylinders. The above mixture is verified with a certificate of analysis guaranteeing that the concentration is accurate to within ± 2% of the recorded concentration. These standard gases are diluted to a nominal working standard concentration of 10 ppbv (parts per billion by volume).

5.3 Certified Internal Standard Gas Cylinder - A cylinder containing the three internal standard compounds, bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5, and the three surrogate standards, 1,2-dichloroethane-d4, toluene-d8, and bromofluorobenzene, at approximately 20 ppmv (Scott Specialty Gases, Troy, MI or equivalent). This standard is subject to the same certification criteria as the standard gas cylinders. This standard is diluted to a nominal working concentration of 50 ppbv.

5.4 Boiled and Purged Deionized Water (BPSQ) - To be used in humidifying the dilution air. It is prepared in the following manner:

5.4.1 Deionized water is passed through a charcoal filter to remove organic impurities.

5.4.2 The filtered water is boiled for approximately one hour to remove any additional impurities.

5.4.3 The boiled water is purged with ultra-high purity nitrogen at 5-10 psi for approximately one hour. (A fritted sparger at the end of the purge line greatly increases the purge efficiency by allowing for the evolution of fine bubbles, thus increasing the effective bubble surface area.)

5.4.4 The purged water is sealed off and put into the apparatus setup before it reaches room temperature.

5.5 Methanol- Reagent grade to be used for cleaning system components.

6.0 **Sample Collection, Preservation, and Handling**

6.1 Samples are stored at room temperature in an environment free of the volatile compounds of interest. Several common laboratory solvents such as methylene chloride and acetone are difficult to completely eliminate and appropriate precautions should be taken to minimize their potential impact. Holding times have not yet been established by the EPA. Analysis within 14 days of receipt should, however, be strived for.

7.0 **Procedure**

Standard Preparation

7.1 Summary - In order to make a working intermediate standard to calibrate the GC/MS system, several standard gas cylinders are mixed with humidified VOC-free dilution air. By controlling the flow rate of each gas cylinder, a final concentration of 10 ppbv (nominal) is achieved for the working standard. An example of a dilution calculation is shown below:

For a 2 ppmv standard gas cylinder to have a final concentration of 10 ppbv given a flow rate of 1000 cm^3/min of dilution air:

$$\text{flow rate of standard gas cylinder} = \frac{(10\text{ppbv})(1000\text{cm}^3/\text{min})}{(2\text{ ppmv})(1{,}000\text{ppbv/ppmv})}$$

$$\text{flow rate of standard gas cylinder} = 5.00\ \text{cm}^3/\text{min}$$

Varying volumes of the working standard are sampled onto the GC/MS system to establish a calibration curve.

7.1.1 Assembly - refer to Figure 1.

7.1.2 The humidification bubbler is filled approximately one third full with BPSQ such that the dip tube is immediately above the water's surface. If the dip tube is submerged, saturation of the dilution air stream with water vapor will occur. Such saturation is unnecessary for passivation of the surfaces with which the compounds come into contact and lower humidity

levels are effective. In addition, complications with respect to cryogenic concentration and chromatography of the target compounds occur when the dilution air stream is water-saturated. The dilution air is passed through this canister before coming into contact with the standard gases. After passing through the canister, the dilution air is at approximately 10-30% relative humidity.

7.1.3 Channel 1 on the mass flow control module is used for the VOC-free dilution air only. The mass flow control module, with a range of 2-1000 cm^3/min, is set to 995 cm^3/min. Verify that the inlet line pressure at the gas cylinder is set to 10 psi. The flow through the module should be maintained for approximately half an hour to allow the flow to stabilize and to purge any residual contamination in the lines.

7.1.4 Channel 4 in the dilution manifold is connected to the standard gas cylinder. The mass flow controller, with a range of 0.2-10 cm^3/min, is set to 5.00 cm^3/min. Verify that the inlet line pressure at the gas cylinder is set to 10 psi. The flow through the modules should be maintained for approximately half an hour to allow the flow to stabilize and to purge any residual contamination in the lines.

7.1.5 The humidified air and standard gas are mixed together in the dilution chamber which is heated to a temperature range between 50-60° Celsius. This prevents condensation of water and reduces the adsorption of compounds on the interior surface. The flow from the dilution chamber, at a rate of 1000 cm^3/min, is split into two streams, one going to the vent and the other going through the isolation valve. The mass flow control module for channel 8 is immediately downstream of the isolation valve and serves to meter the now diluted standard gas stream into the canister. This module's flow is set to 500 cm^3/min. on the operator console.

7.1.6 With the isolation valve closed, an evacuated canister (30" Hg) is connected as in Figure 1. The line between the isolation valve and the

bellows valve on the canister must be purged with the diluted gas stream before the canister can be filled. The line is purged by vacuum, then flooded with the diluted standard gas. This cycle is repeated for three purge/flood series. A fourth purge (vacuum) is performed and the purge/flood valve is closed. The canister bellows valve is opened and the canister is filled with the diluted standard at a rate of 500 cm^3/min to atmospheric pressure.

7.1.7 There are three manifold readings which aid in monitoring the pressure in the sample canister as it is being filled. The first is that from the vacuum/pressure gauge located between the isolation and bellows valves. When the bellows valve is opened initially, the gauge drops to the pressure in the evacuated canister (should read 30" Hg). As the canister is filled, the gauge reflects the changing pressure. When it reads close to 0 psi, the canister is full. The second reading can be monitored on the bubble flow meter connected to the vent line. Initially at 500 cm^3/min (half of the flow from the dilution chamber), this will increase after the canister approaches atmospheric pressure and more of the gas stream from the dilution chamber is diverted to the vent line. The third and most accurate reading is the flow rate reading on channel 8 on the mass flow control console. Initially, it is at 500 cm^3/min when the canister is being filled. As the canister approaches atmospheric pressure, the flow reading on the console begins to drop. When the flow reading is 400 cm^3/min, the bellows valve on the canister is closed. The canister is ready to be analyzed on the GC/MS system.

Analysis

7.2 Instrument conditions:

7.2.1 Preconcentrator (Model 2000/2010, ENTECH, Simi Valley, CA) - The following are the specifications and operating conditions for the concentrator.
- Sample cryotrap: 1/8 inch diameter glass bead trap. Temperature range -180°C to 200°C. (See Figure 2.)

- Cryofocusing trap: Internal megabore focusing trap. Temperature range -190°C to 200°C. (See figure 3.)
- Nafion dryer: Temperature range ambient to 100°C. Flow sensor range 0-1000 cm^3/min.
- Trapping rate-selectable controller: Mass flow from 20 to 180 cm^3/min. Minimum required pressure drop across controller is 2 psia.
- Sample volume: 500cm^3 of sample.
- Sample pressure: subambient (7 psia) to 35 psia.
- Reproducibility: ± 10% for 10 to 30 cm^3 of sample, ± 5% for 30 to 100 cm^3, and ± 3% for over 100 cm^3 of sample.
- 16 port valve temperature: 120°C.
- Manifold transfer line temperature: 100°C.
- 8 port valve temperature: 100°C.
- GC transfer line temperature: 125°C.

Refer to Figures 4 through 6 for sample loading, sample transfer/inject, and system bakeout flow diagrams.

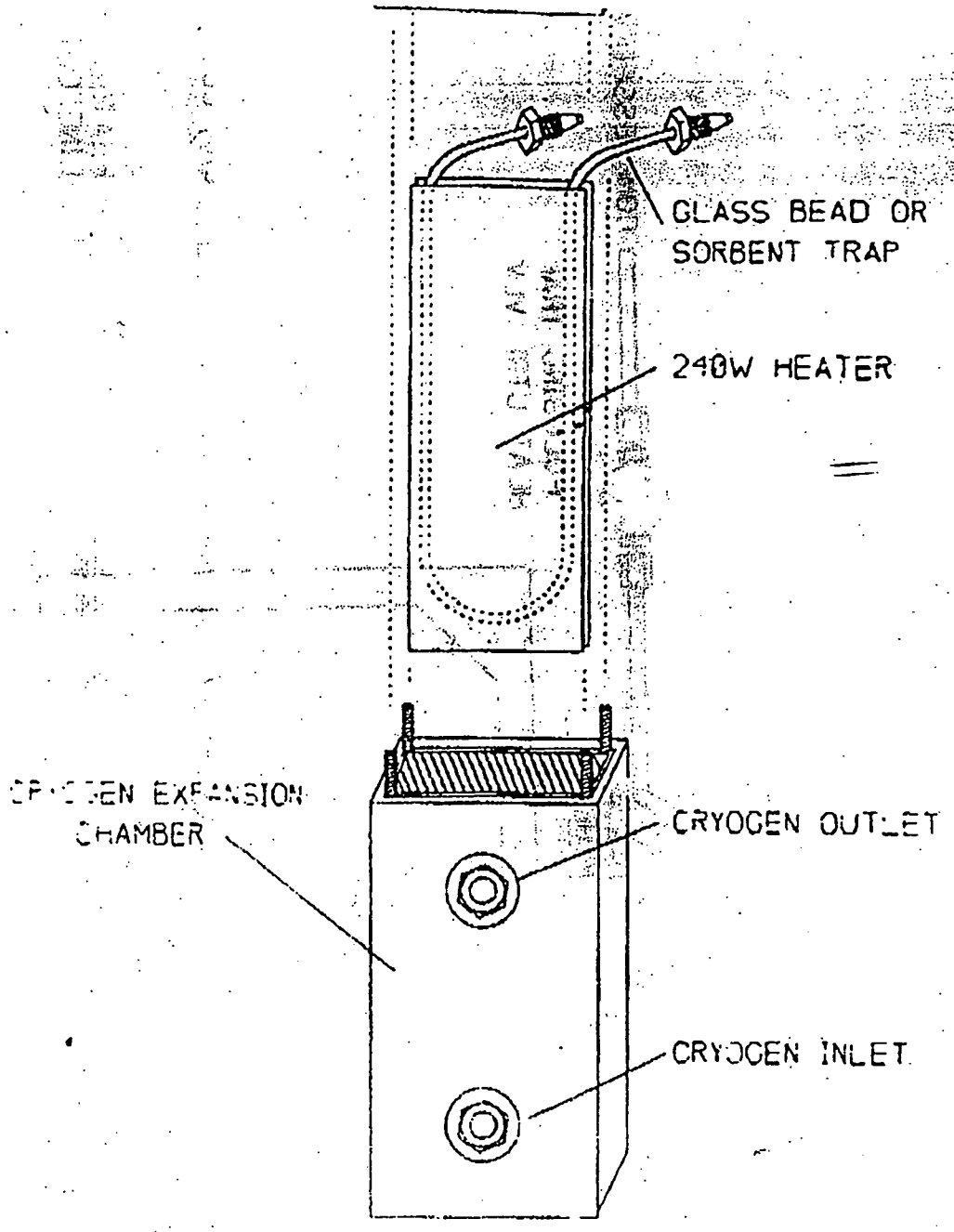


Figure 2: Sample cryotrap (after ENTECH Laboratory Automation).

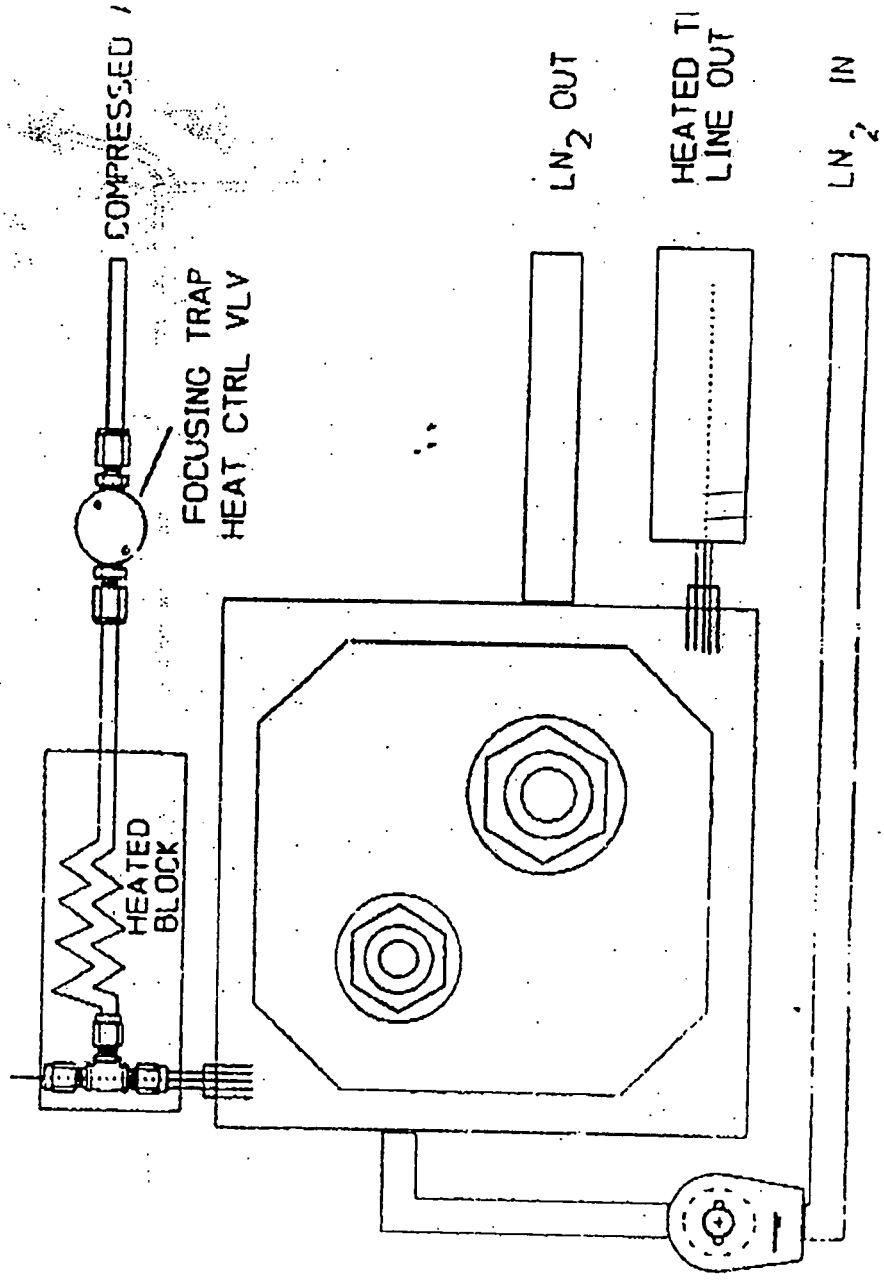


Figure 3: Cryofocusing trap (after ENTECH Laboratory Automation).

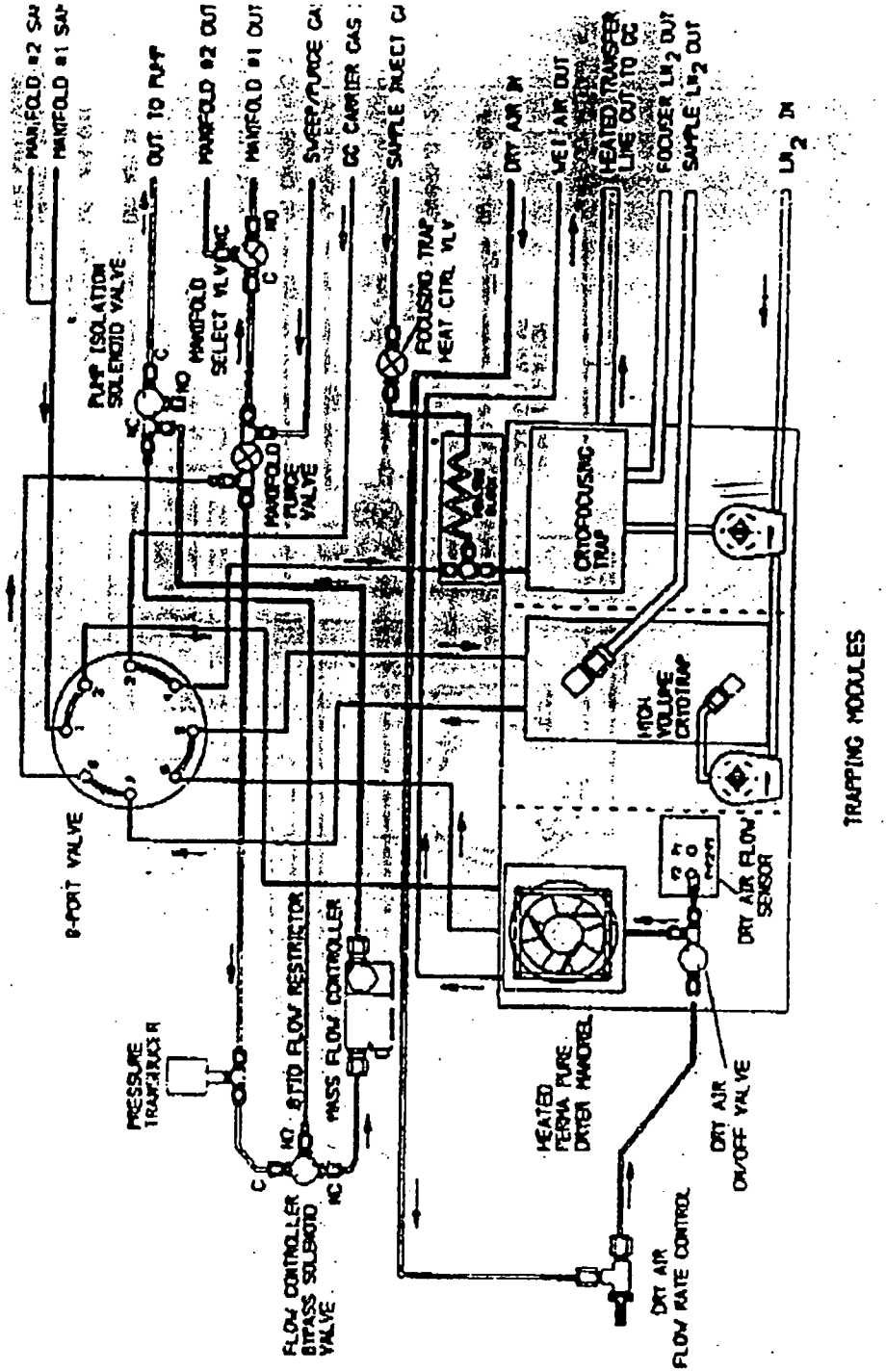


Figure 4: Automated concentrator sample loading flow diagram (after ENTECH Laboratory Automation).

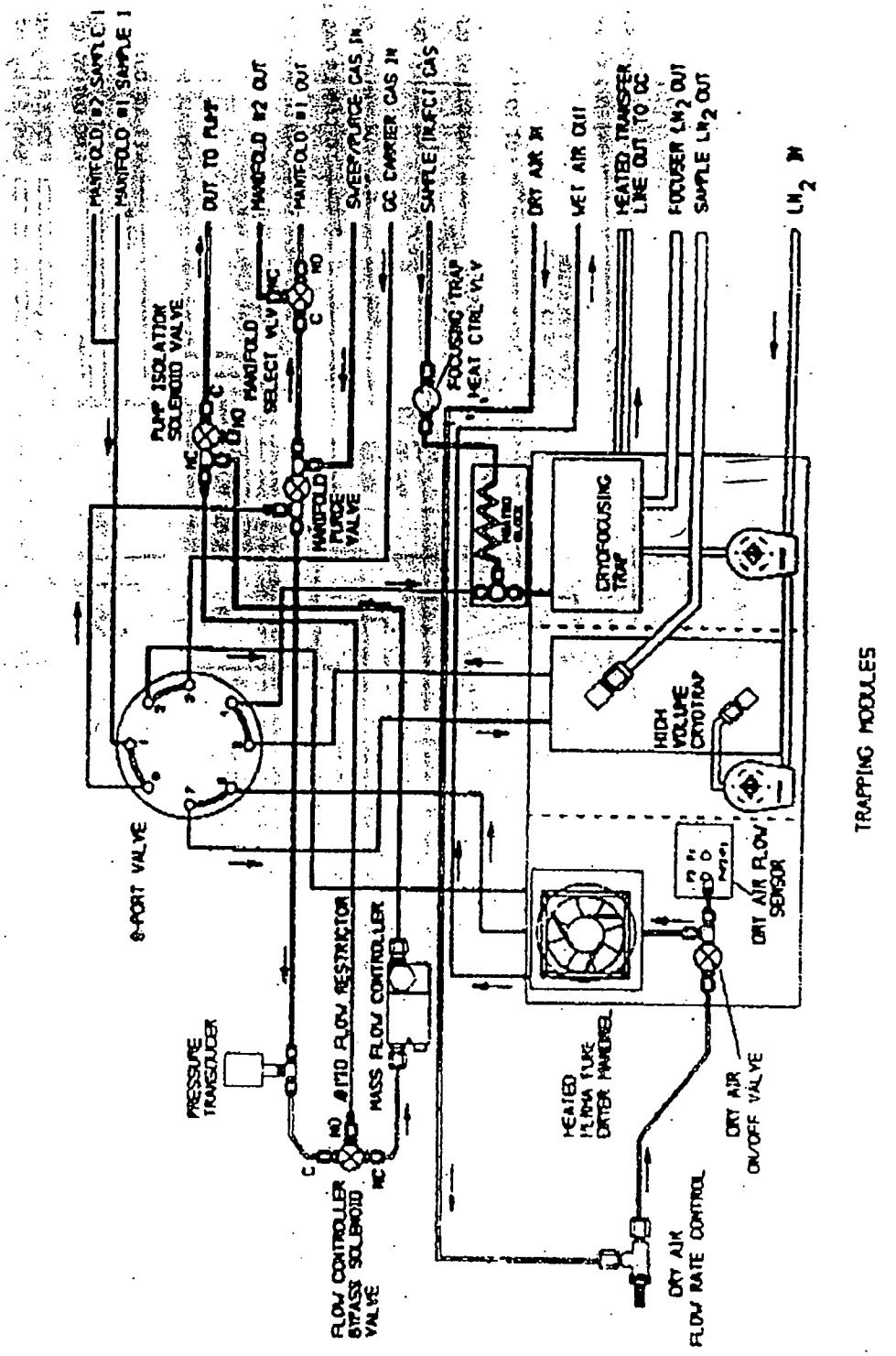


Figure 5: Automated concentrator sample transfer/injection flow diagram (after ENTECH Laboratory Automation).

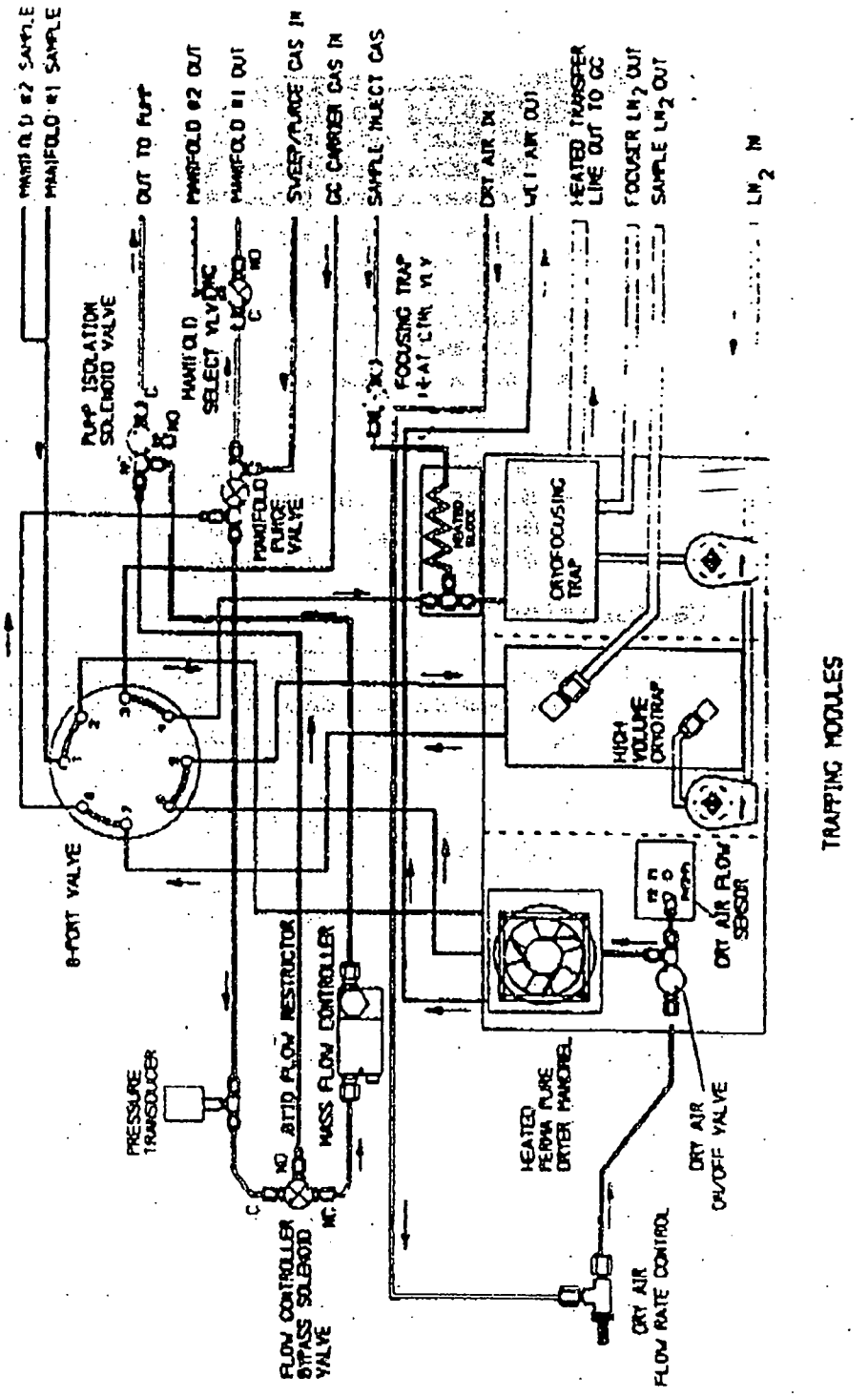


Figure 6: Automated concentrator system bakeout flow diagram (after ENTECH Laboratory Automation).

7.2.2 Gas chromatograph - The following are the operating conditions for the gas chromatograph.
- Initial column temperature: 35°C for 3 minutes.
- Temperature program: 35-150°C at 5°C/min.
- Temperature program: 150°C - 220°C at 10°C/min.
- Final temperature: 220°C for 0.1 minutes.
- Transfer line temperature: 200°C.
- Source temperature: 220°C.
- Carrier gas: Helium at 30 cm/sec.
- Chromatographic column: J&W DB624 0.32mm i.d. X 30m X 1.8um film thickness.

7.2.3 Ion Trap - The following are the operating conditions for the Ion Trap.
- Electron energy: 70 volts.
- Mass range: 35-300 amu.
- Scan time: 1 scan per second.

7.3 Calibration

7.3.1 Prior to the analysis of standards, blanks and any samples, the GC/MS system must meet the mass spectral ion abundance criteria for a 50 ng injection for the instrument performance check solution, bromofluorobenzene(BFB). The ion abundance criteria that must be met are given in Table 2.

TABLE 2
BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criterion
50	8.0 - 40.0% of mass 95
75	30.0 - 66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120.0 % of mass 95
175	4.0 - 9.0% of mass 174
176	Greater than 93.0% but less than 101.0% of mass 174
177	5.0 - 9.0% of mass 176

The instrument performance check solution must be analyzed initially and once per 12 hours of operation. The 12-hour time period for GC/MS

instrument performance check begins at the injection of the BFB which is to be submitted as documentation of a compliant tune. The mass spectral ion abundance criteria for p-bromofluorobenzene must be met before any calibration standards, blanks, or samples are analyzed.

7.3.2 After the instrument performance check solution criteria have been met, the GC/MS system is calibrated with three different concentrations of each compound from those available in the standards cylinders. (Concentrations of three standards are dependent on the initial concentration of the compound in the Certified Stock Standard cylinders). All standards will contain surrogates and internal standards.

7.3.3 The quantitation ions for each internal standard are as follows:

INTERNAL STANDARDS	QUANTITATION ION
Bromochloromethane	128
1,4-Difluorobenzene	114
Chlorobenzene-d5	117

The corresponding assignments of internal standards to compound of interest are given in Table 3. These references are used for quantification purposes.

TABLE 3
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTIFACTION

Bromochloromethane	1,4-Difluorobenzene	D5-Chlorobenzene
Bromomethane	Benzene	Benzyl chloride
Chloroethane	Carbon tetrachloride	Chlorobenzene
Chloroform	1,2-Dichloroethane	1,2-Dibromoethane
Chloromethane	1,2-Dichloropropane	1,2-Dichlorobenzene
3-Chloropropene (Allyl chloride)	cis-1,3-Dichloropropene	1,3-Dichlorobenzene
Dichlorodifluoromethane	1,1,1-Trichloroethane	1,4-Dichlorobenzene
1,1-Dichloroethane	Trichloroethene	trans-1,3-Dichloropropene
1,1-Dichloroethene		Ethylbenzene
cis-1,2-Dichloroethene		4-Ethyltoluene
1,2-Dichlorotetrafluoroethane		Hexachlorobutadiene
Methylene chloride		Styrene
Trichlorofluoromethane		1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-fluoroethane		Tetrachloroethene
Vinyl chloride		Toluene
		1,2,4-Trichlorobenzene
d4-1,2-Dichloroethane(surr.)		1,1,2-Trichloroethane
		1,2,4-Trimethylbenzene
		1,3,5-Trimethylbenzene
		o-Xylene
		m-Xylene
		p-Xylene
		d8-Toluene (surr)
		Bromofluorobenzene (surr)

7.3.4 Analyze different volumes of each calibration standard (the diluted standard which is now in the SUMMA canister) to give three different concentrations and tabulate the area of the primary characteristic ion (as indicated in Table 4, below) against the concentration for each compound. The concentrations of the three standards will be approximately 10.0, 5.0, and 2.0 ppbv. Calculate the response factors (RRFs) for each compound as follows:

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

where

A_x = Area of the characteristic ion for the compound to be measured (from Table 4)

A_{is} = Area of the characteristic ion for the specific internal standard (from Table 4)

C_{is} = Concentration of the internal standard (ppbv)

C_x = Concentration of the compound to be measured (ppbv)

7.3.5 The average response factor (RF_{avg}) is calculated for all compounds from the three different levels of standard analyzed. The percent relative standard deviation (%RSD = 100[sd/RF_{avg}]) is calculated for each compound. The %RSD for each individual compound should be no greater than 30%.

TABLE 4
CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS AND SURROGATES

Parameter	Primary Ion
Benzene	78
Benzyl chloride	91
Bromomethane	94
Carbon tetrachloride	117
Chlorobenzene	112
Chloroethane	49
Chloroform	83
Chloromethane	50
3-Chloropropene (Allyl chloride)	39
1,2-Dibromoethane	107
1,2-Dichlorobenzene	146
1,3-Dichlorobenzene	146
1,4-Dichlorobenzene	146
Dichlorodifluoromethane	85
1,1-Dichloroethane	63
1,2-Dichloroethane	62
1,1-Dichloroethene	96
cis-1,2-Dichloroethene	96
1,2-Dichloropropane	63
1,2-Dichlorotetrafluoroethane	85
cis-1,3-Dichloropropene	75
trans-1,3-Dichloropropene	75
Ethylbenzene	106

TABLE 4 (con't)

Parameter	Primary Ion
4-Ethyltoluene	105
Hexachlorobutadiene	225
Methylene chloride	49
Styrene	104
1,1,2,2-Tetrachloroethane	83
Tetrachloroethene	164
Toluene	92
1,2,4-Trichlorobenzene	180
1,1,1-Trichloroethane	97
1,1,2-Trichloroethane	97
Trichloroethene	130
Trichlorofluoromethane	101
1,1,2-Trichloro-1,2,2-trifluoroethane	151
1,2,4-Trimethylbenzene	105
1,3,5-Trimethylbenzene	105
Vinyl chloride	62
m-Xylene	106
p-Xylene	106
o-Xylene	106

7.4 Sample Analysis - If time remains in the twelve hour sequence and the initial calibration criteria has been met, samples may be analyzed. If time does not remain in the twelve hour sequence, then a new instrument performance check and continuing calibration standard must be analyzed. Samples may be analyzed if the criteria for the instrument performance check and continuing calibration standard have been met.

7.4.1 Before sampling the sample canister, the pressure of the canister is taken with a mechanical pressure gauge (0-15 psi). The pressure is recorded and compared with the final canister pressure recorded in the field.

Note: the same gauge used in the field measurement should be used for the laboratory reading.

7.4.2 The sample canister is connected to the concentrating unit and the Nupro valve is opened.

7.4.3 The concentrator is then flushed with 20 cm^3 of the sample that is going to be analyzed. This is performed to eliminate any carryover resulting from small dead volumes in the concentrator unit.

7.4.4 Due to the volume of sample taken into the concentrator, the system must now be flushed with carrier gas. This is to ensure that when the prescribed sample volume is taken, it samples that amount and not more.

7.4.5 The sample cryofocusing trap is then cooled to -150°C.

7.4.6 A 100cm^3 aliquot of the internal standard and surrogate canister is sampled and trapped on the sample cryofocusing trap. The flow for the internal standard/ surrogate canister is set at 100 cm^3/min.

7.4.7 A 500cm^3 aliquot of the sample is taken and trapped on the sample cryofocusing trap. The flow is set at 150 cm^3/min.

7.4.8 The sample pressure is recorded by the ENTECH unit before and after the desired volume is taken. This is done so that a theoretical calculation can be performed to check that the volume obtained by the system via the mass flow controller is the approximately the same as the theoretical amounts.

7.4.9 The common regions of the concentrator are then swept with carrier gas to ensure recovery of analytes that may have reversibly absorbed onto the surface. A volume of 50 cm³ is used in this step.

7.4.10 The cryofocusing trap is cooled to -170°C.

7.4.11 The sample cryofocusing trap is heated to 150°C. which will transfer the sample to the cryofocusing trap. The total time for desorption is 4 minutes.

7.4.12 After sample transfer to the cryofocusing trap is complete, the trap is heated to 180°C. The sample is then transferred to the GC column.

7.4.13 Upon sample injection onto the column, the GC/MS is signaled by the computer to scan the eluting carrier gas from 35 to 300 amu.

7.4.14 Primary identification is based upon retention time and relative abundance of eluting ions as compared to the spectral libraries stored on the Ion Trap computer.

7.5 Suggested system maintenance - The following is a list of routine maintenance items performed on the concentrator system and Ion Trap system.

7.5.1 Concentrator system - The main area of maintenance is the conditioning of the system before and after analysis. The concentrator should have all lines connecting the sample containers and common transfer lines backflushed with carrier gas. This will sweep out contaminants that may reside in the lines. The transfer line from the concentrator to the GC may have to be changed periodically, due to constant stress from heating and cooling.

7.5.2 Ion Trap - The ion trap will require routine maintenance generally proportional to the usage of the instrument. The most commonly performed maintenance is the cleaning of the ion trap source. This maintenance is performed when the instrument performance check solution(BFB) is unable to meet acceptable ion abundance criteria.

7.6 Calculations

7.6.1 Qualitative analysis - The compounds listed in this method must be identified by the analyst through the comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The two criteria that must be satisfied to verify the identification are

7.6.1.1 The elution of the sample component at the GC relative retention time of the standard component - In order to establish the relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be analyzed on the same shift 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(EICP) for ions unique to the component of interest.

7.6.1.2 Correspondence of the sample component and standard component mass spectra - The relative intensities of the characteristic ions of the sample component must agree within 20% of the relative intensities of those of the standard component. Ions accounting for more than 10% of the sample spectra but not present in the standard spectra for the same component must be considered and accounted for by the analyst making the comparison. If a compound cannot be verified by all of these criteria, but, in the technical judgement of the mass spectral interpretation specialist, the

identification is correct, then the compound shall be reported and quantified.

7.6.2 Quantitative analysis -- The quantitation of an identified compound will be based on the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion (Table 4). The internal standard technique will be used for quantitation. The internal standard used for a given analyte is found in Table 3. The concentration of each identified analyte is calculated as follows:

$$X_s = \frac{A_s \times I_s}{A_{is} \times RRF}$$

where

X_s = analyte air concentration in ppbv.

A_s = area of the characteristic ion for the compound measured.

I_s = amount of internal standard present in ppbv.

A_{is} = area of the characteristic ion for the internal standard.

RRF = response factor for the analyte being measured.

The surrogate concentrations are determined using the same equations as used for analytes. The percent recovery (%R) of the surrogate is calculated as follows:

$$\%R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

The nominal recovery limits for the three surrogates used are found in Table 5. Actual recovery limits may differ and are based on statistical evaluation of historical data. Please refer to the Standard Operating Procedure for the Determination of Control Limits.

Table 5
NOMINAL SURROGATE RECOVERY LIMITS

COMPOUND	%R
Toluene-d8	90-110
Bromofluorobenzene	90-110
1,2-Dichloroethane-d4	90-110

For those compounds where no standard was available, an estimated concentration is determined using the internal standard method. The nearest internal standard free of interferences is used. The formula for calculating concentrations for these compounds is the same as for those compounds for which standards are available. Total peak heights from the total ion chromatograms are used for both the compound to be measured and the internal standard. An RRF of one (1) is assumed.

8.0 Quality Control

8.1 Instrumentation and Sample Canisters

8.1.1 Prior to the analysis of any samples, the GC/Ion Trap system must be tuned daily to meet the tuning criteria for Bromofluorobenzene (BFB) specified in section 7.3.1. All instrument conditions must be identical to those used during sample analysis.

8.1.2 There must be an initial three-point calibration meeting criteria specified in 7.3.

8.1.3 All canisters are required to be certified clean (containing less than LOQ of each target compound) and determined to be leak-free prior to sampling and/or use in the generation of standards. Furthermore, it must be demonstrated, through the analysis of canister blanks and field blanks, that the sampling and/or analytical system does not contribute to the presence of target compounds (i.e. those listed in Table 1) at or above the Limit of Quantification (LOQ). A leak-free analytical system along with the use of boiled and nitrogen-purged reagent water (BPSQ) used in humidification is essential.

8.1.4 The automated canister concentrator provides a QA/QC report for each discrete analysis. An example of the QA/QC report follows; see Figure 7. Information is provided about the concentration procedures which allows the analyst to check for proper system operation. The hardcopy of this report is archived with the raw data documentation. Many of the potential problems that can occur during sample concentration will result in abnormal readings that are saved on the QA/QC report. The report is examined following a run to ensure that all systems were functionally normally. If any readings indicate that concentration/transfer of the sample did not proceed normally, proper corrective action is taken with reanalysis of the sample to follow.

8.1.5 A summary of the primary indicators that are to be examined on a per-sample basis is given below. For a complete treatment, see the concentrator operation manual.

<u>System Temperatures</u>
Temperature zones controlled by the system fall into two categories; those that are held constant during the entire concentration procedure, and those that have different setpoints. The QA/QC report shows the actual temperatures recorded as well as the user specified setpoints. These temperatures are also monitored by the analyst in real-time via the concentrator computer monitor.

<u>Flows and Volumes</u>
The system records actual flow rates and volumes delivered during each concentration procedure. The volumes of internal standard, sample, and dry purge gas are recorded along with their setpoints. System pressures are also recorded. Evaluation will, for example, enable the analyst to determine whether or not mass flow controller operation in the concentrator is normal. Real-time monitoring is also possible.

Sample Pressures Before and After Sampling

The sample pressure is recorded before and after withdrawing an aliquot for concentration. The initial pressure can be used as an indicator to determine if the pressure was maintained from the field to the laboratory and during storage.

Sequence Times

Trapping and desorption/transfer times are recorded for both comparison to setpoints and to give additional insight into conditions during concentration.

QA/QC REPORT

SAMPLE NAME: bfb0228h
INJECT TIME: 10:01:13
DATE: Thu Feb 28 1991
METHOD: to14.CCN
NAMELIST: lin.nam
MANIFOLD POSITION: 3

PRESSURE BEFORE SAMPLING(PSIA) 22.9
AFTER SAMPLING(PSIA) 22.8

NG INT. STD INJECTED IS1(1) IS2(1) IS3(1) IS4(1) IS5(1)

PREHEAT? (N) CRYOFOCUS? (Y) HEAT SAMPLE? (N)

CONDITIONS:

DURING CONCENTRATION	MAX. TEMP	FINAL TEMP	TRAP/SEP TIM
Nafion Dryer	23	21(30)	54
High Volume Cryogenic Trap	-147	-148(-150)	54
Focusing Trap	-145	-193(-180)	180(180)

DESORB/TRANSFER/INJECT	PREHEAT	FINAL TEMP	TIME(secs)
Nafion Dryer	21	21(30)	54(54)
High Volume Cryogenic Trap	-148	153(150)	180(180)
Focusing Trap	-193	123(-180)	90

MEDIUM CONC./TRANSFERRED	VOLUME	FLOW(SCCM)	FINAL PSIA
Internal Standard	50(50)	48(50)	17.5
Sample	102(100)	149(150)	21.4
Sweep/Dry Purge	100(100)	52(50)	41.4
Dry Air	0	635	

REGULATED ZONES	TEMPERATURE
8-PORT VALVE	99(100)
GC TRANSFER LINE	125(120)
MANIFOLD TRANSFER LINE	99(100)
16-POSITION SELECT VALVE	99(100)
SAMPLE CONTAINER	AMBIENT

Figure 7: Sample QA/QC report from the automated canister concentrator.

8.2 Standards

8.2.1 Certified Stock, Calibration, Internal, and Surrogate standards are obtained commercially with a certificate of analysis guaranteeing their accuracy to ± 2% of the listed concentration. The nominal concentration is 20 parts per million by volume (ppmv) per compound for the internal and surrogate standard and 2 parts per million by volume (ppmv) per compound for the stock calibration standard.

8.2.2 Dilution Air (ultra-high purity, 99.999% volatile-free) used for generation of working standards is obtained commercially. Verification that target compounds are absent at or above the LOQ is obtained through the analysis of canister method blanks.

8.2.3 Standard Dilution Manifold mass flow controllers are initially calibrated by the manufacturer with an accuracy specification of ± 1%. These are periodically checked against bubble flow meters at the flows used for working standard generation. (The accuracy of bubble flow meters cannot approach the accuracy at which the mass flow controllers were initially calibrated by the manufacturer.) If the set flow is suspect, it should be verified by additional readings. It is extremely important that the mass flow controllers are protected from fine particles entering the device. In addition, the analyst needs to ensure that the dilution manifold is operating within the temperature range at which it was calibrated and that the manifold is on a level surface. Faulty mass flow controllers will be returned to the manufacturer for recalibration if necessary.

8.2.4 The stability of the working standards is dependent, in part, upon the canister pressure, the humidity level, and the polarity of compounds. Short-term stability is monitored through response factors obtained during initial calibration. Since the standard canisters cannot be pressurized, a limitation of the removal of 3000 cm^3 of standard from a 6-liter SUMMA canister is imposed. This requirement ensures that

standards are made on a relatively frequent basis and, hence, long-term stability (greater than one month) is of reduced concern. Identification of which standards are more susceptible to short-term stability problems is ongoing. In general, the more polar VOCs, such as ketones, exhibit the greatest tendency toward what appears to be adsorption on the interior walls of the canister.

8.2.5 If approved and provided by the EPA, audit cylinders will be used as an additional verification of the validity of the analytical standards.

8.3 Surrogates

8.3.1 Surrogate compounds (see 5.3) are introduced during the canister sub-sampling sequence prior to cryogenic focusing at the following levels:

Table 6

Surrogate Concentrations

Compound	Concentration (ppbv)
Toluene-d8	10
Bromofluorobenzene	10
1,2-Dichloroethane-d4	10

These compounds are those suggested by EPA method 8240 since none are specified in Method TO-14. Nominal recovery windows of 90-110% are based on Method TO-14 QC recovery criteria for audit cylinder results. Internally derived windows are provided in the Method Performance section which follows.

8.4 Method Blanks and Field Blanks

8.4.1 Method Blanks and Field Blanks are analyzed with every batch of samples or every 20 samples, whichever is less, to ensure that the analytical system is free of contaminants and to verify that no target compounds are present at or above the LOQ. It is very difficult to reduce trace levels of common laboratory solvents such as methylene chloride and acetone from the water (BPSQ) used

in humidification below 1ppbv and consequently provision is made in reporting to flag data with a "B". Typical levels encountered for either of these two contaminants is 1-3 ppbv.

8.5 Matrix Spikes and Laboratory Control Samples

It is not feasible with this analysis to fortify samples (matrix spike) or zero air (laboratory control sample) with some or all of the target compounds. Furthermore, a secondary source standard is unavailable at this time.

8.6 Canister Cleaning and Certification

Canisters may be cleaned and certified according to the Standard Operating Procedure for the Cleaning and Certification of SUMMA Passivated Canisters for TO-14 Analysis or by an approved external laboratory.

8.7 Comparison of Canister Pressures, Field vs. Laboratory - If the sample canisters are pressurized during sampling (recommended 5-10 psi), final pressures are obtained at the end of field sampling by using a standard 2.0 inch stainless steel pressure gauge (0-15 psi, 1/2 scale). Readings are obtained again using an identical (or the same) gauge immediately before analysis. Significant pressure losses are cause for concern although sample integrity should not be seriously compromised. In the event that pressure has been shown to have dropped more than 2 psi during the interval between sampling and analysis, the canister should be leak-checked once sample analysis has been completed, and repairs should be initiated if needed. Contamination or leakage into the canister will not occur unless a leak is present in a canister under partial vacuum.

9.0 Method Performance

9.1 Method Detection Limits - The method detection limits for the compounds analyzed by this method were established by analyzing 9 replicates at a test concentration of 0.5 ppbv per compound using the protocol defined in Appendix B of 40 CFR Part 136. The method detection limits for this method are found in Table 7, below.

note: the Method Detection Limits (MDL) which follow were determined under optimal analytical conditions. Most are at such low concentration levels that background levels may be problematic and quantitation at this level is not recommended. Instead, the MDLs should be evaluated in terms of supporting the 1 ppbv Limit of Quantitation (LOQ).

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: TO-14

Method(s)

Sample Prep/Extraction:

Analysis: TO-14

Date(s) of Analysis: [illegible] 6/23/93

Analyst(s): CLC

Instrument Type: GC/MS

Instrument Model: [illegible]

Instrument I.D.: 5973

Instrument Configuration:

GC:

35°C → 3 min → 135°C @ 8°/min → 195°C @ 10°C/min

MS:

Scan Range: 35 - 300 amu

Scan Time: 1sec/scan

Referenced Protocol:

___ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit"

___ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846"

___ Exhibit E, Section V, 10, March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis"

Matrix:

___ Laboratory Reagent Water

___ Aqueous Environmental Sample (specify origin):

___ Soil/Solid Environmental Sample (specify origin):

✓ Other (specify): Summa Canister Air

TABLE 7

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

TO-14 METHOD DETECTION LIMIT STUDY

Method: Volatiles by TO-14
Analyzed on 04/23/93 on Saturn 2T240

Compound	Test Conc. (ppbv)	Replicate Recoveries (ppbv) 1	2	3	4	5	6	7	8	9	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL
Dichlorodifluoromethane	0.500	0.590	0.606	0.592	0.568	0.609	0.590	0.606	0.593	0.600	0.595	0.013	0.036	118.978	0.036
Dichlorotetrafluoroethane	0.500	0.573	0.581	0.578	0.539	0.581	0.553	0.575	0.600	0.581	0.573	0.018	0.051	114.619	0.051
Chloromethane	0.500	0.699	0.692	0.728	0.652	0.702	0.670	0.673	0.720	0.690	0.691	0.024	0.069	138.221	0.069
Vinyl chloride	0.500	0.617	0.635	0.586	0.547	0.628	0.569	0.571	0.597	0.569	0.591	0.020	0.058	118.200	0.058
Bromomethane	0.500	0.648	0.671	0.653	0.603	0.667	0.628	0.626	0.670	0.640	0.622	0.048	0.140	124.373	0.140
Chloroethane	0.500	0.604	0.619	0.641	0.549	0.617	0.608	0.600	0.607	0.619	0.587	0.059	0.172	117.367	0.172
Trichlorofluoromethane	0.500	0.551	0.544	0.546	0.505	0.545	0.521	0.548	0.534	0.551	0.538	0.016	0.047	107.622	0.047
1,1-Dichloroethene	0.500	0.540	0.530	0.535	0.547	0.562	0.530	0.560	0.563	0.550	0.542	0.013	0.038	108.467	0.038
Trichlorotrifluoroethane	0.500	0.552	0.548	0.539	0.472	0.546	0.521	0.547	0.542	0.531	0.533	0.023	0.071	106.572	0.071
3-Chloropropene	0.500	0.570	0.571	0.560	0.489	0.572	0.535	0.569	0.560	0.579	0.551	0.030	0.087	110.111	0.087
Methylene chloride	0.500	0.700	0.701	0.831	0.593	1.211	1.104	1.057	1.086	1.054	0.926	0.222	0.642	185.257	0.642
1,1-Dichloroethane	0.500	0.487	0.477	0.474	0.445	0.487	0.468	0.481	0.490	0.478	0.476	0.014	0.040	95.222	0.040
cis-1,2-Dichloroethene	0.500	0.497	0.500	0.494	0.467	0.504	0.476	0.491	0.508	0.493	0.493	0.013	0.038	98.558	0.038
Chloroform	0.500	0.541	0.545	0.546	0.520	0.547	0.528	0.539	0.537	0.539	0.540	0.011	0.033	108.044	0.033
1,1,1-Trichloroethane	0.500	0.540	0.535	0.533	0.537	0.540	0.528	0.539	0.543	0.545	0.539	0.004	0.011	107.756	0.011
Carbon tetrachloride	0.500	0.517	0.516	0.519	0.514	0.513	0.505	0.519	0.514	0.516	0.515	0.003	0.007	102.933	0.007
Benzene	0.500	0.558	0.544	0.534	0.546	0.547	0.536	0.546	0.555	0.562	0.551	0.009	0.026	110.178	0.026
1,2-Dichloroethane	0.500	0.595	0.587	0.573	0.593	0.592	0.587	0.589	0.597	0.597	0.592	0.007	0.022	118.400	0.022
Trichloroethene	0.500	0.509	0.498	0.493	0.504	0.502	0.505	0.499	0.497	0.503	0.501	0.004	0.013	100.267	0.013
1,3-Dichloropropane	0.500	0.548	0.532	0.542	0.547	0.541	0.537	0.531	0.531	0.537	0.537	0.006	0.022	107.467	0.022
cis-1,3-Dichloropropene	0.500	0.459	0.458	0.450	0.459	0.447	0.456	0.465	0.448	0.457	0.455	0.006	0.017	91.089	0.019
Toluene	0.500	0.593	0.581	0.566	0.575	0.567	0.580	0.579	0.571	0.577	0.577	0.008	0.024	115.333	0.024
trans-1,3-Dichloropropene	0.500	0.458	0.445	0.441	0.445	0.435	0.446	0.441	0.439	0.445	0.446	0.006	0.019	89.222	0.021
1,1,2-Trichloroethane	0.500	0.494	0.470	0.481	0.519	0.493	0.508	0.464	0.488	0.498	0.491	0.017	0.050	98.156	0.051
Tetrachloroethene	0.500	0.608	0.595	0.589	0.593	0.588	0.591	0.583	0.578	0.584	0.591	0.009	0.026	118.178	0.026
1,2-Dibromoethane	0.500	0.518	0.507	0.502	0.505	0.506	0.514	0.515	0.501	0.513	0.509	0.006	0.017	101.822	0.017
Chlorobenzene	0.500	0.504	0.508	0.502	0.500	0.507	0.505	0.509	0.505	0.501	0.505	0.003	0.009	100.911	0.009
Ethylbenzene	0.500	0.528	0.544	0.499	0.492	0.510	0.528	0.530	0.502	0.522	0.517	0.017	0.050	103.467	0.050
m-Xylene	0.500	0.523	0.511	0.511	0.512	0.512	0.510	0.506	0.495	0.501	0.509	0.008	0.023	101.800	0.023
p-Xylene	0.500	0.523	0.511	0.511	0.512	0.512	0.510	0.506	0.495	0.501	0.509	0.008	0.023	101.800	0.023
o-Xylene	0.500	0.620	0.600	0.600	0.597	0.606	0.602	0.596	0.587	0.596	0.601	0.009	0.026	120.223	0.026
Styrene	0.500	0.491	0.498	0.485	0.494	0.490	0.487	0.491	0.478	0.485	0.490	0.008	0.022	97.933	0.022
1,1,2,2-Tetrachloroethane	0.500	0.544	0.529	0.527	0.516	0.523	0.519	0.524	0.507	0.514	0.522	0.011	0.031	104.401	0.031
4-Ethyltoluene	0.500	0.543	0.545	0.535	0.515	0.520	0.527	0.532	0.520	0.520	0.528	0.011	0.031	105.689	0.031
1,3,5-Trimethylbenzene	0.500	0.560	0.556	0.541	0.535	0.541	0.537	0.550	0.539	0.541	0.544	0.009	0.025	108.889	0.025
1,2,4-Trimethylbenzene	0.500	0.557	0.545	0.537	0.535	0.537	0.541	0.545	0.533	0.540	0.541	0.007	0.021	108.222	0.021
1,3-Dichlorobenzene	0.500	0.473	0.470	0.466	0.458	0.457	0.471	0.460	0.455	0.455	0.462	0.008	0.023	92.467	0.025
1,4-Dichlorobenzene	0.500	0.475	0.463	0.458	0.450	0.458	0.454	0.458	0.449	0.452	0.457	0.008	0.023	91.489	0.025
Benzyl chloride	0.500	0.440	0.430	0.430	0.425	0.426	0.421	0.432	0.419	0.419	0.427	0.008	0.021	85.356	0.026
1,2-Dichlorobenzene	0.500	0.566	0.571	0.563	0.547	0.559	0.554	0.559	0.552	0.560	0.557	0.010	0.028	111.356	0.031
1,2,4-Trichlorobenzene	0.500	0.400	0.434	0.421	0.416	0.409	0.396	0.483	0.462	0.359	0.419	0.038	0.109	83.867	0.130
Hexachlorobutadiene	0.500	0.436	0.478	0.473	0.469	0.468	0.461	0.515	0.527	0.423	0.477	0.034	0.098	95.333	0.101

Table 7 (con't.)

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9.2 Limit of Quantification

The Limit of Quantification (LOQ) is 1.0 part per billion by volume (ppbv) per compound listed in Table 7.

9.3 Surrogate Recoveries - Performance

The following list presents the surrogate recovery results for 8 batches of samples where

R = average percent recovery
n = 50
S = percent standard (sample) deviation
Q.C. sets: 2/9/91-7/11/91 inclusive

Surrogate	R	S	R+\-3S
Toluene-d8	100.7	2.10	94-107
Bromofluorobenzene	101.5	2.95	93-110
1,2-Dichloroethane-d4	95.8	3.67	85-107

10.0 References

10.1 Determination of Volatile Organic Compounds (VOCs) in Ambient Air using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis, TO-14, U.S. EPA, May, 1988

10.2 Development of a "Statement-of-Work (SOW) for the Analysis of Air Toxics at Superfund Sites" as Part of the Contract Laboratory Program (CLP), U.S. EPA

10.3 USEPA Contract Laboratory Program Statement of Work for Analysis of Ambient Air, Draft, U.S. EPA, Rev. IAIR01.2, July, 1991

10.4 "Calibration of Low Level Organic Compound Gas Calibration Standards and Cleanup Procedures in Stainless Steel Canisters", R.A. McAllister, J.Rice, R. Moore, D.P. Dayton, Radian Corporation, Research Triangle Park, N.C., May, 1990

10.5 "Model 2000/2010 Automated Concentrator & Sample Manifold - Operator Instruction Manual", ENTECH Laboratory Automation, June, 1990

10.6 "Practical Experience in Analysis of Organic Compounds in Ambient Air Using Canisters and Sorbents", PB90-263039, U.S. EPA, June, 1990

11.0 Provenance

This method was written by

Carrie Brown — Development Chemist

GC/MS Group Leader

Tech. Documentation Officer

Technical Director

It has been reviewed and accepted by

GC/MS Group Leader

Technical Director

APPENDIX TO METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR USING SUMMA PASSIVATED CANISTERS AND ANALYSIS BY GAS CHROMATOGRAPHY/ION TRAP MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 No change from TO14LL.SOP.

1.2 Table 1 indicates compounds and lists the limit of quantification (LOQ) in parts per billion by volume (ppbv).

TABLE 1
VOLATILE COMPOUNDS

TO-14 COMPOUND LIST	CAS #	LOQ[1] (ppbv)
Acetone	666-52-4	10
Benzene	71-43-2	1.0
Benzyl chloride	100-44-7	1.0
Bromomethane	74-83-9	1.0
2-Butanone	78-93-3	10
Carbon tetrachloride	56-23-5	1.0
Chloroethane	75-00-3	1.0
Chloroform	67-66-3	1.0
Chloromethane	74-87-3	1.0
3-Chloropropene (Allyl chloride)	107-05-1	1.0
1,2-Dibromoethane	106-93-4	1.0
1,2-Dichlorobenzene	95-50-1	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	106-46-7	1.0
Dichlorodifluoromethane	75-71-8	1.0
1,1-Dichloroethane	75-34-3	1.0
1,2-Dichloroethane	107-06-2	1.0
1,1-Dichloroethene	75-35-4	1.0
cis-1,2-Dichloroethene	156-60-5	1.0
1,2-Dichloropropane	78-87-5	1.0
1,2-Dichlorotetrafluoromethane	76-14-2	1.0
cis-1,3-Dichloropropene	10061-01-5	1.0
trans-1,3-Dichloropropene	10006-02-6	1.0

[1] LOQ = Limit of Quantification

TABLE 1 (con't.)

TO-14 COMPOUND LIST	CAS #	LOQ[1] (ppbv)
Ethylbenzene	100-41-4	1.0
4-Ethyltoluene	622-96-8	1.0
Hexachlorobutadiene	87-68-3	1.0
2-Hexanone	591-78-6	10
Methylene chloride	75-09-2	1.0
4-Methyl-2-pentanone	108-10-1	10
Styrene	100-42-5	1.0
1,1,2,2-Tetrachloroethane	79-34-5	1.0
Tetrachloroethene	127-18-4	1.0
Toluene	108-88-3	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
1,1,1-Trichloroethane	71-55-6	1.0
1,1,2-Trichloroethane	79-00-5	1.0
Trichloroethene	75-69-4	1.0
Trichlorofluoromethane	75-69-4	1.0
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1.0
1,2,4-Trimethylbenzene	95-63-6	1.0
1,3,5-Trimethylbenzene	108-67-8	1.0
Vinyl chloride	75-01-4	1.0
<u>total</u>-Xylenes	1330-20-7	1.0

[1] LOQ = Limit of Quantification

2.0 SUMMARY OF METHOD

2.1 No change from TO14LL.SOP.sop.

2.2 No change from TO14LL.SOP.sop.

2.3 No change from TO14LL.SOP.sop.

2.4 Quantification is by the internal standard technique with multiple three-point internal standard calibration curves providing response factors for most of the compounds of interest. Those compounds identified for which no analytical standard is available are estimated.

2.5 No change from TO14LL.SOP.sop.

3.0 INTERFERENCES

No change from TO14LL.sop.

4.0 APPARATUS AND MATERIALS

No change from TO14LL.sop.

5.0 REAGENTS

No change from TO14LL.sop.

6.0 SAMPLE COLLECTION , PRESERVATION, AND HANDLING

No change from TO14LL.sop.

7.0 PROCEDURE

7.1 Standard Preparation - No change from TO14LL.sop.

7.2 Analysis- No change from TO14LL.sop.

7.3 Calibration-

7.3.1 Prior to the analysis of standards, blanks and any samples, the GC/MS system must meet the mass spectral ion abundance criteria for 25 ng of the instrument performance check solution, bromofluorobenzene(BFB). The ion abundance criteria that must be met are given in Table 2.

TABLE 2
BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criterion
50	8.0 - 40.0% of mass 95
75	30.0 - 66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120.0 % of mass 95
175	4.0 - 9.0% of mass 174
176	Greater than 93.0% but less than 101.0% of mass 174
177	5.0 - 9.0% of mass 176

The instrument performance check solution must be analyzed initially and once per 12 hours of operation. The 12-hour time period for GC/MS instrument performance check begins at the injection of the BFB which is to be submitted as documentation of a compliant tune. The mass spectral ion abundance criteria for *p*-bromofluorobenzene must be met before any calibration standards, blanks, or samples are analyzed.

7.3.2 No change from TO14LL.sop.

7.3.3 No change from TO14LL.sop.

7.3.4 Analyze different volumes of each calibration standard (the diluted standard which is now in the SUMMA canister) to give three different concentrations and tabulate the area of the primary characteristic ion (as indicated in Table 4, below) against the concentration for each compound. The concentrations of the three standards will be 10.0, 5.0, and 2.0 ppbv nominal. (Concentrations cannot be further defined at this point because they are dependent on the initial concentration in the certified stock standard cylinders; see, also, Sections 7.3.2 and 8.2, above.) Calculate the response factors (RRFs) for each compound as follows:

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

where

A_x = Area of the characteristic ion for the compound to be measured (from Table 4)

A_{is} = Area of the characteristic ion for the specific internal standard (from Table 4)

C_{is} = Concentration of the internal standard (ppbv)

C_x = Concentration of the compound to be measured (ppbv)

7.3.5 No change from TO14LL.sop.

7.3.6 The following criteria must be met before samples are analyzed.

- The spectral ion abundance criteria presented in Table 2.0 must be met.
- The calibration routine detailed in Section 7.3.4, above, must have been performed.
- Alternatively, a continuing calibration using the (nominally 5.0 ppbv) standard may be performed, provided that the RRF values for the continuing calibration analytes are within 25.0% difference from the mean RRF values for the initial calibration analyses.
- Both initial and continuing calibration standards must include all analytes of interest.
- A method blank must be analyzed.

7.4 No change from TO14ll.sop.

7.5 No change from TO14LL.sop.

7.6 No change from TO14LL.sop.

8.0 QUALITY CONTROL

8.1 Instrumentation and Sample Canisters

8.1.1 No change from TO14LL.sop.

8.1.2 There must be an initial three point calibration or a continuing calibration meeting the criteria specified in 7.3.

8.1.3 No change from TO14LL.sop.

8.1.4 No change from TO14LL.sop.

8.1.5 No change from TO14LL.sop.

8.2 No change from TO14LL.sop.

8.3 No change from TO14LL.sop.

8.4 No change from TO14LL.sop.

8.5 No change from TO14LL.sop.

8.6 No change from TO14LL.sop.

8.7 No change from TO14LL.sop.

9.0 METHOD PERFORMANCE

No change from TO14LL.sop

10.0 REFERENCES

No change from TO14LL.sop.

11.0 PROVENANCE

This method appendix was written by

_____ Laboratory Manager

_____ Technical Documentation Officer

It has been reviewed and accepted by

_____ Technical Documentation Officer

_____ Organics Department Manager

GENERAL REQUIREMENTS FOR ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 This SOP summarizes the procedures used in quantitatively extracting volatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in the appropriate method sections.

1.2 Refer to the specific SOP of interest for further details.

2.0 SUMMARY OF METHOD

2.1 Semivolatiles, pesticides, and PCBs: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative method are met.

2.2 Volatiles: Refer to the specific SOP of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the method by the analysis of method blanks.

3.3 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500 mL K-D flasks). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific SOP of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific SOP of interest for a description of the solvents needed.

5.2 Stock Standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.2.1 Purgeable Stock Standards: Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.2.1.1 All standards must be replaced after one (1) month, or sooner if comparison with check standards indicates a problem.

5.2.2 Semivolatile Surrogate and Matrix Spike Stock Standards: Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone or methanol.

5.2.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These

solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.3 Surrogate Solutions: A surrogate solution (i.e., one or more chemically inert compounds not expected to occur in an environmental sample and similar, chemically, to the compounds of interest) should be added to each sample, blank and matrix spike sample just prior to extraction or processing. The recovery of the surrogates is used to monitor for unusual matrix effects, sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow; however, these compounds, or others that better correspond to the analyte group, may be used as well.

5.3.1 Base/neutral and acid surrogate solutions: The following are recommended surrogate solutions.

Base/Neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_5

5.3.1.1 Prepare, in methanol, a surrogate solution containing the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL for water and sediment/soil samples (low- and medium-level).

5.3.2 Organochlorine pesticide, organophosphorus pesticide, and herbicide surrogate solutions: The following are recommended surrogate solutions:

Organochlorine pesticides
Dibutylchlorendate (DBC)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

Organophosphorus pesticides
Triphenylphosphate (TPP)

Chlorinated Phenoxyacid Herbicides
Dichlorprop (DCP)

5.3.2.1 Prepare, in acetone or methanol, surrogate solutions containing the following compounds at the concentrations specified (in ug/mL):

Organochlorine Pesticides

Compound	Water	Soil
DBC	1.0	20
TCMX	2.0	40

Organophosphorus Pesticides

Compound	Water	Soil
TPP	15	30

Chlorinated Phenoxy Acid Herbicides

Compound	Water	Soil
DCP	10	10

5.3.3 Purgeable surrogate solution: The following are recommended surrogates for volatile organics.

Purgeable Organics
p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.3.3.1 Prepare, in methanol, (as described in Paragraph 5.2.1 or through secondary dilution of the stock standard) a solution containing the surrogate compounds at a concentration of 25 ug/mL.

5.4 Matrix spike solutions: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike mixtures. These compounds, or others that better correspond to the analyte group, may be used as well.

5.4.1 Base/neutral and acid matrix spike solution: Prepare, in methanol, a spike solution containing each of the following base/neutral compounds at 100 ug/mL and the acid compounds at 200 ug/mL for both water and sediment/soil samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3 -methylphenol
1,4-Dichlorobenzene	
N-Nitroso-di-n-propylamine	4-Nitrophenol

5.4.2 Organochlorine pesticide matrix spike solution: Prepare, in acetone or methanol, a spike solution that contains the following pesticides in the concentrations (in ug/mL) specified for water and sediment/soil.

Pesticide	Water	Soil
alpha-BHC	0.20	0.4
beta-BHC	0.50	1.0
Lindane (gamma-BHC)[1]	0.20	2.0
delta-BHC	0.25	0.5
Heptachlor[1]	0.20	2.0
Aldrin[1]	0.20	2.0
Hept. Epoxide	0.25	0.5
g-Chlordane	0.25	0.5
a-Chlordane	0.25	0.5
Endosulfan I	0.25	0.5
4,4'-DDE	0.30	0.6
Dieldrin[1]	0.50	5.0
Endrin[1]	0.50	5.0
4,4'-DDD	0.45	0.9
Endosulfan II	0.30	0.6
4,4'-DDT[1]	0.50	5.0
Endrin Aldehyde	0.60	1.2
Endo. Sulfate	0.40	0.8

5.4.3 Organophosphorus pesticide matrix spike solution: Prepare, in acetone or methanol, a spike solution containing the following pesticides in the concentrations (in ug/mL) specified for water and sediment/soil.

Pesticide	Water	Soil
Disulfoton	5.0	10.0
Methyl parathion	3.0	6.0
Thionazin	2.0	4.0
Parathion	2.5	5.0
Phorate	5.0	10.0

[1] Specified per methods 608 and 8080.

5.4.4 Chlorinated phenoxyacid herbicide matrix spike solution: Prepare, in acetone or methanol, a spike solution containing the following herbicides in the concentration (in ug/mL) specified for water and sediment/soil.

Herbicide	Water	Soil
2,4-D	2.5	2.5
2,4,5-TP (Silvex)	0.25	0.25
2,4,5-T	0.50	0.50

5.4.5 Purgeable matrix spike solution: Prepare, in methanol, a spike solution containing the following compounds at a concentration of 25 ug/mL.

Purgeable organics
1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be kept at $\leq$ 4° Celsius from the time of collection until extraction.

6.2 See the specific method for further description of sampling procedures and holding times.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables, organochlorine pesticides, organophosphorus pesticides, and chlorinated phenoxy acid herbicides must undergo solvent extraction prior to analysis. The method that should be used on a particular sample is highly dependent upon the physical characteristics of that sample. Appropriate surrogate solutions and, if necessary, matrix spike solutions are added to the sample prior to extraction for all four methods.

7.1.1 Aqueous samples: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted

using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.2 Soil/sediment samples: This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using Soxhlet or sonication. A known weight of sample is mixed with anhydrous sodium sulfate and solvent-extracted. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with analysis.

7.2 Volatile organic sample preparation

7.2.1 This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and for solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be fortified with surrogate solutions and, if required, with matrix spike solutions.

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of the method described above is followed directly by analysis. Samples prepared for semivolatile or pesticide/PCB analysis may, if necessary, undergo cleanup prior to analysis.

8.0 REFERENCES

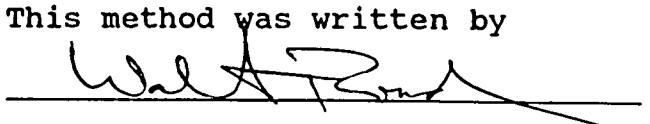
8.1 "Guidelines for Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; Final Rule and Proposed Rule", USEPA 40 CFR, Part 136, Oct. 26,1984.

8.2 "EPA Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewaters", EPA-600/4-82-057, July, 1982.

8.3 Test Methods for Evaluating Solid Waste, SW-846, Rev. 0, Sept, 1986.

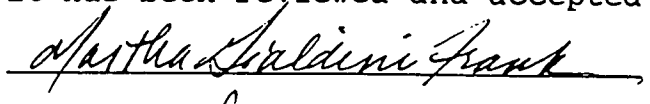
9.0 PROVENANCE

This method was written by



Technical Director

It has been reviewed and accepted by



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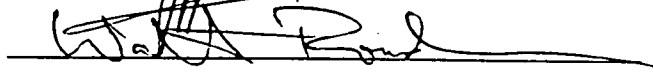

Technical Director

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 Scope and Application

1.1 This method describes a procedure for isolating organic compounds from aqueous samples as well as describing concentration techniques suitable for preparing the extract for the following determinative methods:

1) Semivolatiles (Base/Neutral/Acid Extractables) by GC/MS (625 or 8270).
2) Organochlorine pesticides and polychlorinated biphenyls (PCBs) by GC/ECD (608 or 8080).
3) Organophosphorus pesticides by GC/ECD or GC/NPD (8140).
4) Phenols by GC/FID (604 or 8040).
5) Phthalate esters by GC/FID (606 or 8060).
6) Polynuclear Aromatic Hydrocarbons by GC/FID (610 or 8100).

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step to be used.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method	Extraction pH Initial	Secondary	Exchange Solvent Required For Analysis	Exchange Solvent Required For Cleanup	Extract[1] Volume Required For Cleanup (mL)	Final Extract Volume For Analysis (mL)
608/8080	5-9	none	hexane	hexane	10	10
8140	6-8	none	hexane	hexane	1.0	10
625/8270	>11	<2	none	---	---	1.0
604/8040	<2	none	2-propanol	hexane	1.0	1.0
606/8060	as received	none	hexane	hexane	1.0	1.0
610/8100	as received	none	hexane	cyclohexane	1.0	1.0
612/8120	as received	none	hexane	hexane	1.0	1.0

[1] Suggested volume based on large column (approximately 10-20 g sorbent). Smaller columns may be appropriate depending upon cleanup technique.

3.0 INTERFERENCES

3.1 Refer to **General Requirements for Organic Extraction and Sample Preparation** SOP.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2L, with Teflon stopcock.

4.2 Pyrex powder funnel with acetone-rinsed glass wool pad at the bottom to retain sodium sulfate.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube - 10mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-021 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K- 569001-0219 or equivalent).

4.5.5 Tube heater/concentrator - (Kontes K72003 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - Glass, 2mL and 12mL capacity, with Teflon-lined screw-caps.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Wheaton bottles- 250mL, used for extract collection

4.9 Gas-tight syringe - 1mL.

4.10 Graduated cylinder - Pyrex, 1L.

4.11 Separatory funnel shaker table - Eberbach model 5900, or equivalent.

4.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc. (or equivalent) is suitable.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all procedures. Unless otherwise indicated, it is intended that all 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 ASTM Type II Water (ASTM D1193-99 (1983)): All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium hydroxide solution (10N), NaOH: Dissolve 40 g NaOH in water and dilute to 100 mL.

5.4 Sodium Sulfate (granular, anhydrous), Na_2SO_4: Purify by heating at 400°C for 4 hours in a shallow tray.

5.5 Sulfuric acid (1:1), H_2SO_4: Slowly add 50 mL of H_2SO_4

(sp. gr. 1.84) to 50 mL of water.

5.6 Extraction/exchange solvent: Methylene chloride, hexane, 2-propanol, cyclohexane (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be kept at ≤ 4° Celsius from the time of collection until extraction.

6.2 See the specific method for further description of sampling procedures and holding times.

7.0 PROCEDURE

7.1 Using a 1L graduated cylinder, measure 1 liter (nominal) of sample and transfer it to the separatory funnel; record the volume measured out to the nearest 5 mL. If high concentrations are anticipated, a smaller volume may be used and then diluted with water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see **General Requirements for Organic Extraction and Sample Preparation** SOP for details on the surrogate solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spike solution. For base/neutral-acid analysis, the amount added of the surrogates and matrix spike compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of <80% of the methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.6 Repeat the extraction two more times using fresh portions of solvent (Steps 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, as in 625/8270 extraction, adjust the pH of the aqueous phase to the pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Steps 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis, the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (*e.g.*, if, for regulatory purposes, the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10mL concentrator tube to a 500mL evaporation flask.

7.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot

water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.12 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchanged solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Step 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.13 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. The extract may be either further concentrated by using the techniques outlined in Step 7.14 or adjusted to 10.0 mL with the solvent last used.

7.14 If further concentration is indicated in Table 1 or if additional cleanup steps are to be performed on extracts for pesticide analysis, proceed as follows:

7.14.1 For further concentration: Add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Pre-wet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a tube heater/concentrator unit capable of maintaining a constant temperature at 80° to 90°C. Adjust the vertical position of the apparatus and the heater temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Synder column and rinse the flask and its lower joints into the concentrator tube with 0.2 ml of extraction

solvent. Adjust to the final volume indicated in Table 1.

7.14.2 Pesticides and/or PCBs, nitrogen blowdown technique: Place the concentrator vial in a warm water bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

> Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences.

The internal wall of the vial must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 mL. During evaporation, the vial solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. Adjust the extract volume to that required for cleanup or for the appropriate determinative method.

8.0 REFERENCES

8.1 "Guidelines for Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; Final Rule and Proposed Rule", USEPA 40 CFR, Part 136, Oct. 26,1984.

8.2 "EPA Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewaters", EPA-600/4-82-057, July, 1982.

8.3 Test Methods for Evaluating Solid Waste, SW-846, Rev. 0, July, 1982.

9.0 PROVENANCE

This method was written by

Walter Ford — Technical Director

It has been reviewed and accepted by

Martha Galvani Frank — Senior Chemist/Technical

[illegible] — Organics Extractions Group Leader

Walter Ford — Technical Director

FLORISIL CLEANUP - ORGANOCHLORINE PESTICIDES/PCB ANALYSIS

with Optional Cleanup Procedure for Sulfur

1.0 SCOPE AND APPLICATION

1.1 Cleanup of pesticide residues and/or PCBs is generally necessary for all aqueous samples except finished waters and drinking water. If particular circumstances require the use of a cleanup procedure, the analyst may use the procedures which follow. Additional procedures not documented here and subsequently developed must demonstrate at least an 80 percent recovery of all pesticides and/or PCBs analyzed and be capable of meeting the quality control criteria established in the specific analytical method.

2.0 SUMMARY OF METHOD

2.1 A glass column, packed with Florisil adsorbent and topped with sodium sulfate water adsorbent, is used to selectively remove polar compounds and/or other matrix interferences. Elution is effected with suitable solvents, leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

3.1 The analyst must demonstrate through the use of method blanks that the glassware, sorbent, solvents, and/or mercury do not contribute compounds which would interfere with the analysis of target analytes. In addition, it must be demonstrated that target compounds are not contributed by the cleanup procedure. Any target analytes so detected must be, at most, 0.5 times the reported detection limit.

3.2 Sulfur interferes with GC/ECD analysis.

4.0 APPARATUS AND MATERIALS

4.1 Cleanup column: 20 mm I.D., 200 mm length plus solvent reservoir and stopcock (Teflon).

4.2 Pipets - Disposable, Pasteur type.

4.3 Glass wool - hexane and ethyl ether rinsed.

4.4 Muffle Furnace.

4.5 Kuderna Danish (K-D) Apparatus.

- 4.5.1 Concentrator Tube - 10mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.
- 4.5.2 Evaporation flask - 500mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.
- 4.5.3 Snyder Column - Three-ball macro (Kontes K-50300-021 or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - Glass, 12mL with Teflon-lined screw cap.

4.8 Boiling chips: Solvent rinsed, approximately 10/40 mesh Teflon boiling chips.

4.9 Nitrogen evaporation device equipped with a heated bath that can be maintained at 35-40°C. N-Evap by Organomation Associates, Inc. (or equivalent).

4.10 Vortex mixer.

4.11 Wheaton bottles - glass, 500mL.

5.0 REAGENTS

5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchased activated at 1250°F (667°C). Store in glass containers with ground glass stoppers or foil-lined screw caps.

5.1.1 Activation of Florisil: Just before use, activate each batch at least 16 hrs. at 130°C in a glass container. Store before use in a tightly closed foil-lined container.

5.2 Hexane: Pesticide residue grade or equivalent. It is recommended that each lot of solvent used be analyzed to demonstrate that it is free of interference before use.

5.3 Ethyl ether: Pesticide residue grade or equivalent.

5.3.1 6% Ethyl ether in hexane (v/v): Eluent for Fraction # 1.

5.3.2 15% Ethyl ether in hexane (v/v): Eluent for Fraction # 2.

5.3.3 50% Ethyl ether in hexane (v/v): Eluent for Fraction # 3.

5.4 Sodium Sulfate (Na_2SO_4), granular anhydrous: Reagent grade, purified by heating in a muffle furnace at 400°C for 4 hours. Store in tightly capped glass jars.

5.5 Mercury: Triple distilled, for sulfur cleanup.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 N/A

7.0 PROCEDURE

Florisil Column Cleanup

7.1 The sample extract volume, following Kuderna-Danish concentration, should be 5-10 mL. The solvent should be hexane following solvent exchange from methylene chloride (see **Separatory Funnel Liquid-Liquid Extraction SOP**).

7.2 Add a weight of Florisil (nominimally 20 g) to the cleanup column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the cleanup column. Discard the eluate.

7.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube or 12mL vial to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.4 Drain the column into the 500mL Wheaton bottle until the sodium sulfate layer is **almost** exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) using a drip rate of about 5 mL/min. This is Fraction # 1. Remove the 500mL Wheaton bottle and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v), collecting the eluate. This is Fraction # 2. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v), again collecting the eluate. This is Fraction # 3.

7.5 Concentrate the combined extracts to 10 mL by the Kuderna-Danish technique. Table 1 lists the priority pollutant target compounds and their distribution in the three fractions collected.

Table 1[2]

Compound	Percent Recovery by Fraction 1	2	3
Aldrin	100		
a-BHC	100		
b-BHC	97		
d-BHC	98		
g-BHC (Lindane)	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

7.6 If additional extract concentration below 10 mL is needed for analysis, proceed to Nitrogen Blowdown technique.

7.6.1 Nitrogen Blowdown technique (taken from ASTM Method D 3086) - Place the concentrator tube with an open mini-Snyder column attached in a heating bath (30 to 35°C) and evaporate the extract to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

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[2] From USEPA 40 CFR, Part 136, Oct. 26, 1984, Method 608.

Caution: New plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

7.7 Store the extract at $\leq$ 4°C in the dark until ready for analysis.

Sulfur Removal

7.8 Sulfur contamination will cause a rise in the baseline of the chromatogram that may interfere with the analyses of the early eluting pesticides. If crystals of sulfur are suspected, proceed to sulfur cleanup. Sample analyses showing the presence of sulfur are not acceptable and must be cleaned up and reanalyzed.

7.9 Mercury is a highly toxic metal and, therefore, must be used with great care. Prior to using mercury, the analyst must become acquainted with the proper handling and cleanup techniques.

7.2.1 Add one to three drops of mercury to each hexane extract in a clean vial. (Prolonged mixing may be required. If so, use a vortex mixer.) Tighten the top on the vial and agitate the sample for 2 minutes. Decant to remove all solid mercuric sulfide precipitate and any remaining liquid mercury.

7.2.2 If the mercury turns black, repeat sulfur removal as necessary.

7.2.3 Proceed to analysis of extract.

7.2.4 Dispose of the mercury waste properly per the **Waste Disposal** SOP.

8.0 QUALITY CONTROL

8.1 Column Performance Check: Every lot number of Florisil must be tested by the following procedure prior to use in sample cleanup. Place 1.0 mL of organochlorine pesticide Level 3 standard (in hexane), midpoint concentration, onto the top of a washed Florisil column. Follow the procedures in 7.2-7.6. The recovery of each analyte must be determined for evaluation and reporting purposes. The lot of Florisil is acceptable if all pesticides are recovered at 80 to 110 percent and if no peaks interfere with the target analytes.

9.0 REFERENCES

9.1 "Guidelines for Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; Final Rule and Proposed Rule", USEPA Method 608, 40CFR, Part 136, Oct. 26, 1984.

9.2 Test Methods for Evaluating Solid Waste, SW-846. Rev. 0, Sept. 1986.

10.0 PROVENANCE

This method was written by:

_____ Organic Extractions Group Leader

_____ Technical Director

It has been reviewed and accepted by:

_____ Senior Chemist/Technical

_____ Organic Extractions Group Leader

_____ Technical Director

METHOD FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBS BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTION (GC/ECD)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs) and is based upon procedures defined in EPA Method 8080. Table 1 indicates compounds that may be determined by this method and lists the Limit of Quantification (LOQ) for an aqueous sample, and the EPA Method Detection Limit.

2.0 SUMMARY OF METHOD

2.1 This method provides for gas chromatographic analysis of certain organochlorine pesticides and PCBs with an Electron Capture Detector (ECD). Prior to use of this method, appropriate sampling and extraction techniques must be used. The final sample extract is injected into a gas chromatograph (GC) and the compounds in the GC effluent are detected by an ECD.

2.2 The sensitivity of this method depends on the level of interferences as well as on instrumental limitations. If interferences prevent detection of the analytes of interest, various cleanup procedures may be used to try and reduce the level of interferences.

TABLE I
CHLORINATED PESTICIDES & PCBS

	CAS #	LOQ[1] (ug/L)	EPA MDL[2] (ug/L)
Aldrin	309-00-2	0.05	0.004
Alpha-BHC	319-84-6	0.05	0.003
Beta-BHC	319-85-7	0.05	0.006
Delta-BHC	319-86-8	0.05	0.009
Gamma-BHC (Lindane)	58-89-8	0.05	0.004
Chlordane (technical)	57-74-9	0.50	0.014
4,4'-DDD	72-54-8	0.10	0.011
4,4'-DDE	72-55-9	0.10	0.004
4,4'-DDT	50-29-3	0.10	0.012
Dieldrin	60-57-1	0.10	0.002
Alpha-Endosulfan	959-98-9	0.05	0.014
Beta-Endosulfan	33213-65-9	0.10	0.004
Endosulfan sulfate	1031-07-08	0.10	0.066
Endrin	72-20-8	0.10	0.006
Endrin Aldehyde	7421-93-4	0.10	0.023
Heptachlor	76-44-8	0.05	0.003
Heptachlor Epoxide	1024-57-3	0.05	0.083
Isodrin[3]	465-73-6	0.05	nd
Kepone[3]	143-50-0	0.10	nd
Methoxychlor	72-43-5	0.50	0.176
Toxaphene	8001-35-2	1.0	0.24
PCB-1016	12674-11-2	0.50	nd
PCB-1221	11104-28-2	0.50	nd
PCB-1232	11141-16-5	0.50	nd
PCB-1242	53469-21-9	0.50	0.065
PCB-1248	12672-29-6	0.50	nd
PCB-1254	11097-69-1	1.0	nd
PCB-1260	11096-82-5	1.0	nd

[1] LOQ = Limit of Quantification
[2] MDL = Method Detection Limit specified by EPA Method 8080, SW-846, Rev. 0, Sept., 1986. The laboratory has established MDLs in laboratory reagent water for all these parameters; see Section 11.0 **Method Performance.**
[3] Additional compound analyzed as part of the Appendix IX regulated compounds list.

3.0 INTERFERENCES

3.1 The use of wide or narrow bore capillary columns, which give superior resolution over packed columns, is recommended. A second column with differing polarity from the first will frequently eliminate some interferences and is necessary for confirmation if GC/MS is not used.

3.2 PCBs in the sample may interfere with accurate identification and quantification of individual pesticides.

3.3 Sulfur in the extract will interfere with identification and quantification of some pesticides and PCBs. Sulfur must be removed from the extract. A method for sulfur cleanup is discussed in the SOP, **Florisil Cleanup - Organochlorine Pesticides/PCB Analysis with Optional Cleanup Procedure for Sulfur.**

3.4 Polar compounds, including certain pesticides, can be removed or reduced by using florisil column chromatography. PCBs may be separated from other organochlorine pesticides by column chromatography on silicic acid. Many pesticides may be fractionated into groups using florisil column chromatography.

4.0 MATERIALS

4.1 Vials - Both amber and clear borosilicate glass, with Teflon-lined caps, 2mL to 20mL, for the storage of standards and extracts.

4.2 Balance - Analytical, capable of accurately weighing 0.0001g.

4.3 Gas chromatograph- An analytical system complete with on-column injectors capable of split-splitless injections onto capillary columns, programmable oven temperatures, and equipped with Ni^{63} Electron Capture Detectors. An autosampler capable of 1 to 5 uL injections is highly recommended.

4.4 Chromatographic data system - Capable of measuring peak area or peak height. A system with the ability to generate external standard reports and calculate responses based on linear regression of a standard curve

is required.

4.5 Capillary columns- Capable of resolving all the single component pesticides. A second, confirmation, column is also needed. This column should differ in polarity to the extent that the pesticide will have a different elution order and or retention times from the first column.

4.6 See EPA SW-846 Methods for a list of additional materials.

5.0 REAGENTS

5.1 Stock standard solutions- These can be purchased or formulated in the lab from neat pesticide sources. All standards should be traceable to EPA reference standards or be certified by the manufacturer.

5.2 Calibration standards - As many as five concentration levels are prepared from the stock standard solutions to give final concentrations covering the linear range of the instruments. A list of standards in component table form is appended to this document, as part of the sample data package produced by the Nelson Analytical Chromatography software.

5.5 See EPA SW-846 Methods for a complete list of reagents.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sample extracts are stored at $\leq$ 4° Celsius until analysis. Extracts are to be completely analyzed within 40 days of the date of extraction.

7.0 EXTRACTION AND EXTRACT CLEANUP

See **Separatory Funnel Liquid-Liquid Extraction** and **Florisil Cleanup - Organochlorine Pesticides/PCB Analysis.**

8.0 SAMPLE ANALYSIS

8.1 Gas Chromatography Conditions:

Column 1: 0.32mm X 60m X 0.5um, Rtx-5 or equivalent. Hydrogen carrier gas set to optimal linear velocity (40cm/sec.) using methylene chloride vapor injected at the highest column temperature used in the oven program.

Column 2: 0.32mm X 60m X 0.5um, Rtx-35 or equivalent. Same carrier conditions as for column 1.

The gas chromatograph (GC) oven should be programmed to obtain maximum peak resolution for all compounds of interest. Adjacent peaks must be 75% resolved to baseline and 4,4'-DDT must have a retention time greater than 12.00 minutes.

8.2 Calibration Using External Standards Method - The initial calibration is performed using five concentration levels of the single component pesticides and a one point standard for all multi-component pesticides and PCBs. All method blanks and QC follow the calibration sequence. Samples are then analyzed followed by a continuing calibration standard. Method blanks and instrument blanks must demonstrate that the analytical system is free of any compounds of interest at the LOQ. If multi-component compounds are identified in a sample, the sample must be re-analyzed with a three way standard curve of the component of interest. The standards and their concentrations define the linear range for quantification. The correlation coefficient for each multi-level calibration must be 0.9900 or better if quantification is to be performed. The same criterion applies to the second column used for confirmation. The linearity of the calibration curve must be verified at the beginning of each analysis sequence and at least once every 12 hours using a continuing calibration standard. This continuing calibration standard is the mid-level standard used in the initial calibration sequence. The continuing calibration standard must agree with the initial mid-level standard with a calculated relative percent difference (%RSD) of less that 15 percent. If continuing calibration criteria are not met, GC maintenance procedures as outlined in Section 9.0 may be employed in order to regain continuing calibration criteria. Continued failure (after more than three attempts) to meet these criteria requires that a new calibration curve be analyzed.

8.3 Retention time windows must be set so that all standards run in an analysis sequence fall within the designated windows. Retention time windows are established prior to the analysis sequence whenever a column is changed, modified, or when instrument maintenance has been performed which will affect retention times. Three times the standard deviation of the absolute retention times for each Pesticide/PCB will be used to establish the

retention time window. For multi-response Pesticide/PCBs, the analyst should utilize the retention time window but should rely primarily on pattern recognition.

8.4 Column reactivity and active sites which cause breakdown of Endrin and 4,4'_DDT must not exceed 20 percent for either compound on either column. Evaluate the chromatogram for each Evaluation Mix B run throughout the sequence. The appearance of peaks in addition to the four main pesticide peaks indicates breakdown of Endrin and/or 4,4'-DDT. The breakdown is calculated using Equations 1 and 2. Whenever the breakdown criteria are exceeded, corrective action must be taken before analysis continues.

Equation 1:

$$\% \text{ Breakdown for } 4,4'\text{-DDT} = \frac{\text{Total DDT degradation peak area (DDE+DDD)}}{\text{Total DDT Peak Area (DDT+DDE+DDD)}} \times 100$$

Equation 2:

$$\% \text{ Breakdown for Endrin} = \frac{\text{(TEDPA)}}{\text{(TEPA)}} \times 100$$

where TEDPA = Total Endrin Degradation Peak Area
TEPA = Total Endrin Peak Area

8.5 Samples are analyzed in a set referred to as an analytical sequence. This sequence begins with a solvent blank to check the instrument for contamination. The first standard analyzed is the Evaluation B mix which is used to calculate the percent breakdown of Endrin and 4,4'-DDT. The initial calibration continues with the multi-level standards followed by the single point PCBs and multi-component pesticides. At this point the method is calibrated and if all QC criteria are met, the analysis of samples can begin. Samples are analyzed for the next 12 hours, followed by a Continuing Calibration Standard and the Evaluation B mix. The calibration curve can be used as long as the Continuing Calibration Standard and the Evaluation B mixture continue to meet all criteria.

8.5.1 Analytical Sequence

1. Solvent Blank
2. Evaluation B mix
3. Level 1 Std.
4. Level 2 Std.
5. Level 3 Std.
6. Level 4 Std.
7. Level 5 Std.
8. PCB stds.
9. " "
10. " "
11. " "
12. " "
13. Multi comp. pest Stds.
14. " " " "
15. Method blanks, QC or samples for a period not to exceed 12 hours.
16. Evaluation B mix
17. Continuing Calibration Std.
18. Samples or QC for a period not to exceed 12 hours.
19. Repeat sequence from 16 and ending with a continuing Calibration Std after the last sample.

8.6 Tentative confirmation occurs when a peak from a sample extract falls within the retention time window for that analyte as defined by the initial standard. Tentative I.D. of multi-component compounds will include a retention time match and a pattern match with the appropriate standard.

8.7 Confirmation occurs when the second column analysis of the same extract gives a retention time match and the quantification from both columns agrees with a maximum of 25 percent difference.

8.8 Calculations

8.8.1 External Standard Calibration

Nelson Analytical Chromatography provides for the generation of external standard reports, an example of which is provided with standard chromatograms at the end of this method. Also generated are standard component tables listing the standard concentration for each appropriate standard level, area response, retention time, retention time window, amount/area ratio, correlation coefficient, reference peak, linear regression equation and fit type. Typical component tables for Rtx-5 and Rtx-35 columns follow at the end of this section.

8.8.2 Method for calculating concentration follows.

$$\text{Concentration } (ng/m^3) = \frac{A_x * I_s * V_t * D}{A_s * V_i * V_s}$$

where A_x = Response for the analyte (area or height)
I_s = Amount of standard injected, ng
A_s = Response for external standard (area or height)
V_i = Volume of extract injected, uL
D = Dilution factor
V_t = Volume of total extract, uL
V_s = Volume of sample extracted, in liters

9.0 SUGGESTED GC SYSTEM MAINTENANCE

9.1 The GC instrument should have maintenance scheduled to minimize instrument breakdown and systematic problems which could lead to poor data. The following maintenance should be performed on a regular basis.

9.1.1 Change septa each week or when indicated.

9.1.2 Replace dirty injector liners with new deactivated ones when endrin or DDT breakdown begins to approach 20%

9.1.3 Check entire GC system for leaks which can cause elevated baselines on the ECD.

9.1.4 Use a guard column before the analytical column and replace the guard column when it is contaminated or when breakdown is detected.

9.1.5 Bake out the GC system at elevated temperatures when carry-over contamination is present.

9.1.6 Monitor the autosampler system to assure proper volume and injection.

10.0 QUALITY ASSURANCE: Pesticide/PCB Analysis

In order to assure the quality of the data, the following minimum requirements must be met.

10.1 An initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of the data. Ongoing data quality checks are compared with established performance criteria to determine if the results of the analyses meet the desired limits of acceptability.

10.2 Before processing any samples, it is necessary to demonstrate that there are no unacceptable levels of interferences from the analytical system. This is accomplished through the analysis of a method blank that is carried through all stages of the sample preparation and measurement steps.

10.3 For each set of twenty samples, a Laboratory Control Sample (LCS) is run. This is laboratory reagent water that has been fortified with the following levels of pesticides.

COMPOUND	CONCENTRATION (ug/L)	RECOVERY LIMITS
alpha-BHC	0.200	37%-134%
gamma-BHC	0.250	32%-127%
beta-BHC	0.500	17%-147%
Heptachlor	0.250	34%-111%
delta-BHC	0.250	19%-140%
Aldrin	0.250	42%-122%
Hept. Epoxide	0.250	37%-142%
Isodrin	0.300	29%-173%
g-Chlordane	0.250	20%-193%
a-Chlordane	0.250	27%-163%
Endosulfan I	0.250	45%-153%
4,4'-DDE	0.300	30%-145%
Dieldrin	0.250	36%-146%
Endrin	0.350	30%-147%
4,4'-DDD	0.450	31%-141%
Kepone	2.000	D-130%
Endosulfan II	0.300	D-202%
4,4'-DDT	0.500	25%-160%
Endrin Aldehyde	0.600	13%-145%
Endo. Sulfate	0.400	26%-144%
Methoxychlor	1.500	47%-160%

10.4 Each blank and sample that is analyzed is fortified with two surrogates, 2,4,5,6-Tetrachloro-*m*-xylene and Dibutylchlorendate, in order to monitor the extraction efficiency. The acceptable recovery limits are 50%-150% and 51%-123%, respectively.

10.5 For each set of twenty samples, a matrix spike and matrix spike duplicate are analyzed. These are a sample and a duplicate, representative of the sample group matrix, which are fortified with the analytes listed in 10.3.

10.6 At a minimum, required instrument QC should be in accordance with EPA 8080.

11.0 Method Performance

The method detection limits for this method are found in the MDL tables, attached. The method detection limits for these compounds were established by spiking a known concentration (*i.e.*, test concentration) of analyte into one liter of laboratory reagent water and carrying the mixture through the extraction procedure described in **Separatory Funnel Liquid-Liquid Extraction.**

12.0 References

12.1 Test Methods for Evaluation of Solid Waste, SW-846, Method 8080, Rev. 0, Sept., 1986.

13.0 Provenance

This method was written by

Tim Albrecht — GC/HPLC Group Leader

Martha Gialdini Frank — Senior Chemist/Technical

It has been reviewed and accepted by

Martha Gialdini Frank — Senior Chemist/Technical

Tim Albrecht — GC/HPLC Group Leader

Walt Ford — Technical Director

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 10/31/89

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: DB-5 60M, 0.32mm

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

__X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

__X__ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 QUANT

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
alpha-BHC	0.0067	0.007	0.009	0.007	0.008	0.008	0.005	0.007	0.007	0.001	0.004	108.7	0.004
beta-BHC	0.0187	0.022	0.021	0.019	0.014	0.015	0.013	0.017	0.017	0.003	0.011	92.4	0.012
gamma-BHC	0.0067	0.008	0.006	0.008	0.007	0.006	0.004	0.006	0.006	0.001	0.004	95.9	0.005
delta-BHC	0.0080	0.008	0.010	0.010	0.013	0.012	0.005	0.009	0.010	0.003	0.008	119.6	0.008
HEPTACHLOR	0.0130	0.013	0.011	0.010	0.011	0.010	0.009	0.011	0.011	0.001	0.004	82.4	0.005
ALDRIN	0.0210	0.016	0.015	0.012	0.014	0.012	0.010	0.016	0.014	0.002	0.007	64.6	0.011
HEPT. EPOXIDE	0.0130	0.015	0.016	0.016	0.014	0.016	0.011	0.016	0.015	0.002	0.006	114.3	0.006
g-CHLORDANE	0.0130	0.013	0.014	0.013	0.014	0.014	0.009	0.014	0.013	0.002	0.006	100.0	0.006
ENDOSULFAN I	0.0130	0.016	0.018	0.018	0.018	0.018	0.008	0.014	0.016	0.004	0.012	120.9	0.012
a-CHLORDANE	0.0130	0.015	0.015	0.015	0.015	0.014	0.009	0.014	0.014	0.002	0.007	106.6	0.007
4,4'-DDE	0.0160	0.016	0.015	0.014	0.015	0.016	0.010	0.016	0.015	0.002	0.007	91.1	0.007
DIELDRIN	0.0160	0.014	0.015	0.014	0.015	0.014	0.010	0.015	0.014	0.002	0.006	86.6	0.006
ENDRIN	0.0200	0.019	0.022	0.021	0.022	0.022	0.014	0.022	0.020	0.003	0.009	101.4	0.009
ENDOSULFAN II	0.0187	0.021	0.021	0.020	0.022	0.021	0.013	0.021	0.020	0.003	0.010	106.2	0.010
4,4'-DDD	0.0187	0.016	0.019	0.021	0.020	0.020	0.013	0.019	0.018	0.003	0.009	97.8	0.009
END. ALDEHYDE	0.0267	0.028	0.029	0.025	0.030	0.031	0.019	0.029	0.027	0.004	0.013	102.2	0.013
ENDO. SULFATE	0.0267	0.031	0.032	0.031	0.033	0.034	0.022	0.034	0.031	0.004	0.013	116.1	0.013
4,4'-DDT	0.0267	0.023	0.024	0.025	0.026	0.026	0.017	0.026	0.024	0.003	0.010	89.4	0.011

1) No provision exists in the above protocol for evaluation of the determined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 10/31/89

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: DB-1301 60M, 0.32mm;

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

__X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

__X__ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 CONFIRM

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
alpha-BHC	0.0067	0.007	0.007	0.007	0.007	0.007	0.005	0.007	0.007	0.001	0.002	100.2	0.002
beta-BHC	0.0187	0.015	0.016	0.013	0.015	0.014	0.010	0.016	0.014	0.002	0.007	75.6	0.009
gamma-BHC	0.0067	0.007	0.008	0.007	0.008	0.008	0.005	0.008	0.007	0.001	0.003	108.7	0.003
delta-BHC	0.0080	0.008	0.009	0.008	0.009	0.009	0.006	0.009	0.008	0.001	0.003	103.6	0.003
HEPTACHLOR	0.0130	0.014	0.012	0.014	0.011	0.015	0.007	0.015	0.013	0.003	0.009	96.7	0.009
ALDRIN	0.0210	0.019	0.018	0.014	0.017	0.015	0.015	0.015	0.016	0.002	0.006	76.9	0.008
HEPT. EPOXIDE	0.0130	0.015	0.016	0.015	0.016	0.016	0.016	0.010	0.015	0.002	0.007	114.3	0.007
g-CHLORDANE	0.0130	0.025	0.027	0.024	0.026	0.026	0.026	0.026	0.026	0.001	0.003	197.8	0.003
ENDOSULFAN I	0.0130	0.016	0.016	0.015	0.016	0.015	0.015	0.015	0.015	0.001	0.002	118.7	0.002
a-CHLORDANE	0.0130	0.019	0.020	0.019	0.020	0.019	0.013	0.019	0.018	0.002	0.008	141.8	0.008
4,4'-DDE	0.0160	0.018	0.018	0.017	0.018	0.017	0.012	0.018	0.017	0.002	0.007	105.4	0.007
DIELDRIN	0.0160	0.019	0.020	0.018	0.020	0.019	0.012	0.019	0.018	0.003	0.009	113.4	0.009
ENDRIN	0.0200	0.023	0.025	0.023	0.025	0.024	0.015	0.024	0.023	0.003	0.011	113.6	0.011
ENDOSULFAN II	0.0187	0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.021	0.000	0.000	112.3	0.000
4,4'-DDD	0.0187	0.023	0.023	0.022	0.025	0.023	0.023	0.023	0.023	0.001	0.003	123.8	0.003
END. ALDEHYDE	0.0267	0.040	0.036	0.035	0.039	0.035	0.047	0.039	0.039	0.004	0.013	145.0	0.013
ENDO. SULFATE	0.0267	0.032	0.033	0.032	0.034	0.033	0.020	0.032	0.031	0.005	0.015	115.6	0.015
4,4'-DDT	0.0267	0.019	0.014	0.013	0.017	0.013	0.008	0.013	0.014	0.003	0.011	51.9	0.021

1) No provision exists in the above protocol for evaluation of the determined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 01/29/90

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: Rtx-5, 60M, 0.32mm

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

___X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

___X___ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 QUANT

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
AROCHLOR 1221	1.0000	0.9756	0.9520	1.0676	1.1834	0.9932	0.8892	0.0915	0.8789	0.3597	1.1305	87.9	1.2862
AROCHLOR 1248	1.0000	1.2237	1.2933	1.1163	1.2463	1.1413	1.1619	1.2911	1.2106	0.0717	0.2253	121.1	0.2253
AROCHLOR 1260	1.0000	1.2790	1.3452	1.3323	1.4190	1.3507	1.3023	1.4006	1.3470	0.0499	0.1567	134.7	0.1567

1) No provision exists in the above protocol for evaluation of the determined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 03/30/89; 04/09/90

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: DB-5 60M, 0.32mm;

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

___X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

___X___ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 QUANT

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
AROCHLOR 1016	1.0000	0.847	0.945	1.140	0.971	1.140	1.040	1.130	1.030	0.114	0.359	103.0	0.359
AROCHLOR 1232	1.0000	0.948	0.971	0.913	0.965	0.924	0.922	0.939	0.940	0.022	0.070	94.0	0.074
AROCHLOR 1242	1.0000	1.047	0.988	0.973	1.052	0.879	0.970	0.954	0.980	0.059	0.185	98.0	0.189
AROCHLOR 1254	1.0000	1.036	1.025	1.096	1.086	1.115	1.087	1.110	1.079	0.035	0.111	107.9	0.111

1) No provision exists in the above protocol for evaluation of the determined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 11/13/89

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: DB-5 60M, 0.32mm

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

__X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

__X__ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 CONFIRM

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
TOXAPHENE	1.0000	0.832	0.849	0.898	0.890	0.982	0.980	0.958	0.913	0.061	0.193	91.3	0.212

1) No provision exists in the above protocol for evaluation of the detemined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 11/13/89

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: DB-1301 60M, 0.32mm

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

__X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

__X__ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 QUANT

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL	1)
TOXAPHENE	1.0000	0.935	0.943	0.983	1.112	0.922	1.212	0.930	1.005	0.113	0.354	100.5	0.354	

1) No provision exists in the above protocol for evaluation of the detemined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

Parameter: Organochlorine Pesticides and PCBs

Method(s)

Sample Prep/Extraction: 3510

Analysis: 8080

Date(s) of Analysis: 03/30/90

Analyst(s): Linda Kapala

Instrument Type: Varian Vista

Instrument Model: 6000

Instrument I.D.: 1

Instrument Configuration:

Column: Rtx-5 60M, 0.32mm

Referenced Protocol:

_____ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit".

__X__ Chapter One, Method Detection Limit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846".

_____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis".

Matrix:

__X__ Laboratory Reagent Water

_____ Aqueous Environmental Sample (specify origin):

_____ Soil/Solid Environmental Sample (specify origin):

_____ Other (specify):

ENVIRONMENTAL CONTROL TECHNOLOGY, INC.

METHOD DETECTION LIMIT

METHOD(S): 8080 QUANT

Parameter	Test Conc. ug/L	Replicate Recoveries, ug/L 1	2	3	4	5	6	7	Average	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
CHLORDANE (Technical)	1.0000	0.688	0.748	0.741	0.811	0.736	0.751	0.838	0.759	0.050	0.157	75.9	0.207

1) No provision exists in the above protocol for evaluation of the detemined MDL with respect to analyte recovery. An "Adjusted MDL", taking into account the Average Percent Recovery, is also given.

******* EXTERNAL STANDARD TABLE *******

********** 06-19-1991 19:14:51 Version 5.1 **********

* Sample Name: L3P1 Data File: 0:A56PS10 *

* Date: 06-10-1991 18:02:34 Method: 0:A56PTA 06-19-1991 19:14:28 # 1928*

* Interface: 10 Cycle#: 10 Operator TCA Channel#: 0 Vial#: N.A. *

* Starting Peak Width: 4 Threshold: 5 Area Threshold: 200 *

****

* Instrument Type: 3600-2 PEST/PCB Column Type: DB-5/Rtx-35 0.53 30m *

Solvent Description: H2 Holdup 2.5min.P=14.5 V=42.1 *

* Conditions: 160H2TO240@8H1TO260@10H2TO290@15H6 INJ=240 DET=290 *

Detector 0: R1 at4 320 Detector 1: R1 at4 320 *

* Misc. Information: *

****

Starting Delay: 0.00 Ending retention time: 40.00

Area reject: 2000 One sample per 0.400 sec.

Amount injected: 1.00 Dilution factor: 1.00

Sample Weight: 1.00000

PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in ug/mL	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT	BL	REF PEAK	% DELTA RET TIME	CONC/AREA
3	11.667	TCMX	0.2978	16.3009%	669602	293034	2.3	1	0	0	4.4469E-07
5	12.873		0.0000	0.0000%	8940	3874	2.3	1			0.0000E+00
6	13.187	alpha-BHC	0.0285	1.5629%	89425	40146	2.2	1	0	0	3.1926E-07
8	14.153	beta-BHC	0.0687	3.7616%	93046	38344	2.4	1	0	0	7.3848E-07
9	14.460	gamma-BHC	0.0356	1.9467%	122685	50774	2.4	1	0	0	2.8985E-07
11	15.320	delta-BHC	0.0340	1.8615%	115235	46401	2.5	1	0	0	2.9508E-07
12	15.767		0.0000	0.0000%	5221	2082	2.5	1			0.0000E+00
13	15.940		0.0000	0.0000%	3290	1383	2.4	1			0.0000E+00
15	17.327	Heptachlor	0.0370	2.0254%	99232	36471	2.7	1	0	0	3.7284E-07
18	18.747	Aldrin	0.0358	1.9595%	136181	51410	2.6	1	0	0	2.6285E-07
19	19.927	Isodrin	0.0428	2.3450%	128419	47582	2.7	1	0	0	3.3356E-07
20	20.293	Hept. Epoxide	0.0352	1.9285%	102368	38219	2.7	1	0	0	3.4412E-07
22	21.227	g-Chlordane	0.0351	1.9221%	114002	41669	2.7	2	0	0	3.0798E-07
23	21.767	Endosulfan I	0.0374	2.0448%	128731	43429	3.0	2	0	0	2.9015E-07
24	21.827	a-Chlordane	0.0335	1.8330%	112342	42499	2.6	2	0	0	2.9805E-07
25	22.473	4,4'-DDE	0.0427	2.3360%	136952	51921	2.6	1	0	0	3.1159E-07
26	22.793	Dieldrin	0.0333	1.8256%	92159	32487	2.8	1	0	0	3.6185E-07
28	23.687	Endrin	0.0504	2.7618%	94433	32354	2.9	1	0	0	5.3424E-07
29	24.020	Endosulfan II	0.0428	2.3451%	111076	39580	2.8	2	0	0	3.8566E-07
30	24.127	4,4'-DDD	0.0583	3.1938%	110360	40471	2.7	3	0	0	5.2864E-07
33	24.687	Endrin Aldehyde	0.0853	4.6705%	155705	58872	2.6	1	0	0	5.4794E-07
34	24.960	Kepone	0.2841	15.5517%	443746	173335	2.6	1	0	0	6.4019E-07
35	25.413	Endosulfan Sulfate	0.0649	3.5515%	93031	42307	2.2	2	0	0	6.9735E-07
36	25.467	4,4'-DDT	0.0588	3.2200%	131930	52758	2.5	2	0	0	4.4585E-07
39	26.633		0.0000	0.0000%	8403	2473	3.4	1			0.0000E+00
41	27.007	Endrin Ketone	0.0549	3.0029%	134329	52384	2.6	2	0	0	4.0836E-07
42	27.087	Methoxychlor	0.1873	10.2546%	86642	34468	2.5	2	0	0	2.1620E-06
44	27.820		0.0000	0.0000%	8870	3417	2.6	1			0.0000E+00
46	28.167	DBC	0.1424	7.7948%	262583	96629	2.7	1	0	0	5.4226E-07
48	29.000		0.0000	0.0000%	2156	733	2.9	1			0.0000E+00

TOTAL AMOUNT = 1.8267

Method file name: O:A56PTA
Default Sample Name: PEST/PCB'S Analysis on 3600-2 GC
Operator: TCA Date-time: 06-19-1991 17:12:13 version: 1927

ACQUISITION PARAMETERS

SINGLE OR DUAL CHANNEL (1 OR 2)	1.00
RUN TIME (minutes)	40.00
END TIME FOR PLOTS (default=RUN TIME)	40.00
SOLVENT DELAY TIME (minutes)	0.00
PEAK DETECTION THRESHOLD (microv/sec)	5.00
Area Threshold	200.00
MINIMUM PEAK WIDTH (seconds)	4.00
TIME FOR ONE SAMPLE (seconds)	0.40
NUMBER OF REAL TIME CRT PAGES TO PLOT (0 TO 99)	1.00
REAL TIME PLOT FULL SCALE FOR CH.0 (millivolts)	100.00
REAL TIME FULL SCALE FOR CH.1 (millivolts)	100.00
HARD COPY REAL TIME PLOT	NO
AUTO ZERO REAL TIME PLOT	NO
Pre Version 4 method	YES
RECORD AREA TABLES ON DISK	NO
RECORD RAW DATA	NO
NUMBER OF CRT PAGES FOR REPLOT (1 TO 99)	4.00
VERTICAL SCALE FACTOR FOR REPLOT (units of largest peak)	0.00
OFFSET FOR THE REPLOT (millivolts)	0.00
PUT NAMES ON REPLOT?	YES
PRINT AREA PERCENT REPORT	NO
PRINT EXTERNAL STANDARD REPORT	YES
PRINT INTERNAL STANDARD REPORT	NO
FINAL REPORT AREA REJECT (microvolt-sec)	2000.00
LINK TO USER PROGRAM	NO
FORCE DROP LINE INTEGRATION	NO
FORCE COMMON BASE LINE	NO
FULL SCALE RANGE FOR A.D.C. (3=1VOLT, 1=2VOLT, 0=10VOLT)	0.00
AREA REJECT FOR REFERENCE PEAKS?	%1000000000.00
% RET TIME WINDOW FOR REFERENCE PEAKS	0.50
RET TIME WINDOW IN SECONDS FOR REF. PEAKS	0.00
AREA OR PEAK HEIGHT QUANTITATION (0 OR 1)	0.00
PRINT GROUP REPORT	NO
NUMBER OF CALIBRATION LEVELS (1 TO 6)	5.00
LIST COMPONENTS NOT FOUND IN SAMPLE?	NO
INCLUDE UNKNOWN PEAKS IN REPORTS?	YES
UPDATE RESPONSE FACTORS WITH REPLACEMENT (0) OR AVERAGE (1)	1.00
DEFAULT DILUTION FACTOR	1.00
DEFAULT SAMPLE WEIGHT	1.00
DEFAULT AMOUNT INJECTED	1.00
DEFAULT AMOUNT OF INTERNAL STANDARD	1.00
PRINT GPC MW DISTRIBUTION	NO
PRINT SIMULATED DISTILLATION REPORT	NO

Response factor for unknowns= 0.0000E+00
Component Units = ug/mL

\ TCMX Ret. Time = 11.67 min. Pit.type = 2
Ref. peak: DBC Int Std: TCMX Window size: 0.6%
AREA = 2.2487D+06 * AMOUNT + 0.0000D+00

Correlation (R squared) = 0.9992

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	98176	0.04000	0.00000041
2	289804	0.12000	0.00000041
3	461308	0.20000	0.00000043
4	649448	0.30000	0.00000046
5	905782	0.40000	0.00000044

2 alpha-BHC Ret. Time = 13.19 min. Fit.type = 2
Ref. peak: DBC Int Std: alpha-BHC Window size: 0.6%
AREA = 3.1322D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9995

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12493	0.00400	0.00000032
2	39486	0.01200	0.00000030
3	64318	0.02000	0.00000031
4	91050	0.03000	0.00000033
5	126074	0.04000	0.00000032

3 beta-BHC Ret. Time = 14.15 min. Fit.type = 2
Ref. peak: DBC Int Std: beta-BHC Window size: 0.6%
AREA = 1.3541D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9992

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	14444	0.01000	0.00000069
2	43415	0.03000	0.00000069
3	69998	0.05000	0.00000071
4	97835	0.07500	0.00000077
5	136134	0.10000	0.00000073

4 gamma-BHC Ret. Time = 14.46 min. Fit.type = 2
Ref. peak: DBC Int Std: gamma-BHC Window size: 0.5%
AREA = 3.4500D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9994

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	17267	0.00500	0.00000029
2	54722	0.01500	0.00000027
3	88929	0.02500	0.00000028
4	125104	0.03750	0.00000030
5	173473	0.05000	0.00000029

5 delta-BHC Ret. Time = 15.32 min. Fit.type = 2
Ref. peak: DBC Int Std: delta-BHC Window size: 0.5%
AREA = 3.3889D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9994

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	15904	0.00500	0.00000031
2	52417	0.01500	0.00000029
3	86376	0.02500	0.00000029
4	122264	0.03750	0.00000031
5	171865	0.05000	0.00000029

6 Heptachlor Ret. Time = 17.33 min. Fit.type = 2
Ref. peak: DBC Int Std: Heptachlor Window size: 0.5%
AREA = 2.6821D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9990

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12952	0.00500	0.00000039
2	42568	0.01500	0.00000035
3	69370	0.02500	0.00000036

4	95984	0.03750	0.00000039
5	135741	0.05000	0.00000037

7 Aldrin Ret. Time = 18.75 min. Fit.type = 2
Ref. peak: DBC Int Std: Aldrin Window size: 0.6%
AREA = 3.8045D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9993

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	19635	0.00500	0.00000025
2	60841	0.01500	0.00000025
3	98327	0.02500	0.00000025
4	137657	0.03750	0.00000027
5	191180	0.05000	0.00000026

8 Isodrin Ret. Time = 19.92 min. Fit.type = 2
Ref. peak: DBC Int Std: Isodrin Window size: 0.6%
AREA = 2.9979D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9993

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	18675	0.00600	0.00000032
2	57020	0.01800	0.00000032
3	91745	0.03000	0.00000033
4	129953	0.04500	0.00000035
5	181704	0.06000	0.00000033

9 Hept. Epoxide Ret. Time = 20.29 min. Fit.type = 2
Ref. peak: DBC Int Std: Hept. Epoxide Window size: 0.5%
AREA = 2.9059D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9992

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	14645	0.00500	0.00000034
2	44800	0.01500	0.00000033
3	74675	0.02500	0.00000033
4	104180	0.03750	0.00000036
5	147504	0.05000	0.00000034

10 g-Chlordane Ret. Time = 21.23 min. Fit.type = 2
Ref. peak: DBC Int Std: g-Chlordane Window size: 0.6%
AREA = 3.2469D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9992

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	16552	0.00500	0.00000030
2	50953	0.01500	0.00000029
3	83297	0.02500	0.00000030
4	116482	0.03750	0.00000032
5	164536	0.05000	0.00000030

11 Endosulfan I Ret. Time = 21.77 min. Fit.type = 2
Ref. peak: DBC Int Std: Endosulfan I Window size: 0.3%
AREA = 3.4465D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9981

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	17711	0.00500	0.00000028
2	54437	0.01500	0.00000028
3	90915	0.02500	0.00000027
4	120810	0.03750	0.00000031
5	175400	0.05000	0.00000029

12 a-Chlordane Ret. Time = 21.83 min. Fit.type = 2
Ref. peak: DBC Int Std: a-Chlordane Window size: 0.3%

AREA = 3.3552D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9997

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	17063	0.00500	0.00000029
2	52704	0.01500	0.00000028
3	83758	0.02500	0.00000030
4	123182	0.03750	0.00000030
5	169054	0.05000	0.00000030

13 4,4'-DDE Ret. Time = 22.47 min. Fit.type = 2
Ref. peak: DBC Int Std: 4,4'-DDE Window size: 0.6%
AREA = 3.2094D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9987

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	19227	0.00600	0.00000031
2	59617	0.01800	0.00000030
3	99851	0.03000	0.00000030
4	136567	0.04500	0.00000033
5	196116	0.06000	0.00000031

14 Dieldrin Ret. Time = 22.79 min. Fit.type = 2
Ref. peak: DBC Int Std: Dieldrin Window size: 0.6%
AREA = 2.7636D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9987

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12979	0.00500	0.00000039
2	42526	0.01500	0.00000035
3	71057	0.02500	0.00000035
4	97840	0.03750	0.00000038
5	141303	0.05000	0.00000035

15 Endrin Ret. Time = 23.69 min. Fit.type = 2
Ref. peak: DBC Int Std: Endrin Window size: 0.6%
AREA = 1.8718D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9978

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12812	0.00700	0.00000055
2	39894	0.02100	0.00000053
3	67302	0.03500	0.00000052
4	91150	0.05250	0.00000058
5	135328	0.07000	0.00000052

16 Endosulfan II Ret. Time = 24.02 min. Fit.type = 2
Ref. peak: DBC Int Std: Endosulfan II Window size: 0.4%
AREA = 2.5930D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9986

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	15227	0.00600	0.00000039
2	47673	0.01800	0.00000038
3	80026	0.03000	0.00000037
4	110042	0.04500	0.00000041
5	159174	0.06000	0.00000038

17 4,4'-DDD Ret. Time = 24.13 min. Fit.type = 2
Ref. peak: DBC Int Std: Kepone Window size: 0.4%
AREA = 1.8916D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9982

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	15748	0.00900	0.00000057
2	51058	0.02700	0.00000053

3	88090	0.04500	0.00000051
4	119486	0.06750	0.00000056
5	175046	0.09000	0.00000051

18 Endrin Aldehyde Ret. Time = 24.69 min. Fit.type = 2
Ref. peak: DBC Int Std: Endrin Aldehyde Window size: 0.5%
AREA = 1.8250D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9990

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	21848	0.01200	0.00000055
2	69877	0.03600	0.00000052
3	106824	0.06000	0.00000056
4	157818	0.09000	0.00000057
5	223920	0.12000	0.00000054

19 Kepone Ret. Time = 24.96 min. Fit.type = 5
Ref. peak: DBC Int Std: Kepone Window size: 0.5%
AREA = 1.5883D+06 * AMOUNT + -7.4572D+03
Correlation (R squared) = 0.9982

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	56211	0.04000	0.00000071
2	187189	0.12000	0.00000064
3	305517	0.20000	0.00000065
4	450998	0.30000	0.00000067
5	646371	0.40000	0.00000062

20 Endosulfan Sulfate Ret. Time = 25.41 min. Fit.type = 2
Ref. peak: DBC Int Std: Endosulfan Sulfate Window size: 0.2%
AREA = 1.4340D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9982

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12095	0.01000	0.00000083
2	40771	0.03000	0.00000074
3	68344	0.05000	0.00000073
4	103407	0.07500	0.00000073
5	149083	0.10000	0.00000067

21 4,4'-DDT Ret. Time = 25.47 min. Fit.type = 2
Ref. peak: DBC Int Std: 4,4'-DDT Window size: 0.3%
AREA = 2.2429D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9989

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	18748	0.00800	0.00000043
2	57029	0.02400	0.00000042
3	93786	0.04000	0.00000043
4	128275	0.06000	0.00000047
5	181083	0.08000	0.00000044

22 Endrin Ketone Ret. Time = 27.01 min. Fit.type = 2
Ref. peak: DBC Int Std: Endrin Ketone Window size: 0.3%
AREA = 2.4488D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9992

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	18897	0.00800	0.00000042
2	60295	0.02400	0.00000040
3	101329	0.04000	0.00000039
4	140782	0.06000	0.00000043
5	198441	0.08000	0.00000040

23 Methoxychlor Ret. Time = 27.09 min. Fit.type = 2

Ref. peak: DBC Int Std: Methoxychlor Window size: 0.3%
AREA = 4.6253D+05 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9991

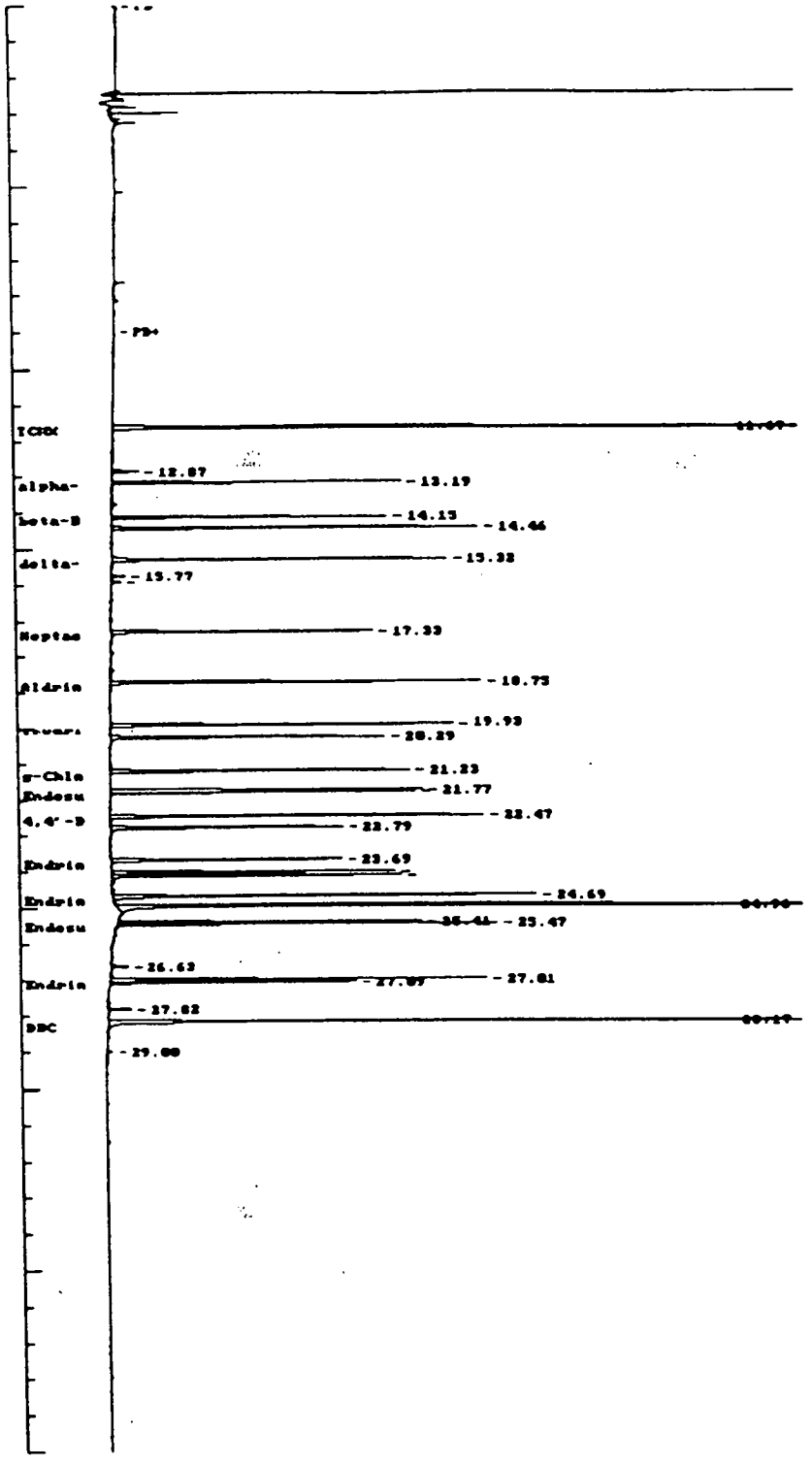
LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	12110	0.03000	0.00000248
2	41367	0.09000	0.00000218
3	68013	0.15000	0.00000221
4	100291	0.22500	0.00000224
5	142528	0.30000	0.00000210

24 DBC Ret. Time = 28.17 min. Fit.type = 2
Ref. peak: DBC Int Std: DBC Window size: 0.4%
AREA = 1.8441D+06 * AMOUNT + 0.0000D+00
Correlation (R squared) = 0.9987

LEVEL	AREA	AMOUNT	RATIO (amount/area)
1	35477	0.02000	0.00000056
2	114169	0.06000	0.00000053
3	191505	0.10000	0.00000052
4	261832	0.15000	0.00000057
5	375453	0.20000	0.00000053

Ev#	Time	Event	Description
1	0.00	PD-	Peak Detection (on/off)
2	9.00	PD+	Peak Detection (on/off)

Areas, times, and heights stored in: O:A56PS10.ATB
Data File = O:A56PS10.PTS Printed on 06-19-1991 at 17:32:28
Start time: 0.00 min. Stop time: 40.00 min. Offset: 0 mv.
Full Range: 100 millivolts



STANDARD OPERATING PROCEDURE
FOR
IDENTIFICATION AND QUANTITATION
OF POLYCHLORINATED BIPHENYLS (PCBs)

1.0 PURPOSE

The following procedures are to be used in the identification and quantitation of polychlorinated biphenyls (PCBs) by GC/ECD in water, soil, oil, and wipe matrices.

2.0 APPLICABILITY

This method is intended for use in conjunction with the SOPs entitled **Gas Chromatography - Polychlorinated Biphenyls (PCBs)** and **Method for the Determination of Organochlorine Pesticides and PCBs by Gas Chromatography/Electron Capture Detection (GC/ECD)**. A set of guidelines follows for the identification and quantitation of specific aroclors.

3.0 BACKGROUND

This procedure is applicable to the seven most common aroclors which were commercially produced until 1977. They are identified by a numerical sequence: 1016, 1221, 1232, 1242, 1248, 1254, and 1260. Except for 1016, the last two digits represent the percent chlorine contained in the mixture. The analysis of aroclors by GC/ECD produces a chromatogram containing a complex pattern of peaks. Each aroclor pattern is unique due to the specific mixture of congeners present at different concentrations. Environmental samples may contain aroclors which have undergone physical and/or chemical degradation; matrix interference present in this type of sample can make identification and quantitation difficult.

Calculations for the less common aroclors 1262, 1268, and polychlorinated terphenyls may be treated in a similar manner but are not specifically addressed in the procedures which follow.

4.0 RESPONSIBILITIES

4.1 Analyst - responsible for correctly identifying aroclors by pattern recognition and determining the level of concentration for the given analyte. When necessary, the presence of two or more aroclors requires calculation by the area subtraction method.

4.2 Reviewer - responsible for verifying the identification and quantitation performed by the analyst. The reviewer ensures the accuracy of any hand calculations performed and reviews the identifications made.

5.0 DEFINITIONS

5.1 Aroclor - trade name for any polychlorinated biphenyl (PCB) mixture identified by a four digit numerical designation.

5.2 Congener - one of 209 discrete chlorinated biphenyl compounds in which one to ten chlorine atoms are substituted on the biphenyl ring.

5.3 External Standard Table (EST) - a computer printout of information pertaining to the analysis.

5.3 Component peak - one of three to six chromatographic peaks chosen as characteristic of the aroclor and used in quantitation. It is identified by a four digit aroclor designation followed by Ci where i is the component peak number.

6.0 PROCEDURE

6.1 A method component table is developed for each analytical sequence from the nine standards analyzed at the beginning of the sequence. For each aroclor, three peaks are chosen to establish a calibration curve and each must have a height of at least 30% of the tallest peak in the aroclor. Generally, the same three peaks are chosen from sequence to sequence to provide consistency between analytical runs.

6.1.1 The calibration curve for each aroclor is comprised of the chosen component peaks at three concentration levels. The average retention time for a component peak is determined and entered into the method component table along with the component peak area for each concentration level. Linear regression analysis provides the correlation coefficient for each component peak within the method. The correlation coefficient must be greater than 0.9900 in order for the component peak to be used for quantitation.

6.2 The choice of alternate peaks for quantitation is restricted to those which meet the criteria for major peaks (peak height must be greater than 30% of the highest peak in the aroclor).

6.2.1 Determine if the concentration of each component peak used for quantitation is within 10% of the average value of the three peaks for that component. If one of the chosen peaks does not meet the 10% criterion, from one to nine alternate peaks are available depending upon the aroclor. After an alternate peak has been chosen and a new method developed, the sample is reprocessed and the new peak is evaluated in order to determine if it meets the 10% criterion.

6.3 Four general categories exist, each requiring the analyst to take a different action, in determining the presence and quantity of an aroclor within a sample:

6.3.1 A single aroclor is tentatively identified in the sample and the software correctly identifies all component peaks within the linear range of the calibration curve.

6.3.1.1 Compare the sample pattern to the aroclor standard patterns. If a match is evident, check the external standard table and note the retention times and concentrations of the component peaks in the sample. The concentration of each component peak used for quantitation must be within 10% of the average value of the three component peaks. If it is, use the average concentration to calculate the final concentration in the original sample.

6.3.2 An aroclor is suspected but the pattern is degraded. Generally, two situations predominate:

6.3.2.1 One or several component peaks appear degraded or are even missing, but the overall pattern is not diminished.

If any component peaks vary by more than 10% from the other two peaks, create another method with a different peak having a calculated concentration which is within the criteria specified (see 6.2).

6.3.2.2 Several major peaks are degraded, resulting in a localized region of the pattern having peak heights that are suppressed but still present.

Develop a method containing 6 peaks; 3 peaks from the verified region of the pattern and 3 peaks from the suppressed region of the pattern. Take the average of the 6 peaks so that the resultant concentration is the average of the verified and suppressed peaks.

6.3.3 The sample matrix may interfere with the overall pattern or a section of the pattern. When cleanup procedures fail to remove the interferences and there is not enough pattern to confirm the presence of an aroclor, dilute the sample. If the aroclor still cannot be positively identified at the elevated detection limit, mark the bench sheet "MI" to indicate matrix interference.

6.3.4 Environmental samples may contain a mixture of aroclors and it may be necessary to choose peaks for quantitation which are different than those normally used to establish a calibration curve. First, tentatively identify the mixture of aroclors present in the sample and the retention times of the characteristic component peaks. Select peaks from each aroclor which do not interfere with the other aroclor(s) present in the sample. In the event that this is not possible, a method of area subtraction is used to determine concentration. An example of the method is described below.

6.3.4.1 Consider a sample in which both 1254 and 1260 have been tentatively identified.

This example uses a standard containing 0.20 ug/mL each of 1254 and 1260 (see Appendix A, EST and chromatogram file ID2) as a "sample", the average concentration for 1260 as determined from the 1260 calibration curve is 0.2321 ug/mL. Note: the positive deviation from the theoretical value in this example is due to a slight peak area contribution of 1254 to 1260 in the standard. It is not normally present.

Since both 1254 and 1260 contain the same congener (although at different concentrations) at the retention time for 1254C1, the peak area for 1254C1 in the sample needs to be corrected for contribution from 1260.

Assuming that the standard calibration has been successful, linearity over the calibration range has been demonstrated. Choose the calibration standard nearest in concentration to the estimated sample concentration. In the example which follows, the 0.5 ug/mL 1254 and 1260 standards are used (see Appendix A for ESTs and chromatograms).

The determination of corrected component peak concentration is a three-step calculation as follows.

Step 1: Based upon the 1254Ci peak area and theoretical concentration for the 1260 standard, and the calculated concentration of 1260 in the sample, a peak area for the 1260 contribution to 1254Ci in the sample can be derived.

$$\frac{\text{Area}_{1260\ std}}{\text{Conc.}_{1260\ std}} = \frac{x_i}{\text{Conc.}_{1260\ sample}}$$

where:

x_i = peak area for 1260 contribution to 1254Ci in sample and i equals the component peak number

In this example,

$$\frac{60,529}{0.5\ ug/mL} = \frac{x_1}{0.2321\ ug/mL}$$

$x_1 = 28,098$

Step 2: Subtract x_i from the peak area for 1254Ci in the sample to obtain the corrected 1254Ci peak area.

$$Area_{1254Ci} - x_i = y_i$$

where:

y_i = corrected 1254Ci peak area and i equals the component peak number

In this example,

$$Area_{1254Ci} - x_1 = y_1$$

$$191,231 - 28,098 = y_1$$

$$y_1 = 163,133$$

Step 3: Based upon the 1254Ci peak area and the theoretical concentration from the 1254 calibration standard, calculate a new concentration for 1254Ci in the sample based upon y_i calculated in step 2.

$$\frac{Area_{1254Ci\ std}}{Conc._{1254Ci\ std}} = \frac{y_i}{z_i}$$

where: z_i = new concentration for 1254Ci in the sample and i equals the component peak number

In this example,

$$\frac{403,887}{0.5\ ug/mL} = \frac{163,133}{z_1}$$

$$z_1 = 0.2020\ ug/mL$$

Similarly for component peaks 2 and 3:

Component Peak #2:

$$\frac{228,862}{0.5 \text{ ug/mL}} = \frac{x_2}{0.2321 \text{ ug/mL}}$$

$x_2 = 106,238$

$395,886 - 106,238 = y_2$

$y_2 = 289,648$

$$\frac{721,103}{0.5 \text{ ug/mL}} = \frac{289,648}{z_2}$$

$z_2 = 0.2008$ ug/mL

Component Peak #3:

$$\frac{533,571}{0.5 \text{ ug/mL}} = \frac{x_3}{0.2321 \text{ ug/mL}}$$

$x_3 = 247,684$

$499,374 - 247,684 = y_3$

$y_3 = 251,690$

$$\frac{643,015}{0.5 \text{ ug/mL}} = \frac{251,690}{z_3}$$

$z_3 = 0.1957$ ug/mL

6.3.4.2 Finally, calculate the average concentration for 1254 in the sample:

$$\frac{z_1 + z_2 + \ldots z_n}{n} = \text{Avg.Conc.}_{1254}$$

where n = total number of component peaks

In this example,

$$\frac{0.2021 + 0.2008 + 0.1957}{3} = 0.1995 \text{ ug/mL}$$

The three concentrations should agree within 25% of the mean value. If they do not, choose other peaks which qualify. If the sample matrix or complexity of the aroclor mixture does not permit this, consult a supervisor before arriving at an estimated concentration. Such values should be flagged with an "E" according to the **SOP on Data Reporting Conventions.**

7.0 RECORDS

7.1 Chromatogram - produced for each sample with the aid of chromatography software.

7.2 External Standard Table - The chromatogram is accompanied by an external standard table which provides a record of the retention time, area count, and height of each peak found in the chromatogram. The analyst uses the external standard table and chromatogram for identification and quantitation of all aroclors. All calculations pertaining to the concentration of an aroclor and detection level for the sample are recorded on the chromatogram, EST, or on a separate calculation sheet, in black ink.

7.3 Calculation sheets - used in the area subtraction method. All calculations used to derive the concentration of an aroclor by this method are included with the chromatogram as a permanent record.

8.0 REFERENCES

8.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition.

8.2 Analytical Chemistry of PCBs; Erickson, Mitchell.D., Ann Arbor Science, 1986.

9.0 PROVENANCE

This method has been written by

Donald K. Ward _____ Chemist III

_____ Technical Director

Jane Hancock _____ QC Chemist

It has been read and approved by

Martha Waldron Frank _____ Technical Documentation Officer

_____ Group Leader

_____ Technical Director

***** EXTERNAL STANDARD TABLE *****

******************** 12-23-1992 09:06:41 Version 5.1 ********************

* Sample Name: AR1260/AR1254, 0.2[illegible]9/ML/0.2[illegible]6/ML Data File: [illegible]

* Date: 12-21-1992 18:55:05 Method: 0:PCBID 12-22-1992 09:04:2[illegible] [illegible]

* Interface: 2 Cycle#: 2 Operator DW Channel#: 1 Vial#: N.A.

* Starting Peak Width: 5 Threshold: 15 Area Threshold: 75[illegible]

****

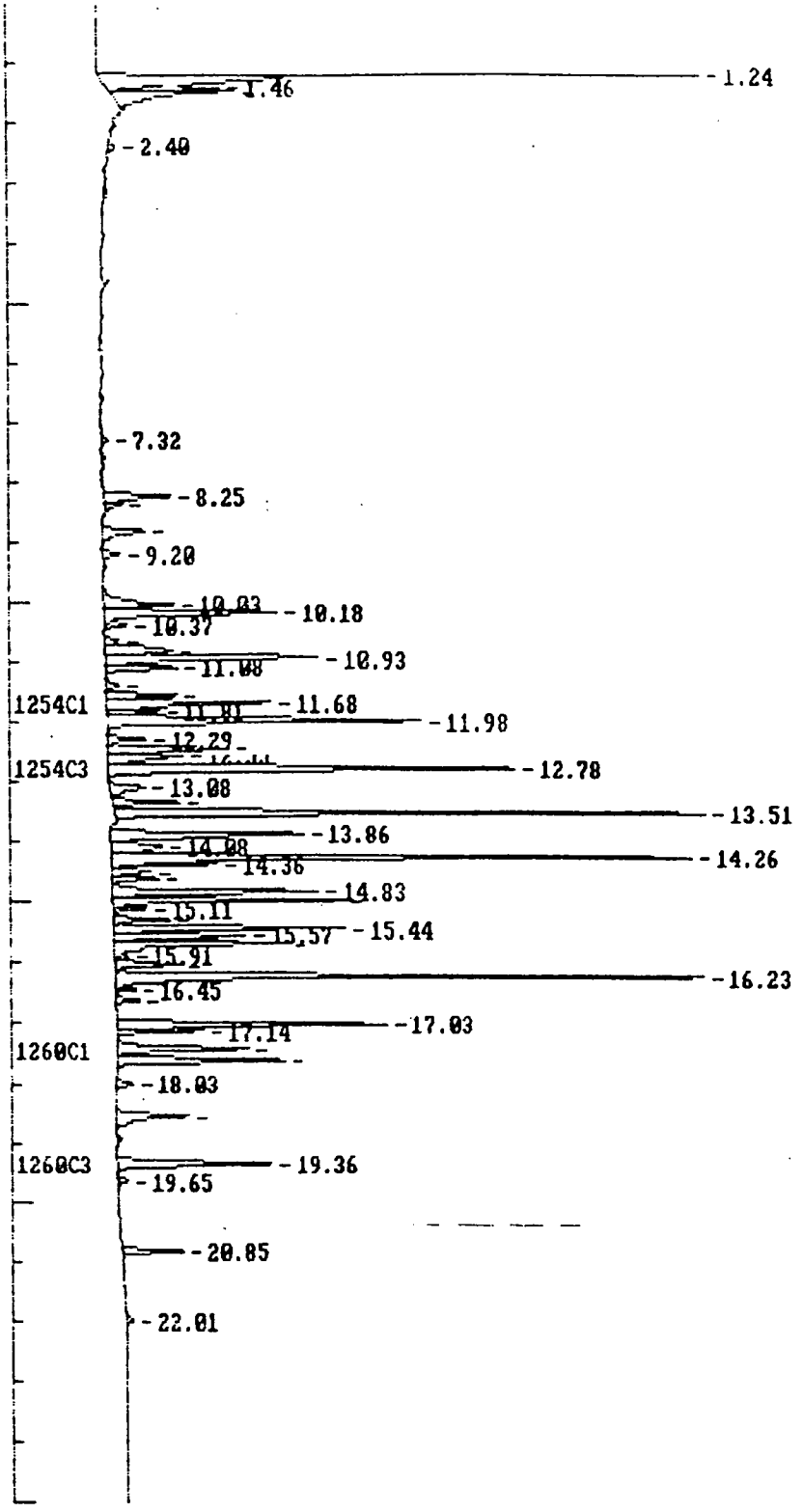
Starting Delay: 0.00
Area reject: 6000
Amount injected: 1.00
Sample Weight: 1.00000

Ending retention time. [illegible]
One sample per 0.500 sec.
Dilution factor. 1.00

PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in ug/ml	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT	BL	REF PEAK	% DELTA RET TIME	CONC/AREA
1	1.242		0.0000	0.0000%	459481	131819	3.5	3			0.0000E+00
2	1.458		0.0000	0.0000%	68901	21967	3.1	4			0.0000E+00
3	1.508		0.0000	0.0000%	177437	27362	6.5	2			0.0000E+00
4	2.400		0.0000	0.0000%	10005	1509	6.6	1			0.0000E+00
8	7.317		0.0000	0.0000%	9205	1388	6.6	1			0.0000E+00
10	8.250		0.0000	0.0000%	79770	14824	5.4	2			0.0000E+00
11	8.383		0.0000	0.0000%	22445	3837	5.8	2			0.0000E+00
12	8.833		0.0000	0.0000%	56968	9415	6.1	1			0.0000E+00
13	9.200		0.0000	0.0000%	21007	3876	5.4	1			0.0000E+00
14	10.033		0.0000	0.0000%	102235	15852	6.4	2			0.0000E+00
15	10.175		0.0000	0.0000%	233912	38607	6.1	3			0.0000E+00
16	10.367		0.0000	0.0000%	24391	4674	5.2	4			0.0000E+00
17	10.633		0.0000	0.0000%	15533	3296	4.7	2			0.0000E+00
18	10.800		0.0000	0.0000%	111012	15125	7.3	2			0.0000E+00
19	10.925		0.0000	0.0000%	264247	47563	5.6	2			0.0000E+00
20	11.083		0.0000	0.0000%	85026	16001	5.3	2			0.0000E+00
21	11.392		0.0000	0.0000%	16825	3025	5.6	2			0.0000E+00
22	11.550		0.0000	0.0000%	75434	15836	4.8	2			0.0000E+00
23	11.675	1254C1	0.2020 0.2367	14.8345%	191231	36540	5.2	2	29	0	1.2380E-06
24	11.808		0.0000	0.0000%	53941	11627	5.1	2			0.0000E+00
25	11.975	1254C2	0.2008 0.2745	17.2007%	395886	69702	5.7	2	29	.0626	6.9338E-07
26	12.292		0.0000	0.0000%	38714	8541	4.5	2			0.0000E+00
27	12.442	0.1995	0.0000	0.0000%	128752	26886	4.8	2			0.0000E+00
28	12.550		0.0000	0.0000%	131698	16690	7.9	2			0.0000E+00
29	12.775	1254C3	0.1957 0.3883	24.3320%	499374	89566	5.6	2	29	0	7.7759E-07
30	13.083		0.0000	0.0000%	51724	7775	6.7	2			0.0000E+00
31	13.333		0.0000	0.0000%	61520	14908	4.1	2			0.0000E+00
32	13.508		0.0000	0.0000%	597838	129977	4.6	2			0.0000E+00
33	13.858		0.0000	0.0000%	250702	42810	5.9	2			0.0000E+00
34	14.075		0.0000	0.0000%	84969	11237	7.6	2			0.0000E+00
35	14.258		0.0000	0.0000%	629223	127804	4.9	3			0.0000E+00
36	14.358		0.0000	0.0000%	65032	16920	3.8	4			0.0000E+00
37	14.483		0.0000	0.0000%	36670	8568	4.3	2			0.0000E+00
38	14.606		0.0000	0.0000%	44957	10152	4.4	2			0.0000E+00
39	14.825		0.0000	0.0000%	214471	45730	4.7	2			0.0000E+00
40	14.975		0.0000	0.0000%	233276	51207	4.6	3			0.0000E+00
41	15.108		0.0000	0.0000%	26434	7045	3.8	4			0.0000E+00
42	15.292		0.0000	0.0000%	50652	12447	4.1	2			0.0000E+00
43	15.442		0.0000	0.0000%	219142	51444	4.3	2			0.0000E+00
44	15.567		0.0000	0.0000%	126785	29191	4.3	2			0.0000E+00
45	15.700		0.0000	0.0000%	195584	38292	5.1	3			0.0000E+00
46	15.908		0.0000	0.0000%	8893	2470	3.6	4			0.0000E+00
47	16.050		0.0000	0.0000%	77292	14639	5.3	2			0.0000E+00
48	16.233		0.0000	0.0000%	602368	129940	4.6	3			0.0000E+00
49	16.450		0.0000	0.0000%	15560	3878	4.0	4			0.0000E+00
50	16.633		0.0000	0.0000%	22046	5078	4.3	2			0.0000E+00
51	17.033		0.0000	0.0000%	282799	59784	4.7	2			0.0000E+00
52	17.142		0.0000	0.0000%	87643	19176	4.6	2			0.0000E+00
53	17.442	1260C1	0.2327	14.5836%	152923	29077	5.3	2	58	0	1.5219E-06
54	17.633	1260C2	0.2321	14.5413%	184210	37023	5.0	2	58	0	1.2598E-06
55	18.025	0.2321	0.0000	0.0000%	17534	3641	4.8	1			0.0000E+00
56	18.575		0.0000	0.0000%	99701	16223	6.1	1			0.0000E+00
58	19.358	1260C3	0.2315	14.5080%	200188	34370	5.8	1	58	0	1.1566E-06
59	19.550		0.0000	0.0000%	11379	2133	5.3	1			0.0000E+00
60	20.850		0.0000	0.0000%	66755	13564	4.9	1			0.0000E+00
61	22.008		0.0000	0.0000%	7022	1358	5.2	1			0.0000E+00

TOTAL AMOUNT = 1.5959

reas, times, and heights stored in: O:ID2.ATB
Data File = O:ID2.PTS Printed on 12-23-1992 at 09:07:30
Start time: 0.00 min. Stop time: 25.00 min. Offset: 0 m..
Full Range: 200 millivolts



**** EXTERNAL STANDARD TABLE ****

************** **** 12-23-1992 09:09:11 Version 5.. ************

Sample Name: AR1660, 0.5 Data File: [illegible]

Date: 12-21-1992 19:53:48 Method: C:PCBID 12-23-1992 09:04:11

Interface: 2 Cycle#: 4 Operator DW Channel#: 1 Vial#: N.A.

Starting Peak Width: 5 Threshold: 15 Area Threshold: [illegible]

****

tarting Delay: 0.00 Ending retention time: 25. [illegible]

rea reject: 6000 One sample per [illegible]

mount injected: 1.00 Dilution factor: [illegible]

ample Weight: 1.00000

RET TIME	PEAK NAME	CONCENTRATION in ug/ml	NORMALIZED CONC	AREA	HEIGHT	AREA/HEIGHT	BL	REF PEAK	% DELTA RET TIME	CONC/AREA
1.242		0.0000	0.0000%	1451120	220691	4.6	1			0.0000E+00
3.133		0.0000	0.0000%	10754	1755	6.1	1			0.0000E+00
4.425		0.0000	0.0000%	21147	3741	5.7	1			0.0000E+00
4.900		0.0000	0.0000%	39254	6385	6.2	2			0.0000E+00
5.092		0.0000	0.0000%	40685	8352	4.8	2			0.0000E+00
5.217		0.0000	0.0000%	249277	36107	6.9	2			0.0000E+00
5.642		0.0000	0.0000%	23225	4285	5.4	2			0.0000E+00
6.150		0.0000	0.0000%	168420	41493	4.1	2			0.0000E+00
6.200		0.0000	0.0000%	258437	41481	6.2	2			0.0000E+00
6.417		0.0000	0.0000%	62335	8528	7.3	2			0.0000E+00
6.608		0.0000	0.0000%	298575	45441	6.6	2			0.0000E+00
7.058		0.0000	0.0000%	71562	14623	4.9	2			0.0000E+00
7.125		0.0000	0.0000%	66372	13497	4.9	2			0.0000E+00
7.317		0.0000	0.0000%	838413	105637	7.9	2			0.0000E+00
7.575		0.0000	0.0000%	360055	59443	6.1	2			0.0000E+00
7.758		0.0000	0.0000%	284247	46124	6.2	2			0.0000E+00
7.925		0.0000	0.0000%	77257	12135	6.4	2			0.0000E+00
8.125		0.0000	0.0000%	24072	4620	5.2	2			0.0000E+00
8.250		0.0000	0.0000%	172559	30508	5.7	2			0.0000E+00
8.392		0.0000	0.0000%	176133	30622	5.8	2			0.0000E+00
8.525		0.0000	0.0000%	187521	22911	9.2	2			0.0000E+00
8.833		0.0000	0.0000%	232035	41915	5.5	2			0.0000E+00
8.942		0.0000	0.0000%	204236	33373	6.1	2			0.0000E+00
9.200		0.0000	0.0000%	335722	50991	6.6	2			0.0000E+00
9.425		0.0000	0.0000%	77505	13038	6.0	2			0.0000E+00
10.025		0.0000	0.0000%	82722	10411	7.9	2			0.0000E+00
10.175		0.0000	0.0000%	221309	35934	6.2	3			0.0000E+00
10.367		0.0000	0.0000%	7942	1573	5.0	4			0.0000E+00
10.633		0.0000	0.0000%	7033	1614	4.4	2			0.0000E+00
10.750		0.0000	0.0000%	36709	5816	6.3	2			0.0000E+00
10.925		0.0000	0.0000%	195277	37509	5.2	2			0.0000E+00
11.550		0.0000	0.0000%	8141	1902	4.3	2			0.0000E+00
11.675	1254C1	0.0749	3.4877%	60529	11734	5.2	2	41	.1933	1.2380E-06
11.975	1254C2	0.1587	7.3860%	228882	31744	7.2	2	41	.1933	6.9338E-07
12.442		0.0000	0.0000%	240643	49991	4.8	2			0.0000E+00
12.550		0.0000	0.0000%	172805	24107	7.2	2			0.0000E+00
12.758	1254C3	0.4149	19.3109%	533571	107787	5.0	2	41	0	7.7759E-07
13.083		0.0000	0.0000%	47715	7994	6.0	1			0.0000E+00
13.333		0.0000	0.0000%	97047	22981	4.2	2			0.0000E+00
13.508		0.0000	0.0000%	761277	167297	4.6	2			0.0000E+00
13.867		0.0000	0.0000%	452281	73512	6.2	2			0.0000E+00
14.142		0.0000	0.0000%	87904	15060	5.8	2			0.0000E+00
14.250		0.0000	0.0000%	878741	180320	4.9	3			0.0000E+00
14.358		0.0000	0.0000%	78293	21279	3.7	4			0.0000E+00
14.483		0.0000	0.0000%	24655	5713	4.3	2			0.0000E+00
14.600		0.0000	0.0000%	95800	21832	4.4	2			0.0000E+00
14.825		0.0000	0.0000%	446874	98117	4.6	2			0.0000E+00
14.975		0.0000	0.0000%	339438	73849	4.6	3			0.0000E+00
15.100		0.0000	0.0000%	27941	7419	3.8	4			0.0000E+00
15.283		0.0000	0.0000%	113691	27176	4.2	2			0.0000E+00
15.433		0.0000	0.0000%	457842	105341	4.3	2			0.0000E+00
15.567		0.0000	0.0000%	259229	59163	4.4	2			0.0000E+00
15.700		0.0000	0.0000%	272880	53445	5.1	2			0.0000E+00
15.908		0.0000	0.0000%	22347	5701	3.9	2			0.0000E+00
16.050		0.0000	0.0000%	162210	29135	5.6	2			0.0000E+00
16.233		0.0000	0.0000%	1312450	289355	4.5	3			0.0000E+00
16.450		0.0000	0.0000%	35130	8815	4.0	4			0.0000E+00
16.625		0.0000	0.0000%	51561	11694	4.4	2			0.0000E+00
17.025		0.0000	0.0000%	571599	122241	4.7	2			0.0000E+00
17.142		0.0000	0.0000%	177407	39381	4.5	2			0.0000E+00
17.442	1260C1	0.5000	23.2718%	328536	62518	5.3	2	70	0	1.5219E-06
17.633	1260C2	0.5000	23.2718%	396903	79736	5.0	2	70	0	1.2598E-06
18.025		0.0000	0.0000%	37454	7690	4.9	1			0.0000E+00
18.575		0.0000	0.0000%	223732	34544	6.5	2			0.0000E+00
18.967		0.0000	0.0000%	15783	3000	5.3	2			0.0000E+00
19.358	1260C3	0.5000	23.2718%	432315	71437	6.1	2	70	0	1.1566E-06
19.650		0.0000	0.0000%	28945	5205	5.6	2			0.0000E+00
20.842		0.0000	0.0000%	149255	29949	5.0	1			0.0000E+00
21.042		0.0000	0.0000%	7023	1322	5.3	1			0.0000E+00
22.000		0.0000	0.0000%	18303	3446	5.3	1			0.0000E+00

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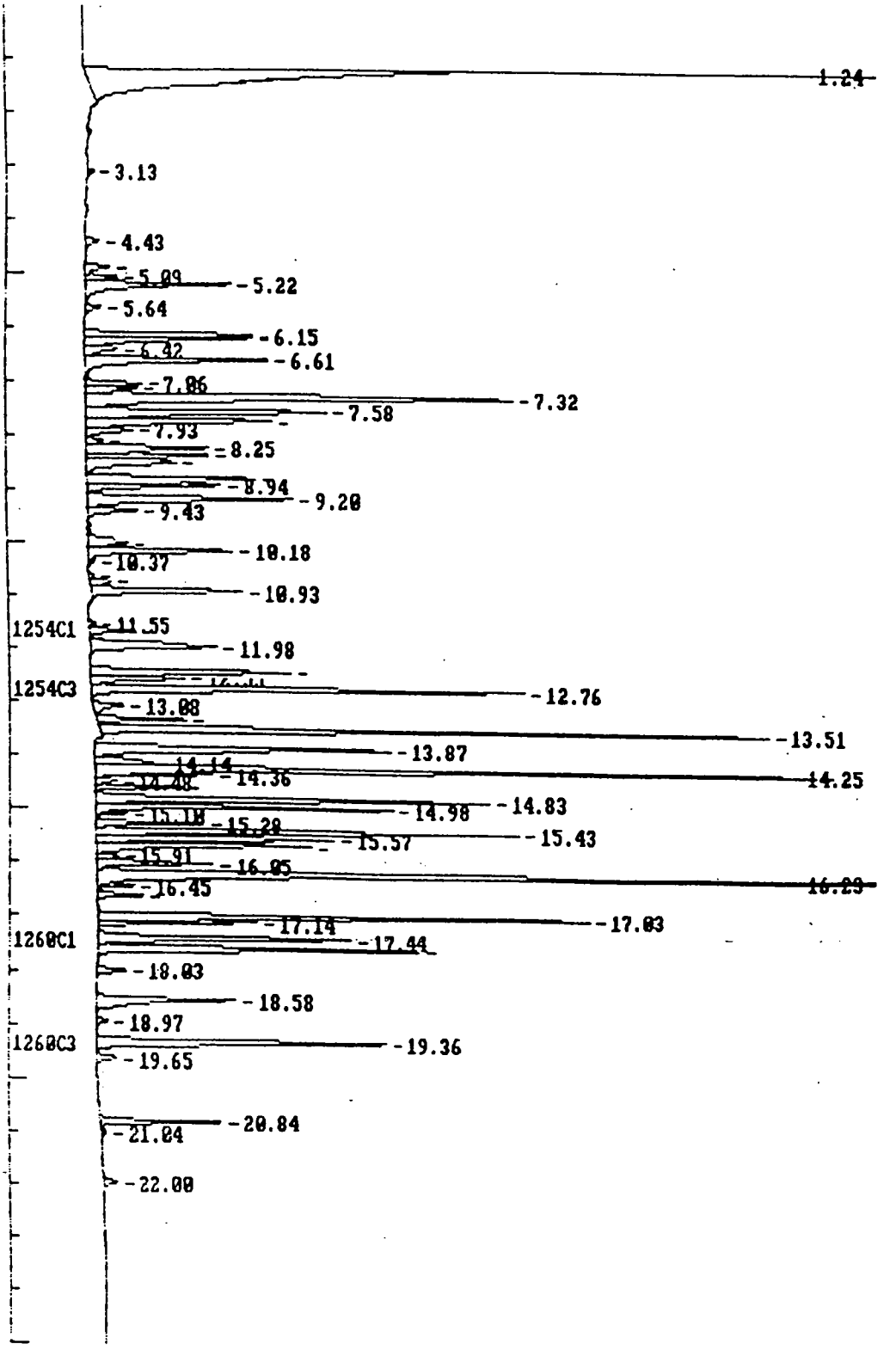

***** EXTERNAL STANDARD TABLE *****

********** 12-23-1992 09:11:10 Version 5.1 **********

* Sample Name: AR1254, 0.5 Data File: D:???

* Date: 12-21-1992 20:23:11 Method: D:PCBID 12-23-1992 09:04:23 # 907

* Interface: 2 Cycle#: 5 Operator DW Channel#: 1 Vial#: N.A.

* Starting Peak Width: 5 Threshold: 15 Area Threshold: 750

Starting Delay: 0.00 Ending retention time: 25.00

Area reject: 6000 One sample per 0.500 sec.

Amount injected: 1.00 Dilution factor: 1.00

Sample Weight: 1.00000

PEAK NUM	RET TIME	PEAK NAME	CONCENTRATION in ug/ml	NORMALIZED CONC	AREA	HEIGHT	AREA/ HEIGHT	BL	REF PEAK	? DELTA RET TIME	CONC/AREA
1	1.242		0.0000	0.0000I	1171994	321593	3.6	3			0.0000E+00
2	1.508		0.0000	0.0000I	170521	26281	6.5	4			0.0000E+00
4	3.142		0.0000	0.0000I	8975	1451	6.2	1			0.0000E+00
6	4.642		0.0000	0.0000I	273116	41144	6.6	1			0.0000E+00
10	7.308		0.0000	0.0000I	20050	2755	7.3	1			0.0000E+00
11	7.583		0.0000	0.0000I	10479	1821	5.8	2			0.0000E+00
13	8.250		0.0000	0.0000I	184044	31945	5.8	2			0.0000E+00
14	8.383		0.0000	0.0000I	78293	11313	6.9	2			0.0000E+00
15	8.233		0.0000	0.0000I	146557	22779	6.4	1			0.0000E+00
16	9.200		0.0000	0.0000I	70212	11825	5.9	3			0.0000E+00
17	9.425		0.0000	0.0000I	8317	1723	4.8	4			0.0000E+00
19	10.033		0.0000	0.0000I	252288	38236	6.6	2			0.0000E+00
20	10.175		0.0000	0.0000I	404322	64260	6.3	2			0.0000E+00
21	10.367		0.0000	0.0000I	70100	12429	5.6	2			0.0000E+00
22	10.633		0.0000	0.0000I	49014	10252	4.8	2			0.0000E+00
23	10.800		0.0000	0.0000I	230846	31892	7.2	2			0.0000E+00
24	10.925		0.0000	0.0000I	437899	79517	5.5	2			0.0000E+00
25	11.083		0.0000	0.0000I	200019	37440	5.3	2			0.0000E+00
26	11.383		0.0000	0.0000I	42861	7334	5.8	2			0.0000E+00
27	11.550		0.0000	0.0000I	174267	35268	4.9	2			0.0000E+00
28	11.675	1254C1	0.5000	32.8532I	403887	75133	5.4	2	34	C	1.2380E-06
29	11.808		0.0000	0.0000I	154649	29198	5.3	2			0.0000E+00
30	11.975	1254C2	0.5000	32.8532I	721103	138757	5.2	2	34	C	6.9338E-07
31	12.292		0.0000	0.0000I	91379	20253	4.5	1			0.0000E+00
32	12.442		0.0000	0.0000I	30030	9810	3.4	1			0.0000E+00
33	12.550		0.0000	0.0000I	21589	6301	3.4	1			0.0000E+00
34	12.783	1254C3	0.5000	32.8532I	643015	128112	5.0	1	34	C	7.7759E-07
35	13.100		0.0000	0.0000I	91252	12556	7.3	2			0.0000E+00
36	13.333		0.0000	0.0000I	57925	14148	4.1	2			0.0000E+00
37	13.508		0.0000	0.0000I	746716	165009	4.5	2			0.0000E+00
38	13.858		0.0000	0.0000I	148654	32165	4.6	2			0.0000E+00
39	14.058		0.0000	0.0000I	119622	19875	6.0	2			0.0000E+00
40	14.250		0.0000	0.0000I	645868	141909	4.6	2			0.0000E+00
41	14.358		0.0000	0.0000I	122193	29734	4.1	2			0.0000E+00
42	14.483	--	0.0000	0.0000I	-61794	14781	4.2	2			0.0000E+00
43	14.708		0.0000	0.0000I	6136	1669	3.7	2			0.0000E+00
44	14.825		0.0000	0.0000I	30827	7421	4.2	2			0.0000E+00
45	14.967		0.0000	0.0000I	231170	53106	4.4	2			0.0000E+00
46	15.100		0.0000	0.0000I	46056	11060	4.2	2			0.0000E+00
48	15.442		0.0000	0.0000I	47341	11367	4.2	2			0.0000E+00
49	15.567		0.0000	0.0000I	26283	6529	4.0	2			0.0000E+00
50	15.700		0.0000	0.0000I	172882	40709	4.2	2			0.0000E+00
51	15.817		0.0000	0.0000I	30196	7995	3.8	2			0.0000E+00
52	16.050		0.0000	0.0000I	15031	3836	3.9	1			0.0000E+00
53	16.233		0.0000	0.0000I	127111	29199	4.4	1			0.0000E+00
54	17.025		0.0000	0.0000I	107472	23106	4.7	2			0.0000E+00
55	17.142		0.0000	0.0000I	25197	5807	4.3	2			0.0000E+00
57	17.633	1260C2	0.0095	0.6247I	7548	1716	4.4	1	34	C	1.2598E-06
58	18.025		0.0000	0.0000I	8216	1716	4.8	1			0.0000E+00
60	18.683		0.0000	0.0000I	7735	1408	5.5	2			0.0000E+00
62	19.358	1260C2	0.0124	0.8157I	10734	1943	5.5	1	34	C	1.1566E-06
63	20.850		0.0000	0.0000I	16513	3431	4.8	1			0.0000E+00
65	22.000		0.0000	0.0000I	1104845	190651	5.8	1			0.0000E+00

TOTAL AMOUNT = 1.5219

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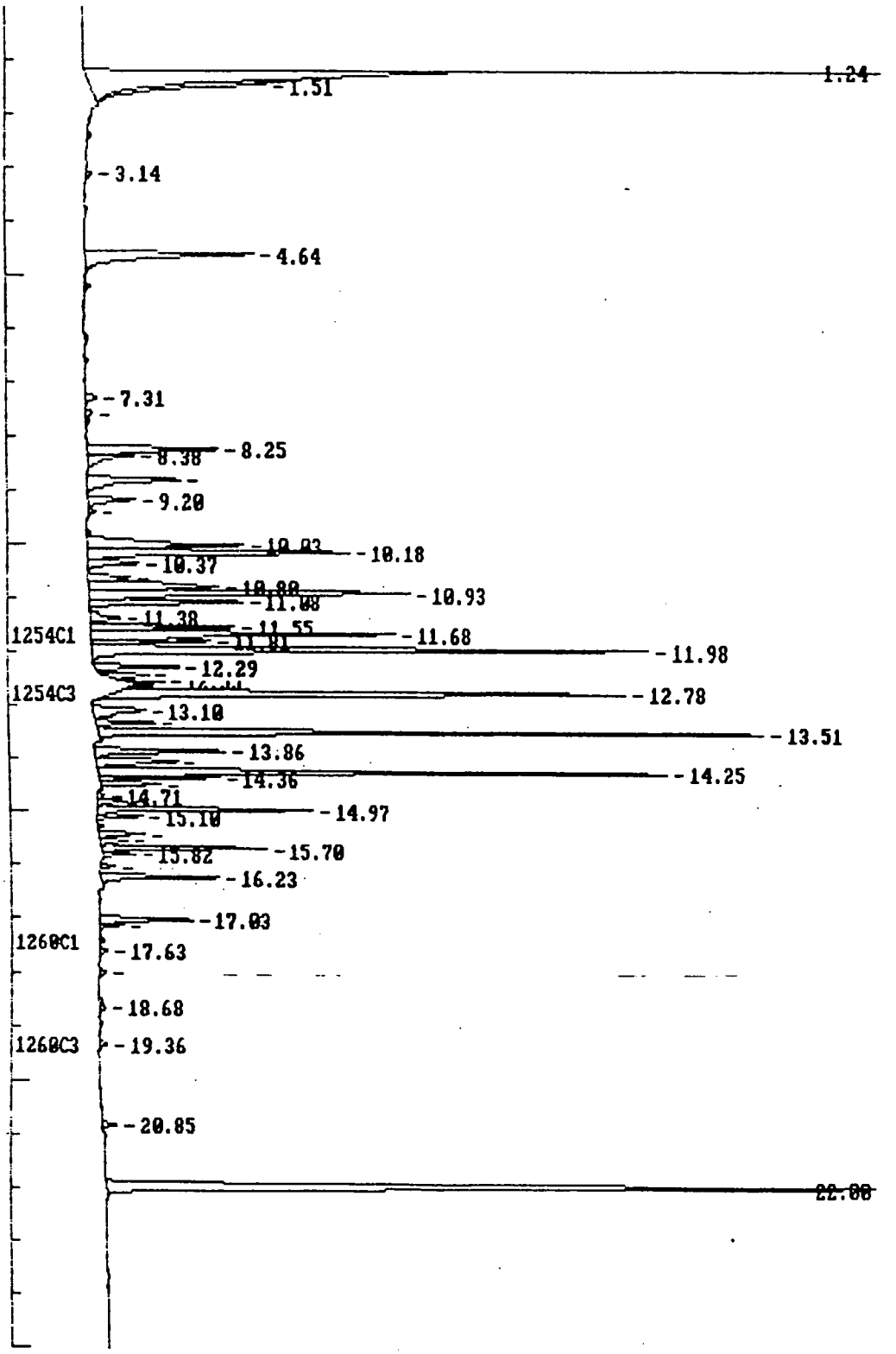


ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS ANALYSIS BY FLAME-AA OR ICP (DIG)

A. Introduction

1. Applicability: This method is applicable to drinking, surface, and waste waters, and to TCLP/EPTOX extracts.
2. Purpose of Testing: Since many metals are acutely or chronically toxic, it is frequently necessary to characterize the metal content of waters and waste waters. The analyses require that the samples be treated so as to be reasonably certain that the subject metals have been liberated from whatever complexes and/or compounds might be holding them at the time of sample collection. In addition, the regulations governing the analysis of EPTOX and TCLP extracts for metal content call for digestion of the extracts prior to analysis. This method deals with the procedure for treating all these aqueous samples for analysis by flame-AA or ICP.
3. Method Detection Limit: N/A
4. Reference Methods: CLP SOW 3/90, Exhibit C, Sec. III; RCRA SW-846, 3rd ed., Rev. 1, Method 3010.
5. Summary of Method: An aliquot of sample is digested in nitric and hydrochloric acid in order to release complexed or encapsulated metallic species into solution. The product of the digestion is brought up to a specified volume, using Type II water. It is then ready for analysis for total metals content.
6. Interferences: With the exception of analysis for Antimony, this treatment is not a suitable preparation of samples requiring furnace (GFAA) analysis, because hydrochloric acid can cause interferences during atomization. When furnace level determination is required, use **Acid Digestion of Aqueous Samples for Total Metals Analysis by Furnace-AA (DIG)**. For further discussion of interferences, refer to **Analysis for Total Metals by Simultaneous ICP.**
7. Sample Collection and Preservation: Aqueous samples should be collected in 500mL polyethylene bottles and acidified to pH<2 with nitric acid. (EPTOX and TCLP filtrates are also preserved with nitric acid.)
8. Holding Time: 180 days (6 months) from date of sampling to date of analysis.
9. Safety Precautions: Many environmental samples are known or suspected health hazards. EPTOX and TCLP extracts may be relatively acidic and have usually been derived from probable or known hazardous substances. Please use standard lab safety practices when handling samples. Laboratory coats and protective eyewear are required. All digestions must be

protective eyewear are required. All digestions must be performed in a fume hood.

B. Apparatus

1. Hotplates.
2. 250mL Erlenmeyer flasks.
3. Watch glasses.
4. GFAA 4.5 micron filter paper, such as Gelman GF/F.
5. Eppendorf calibrated micropipet, 2mL.
6. Vacuum flasks and frits.
7. 250mL graduated cylinders.
8. 250mL polyethylene or glass bottles with tight-fitting caps, for storing the finished digestates.

C. Reagents and Standards

1. Reagents: Reagent grade chemicals shall be used in all analyses.
   a. ASTM Type II water (ASTM d1193-99, 1983), a.k.a. Super Q water.
   b. Concentrated nitric acid (HNO_3): Commercially available.
   c. Concentrated hydrochloric acid (HCl): Commercially available.
   d. Hydrogen peroxide (H_2O_2), 30%: Commercially available.
2. Spiking Standards: Multi-element standard solutions are used to prepare matrix spikes at approximately mid-range of ICP/FLAA calibration curves. The usual solutions are compounded from stocks supplied to company specifications by SPEX, but special spiking solutions may be required for particular jobs; the analyst should check whether such requirements apply before setting up spiked aliquots. (Present spiking solution constituents and concentrations are listed in the **Appendix** at the end of this method.)
3. Calibration Verification Source: N/A
4. Spiking Protocol: Using an Eppendorf micropipet, add 2 mL of the appropriate spiking standard to the sample aliquot designated as a digested matrix spike prior to digestion.

D. Method

1. Check the latest preparation bin to determine the numbering of the current preparation bin. Preparation bins are labeled in the format YY-###, where YY are the last two digits of the year and ### is an incrementing sequential number. Record the new preparation bin number on a blank digestion log sheet, and determine which samples are to be included in the digestion set. Record those samples, determining which will be getting spiked and/or duplicated and noting that as well.

2. Shake a sample bottle vigorously, to homogenize the contents. For each sample, spiked sample, duplicate or duplicate spiked sample measure out 200 mL, using a graduated cylinder, and transfer the aliquot into a 250mL Erlenmeyer flask. Record the sample I.D. and QC designation (if any), along with the initial volume on the digestions log sheet. Record the sample I.D. and QC information on the Erlenmeyer.

3. Add 2 mL of concentrated HNO_3 and 10 mL of concentrated HCl to the sample. Cover with a watch glass and heat on the hotplate, making certain that the sample does not boil, for 2 hrs, or until the sample volume is reduced to between 25 and 50 mL.

4. While the samples are being reduced in volume, make up labels for the sample digestate bottles. Each label should include the sample I.D., the QC designation (if any), the preparation bin number, the preparation date, the initial volume of sample used, and the final volume of digestate. Waters' digestates are labeled with white tape; filtrates' digestates are labeled with red tape, TCLP extracts' digestates with orange tape.

5. Cool the sample and inspect it for presence of suspended material which might clog nebulizers. If there appears to be a probability of such interference, filter the sample through Gelman GF/F paper. (Be sure to use thoroughly cleaned equipment, prerinsed with dilute HNO_3, so as to reduce the chance of sample contamination.) Bring the filtrate up to a final volume of 200 mL, using a graduated cylinder, and transfer it to the previously labeled 250mL digestate bottle. At this point the sample is 5% (v/v) HCL and approximately 5% (v/v) HNO_3, and is ready for analysis.

E. Calculations N/A

F. Quality Control

1. Preparation Blank (PB): The preparation bin shall include a digestion blank, which is a 200 mL aliquot of Super Q water carried through the entire digestion procedure. The digestate bottle containing this sample is to be labeled with PBYY-###, where YY-### is the code number assigned to the preparation bin.
2. Laboratory Control Sample (LCS): *i*.e., Preparation Blank Spike. In addition to the PB, the preparation bin will have a 200 mL aliquot of Super Q water to which has been added 2 mL of the spiking standard, before the aliquot is carried through the digestion procedure. The digestate bottle containing this sample is to be labeled PBSYY-###, where YY-### is the code number assigned to the preparation bin.
3. Matrix Spike (#####S): The spiking protocol is to be applied to a minimum of 1 sample/bin or 1 in 20 samples, whichever gives the greater number of spiked samples. Matrix spikes may be required more often than this frequency, depending on the needs of the clients represented in the bin's set of samples. It is up to the analyst to check that all clients' requirements, as well as the default levels described here, are met. Label the spiked sample digestate bottle with the sample I.D. followed immediately by an 'S'. Note on the digestion log sheet the spiking standard used and the volume of standard added.
4. Matrix Duplicate (#####D): One sample/bin or 1 in every 20 samples, whichever generates the greater number of duplicates, is to be carried through the digestion procedure in two replicate aliquots. As with matrix spikes, specific client demands may lead to a greater frequency of duplicates than 1 in 20 samples, and the analyst will have to determine this before starting the digestion procedure. Label the sample duplicate digestate bottle with the sample I.D. followed immediately by D.

5. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked at the same level. It is the analyst's responsibility to find out whether the samples included in the set to be prepared require this level of QC. If so, code the second spiked sample on the sample digestate bottle and in the Digestion Log sheet by placing "SD" immediately after the ENCOTEC identification for the sample.

G. Provenance

This method was written by

Martha Gialdini Frank Senior Chemist/Technical

It has been reviewed and accepted by

Sharon K. Weindorf Supervisor/Group Leader

Department Manager

Technical Director

APPENDIX

A. Aqueous Sample Spiking Solution

Parameter	Stock Solution mg/L	Final Solution mg/L
Al	5000	50
Sb	100	1
As	200	1
Ba	100	1
Be	20	0.2
Cd	20	0.2
Ca	5000	50
Cr	100	1
Co	100	1
Cu	100	1
Fe	500	5
Pb	100	1
Mn	20	0.2
Mg	5000	50
Ni	100	1
K	5000	50
Se	200	2
Ag	50	0.2
Na	5000	50
Tl	100	1
V	100	1
Zn	100	1

B. TCLP Extract Spiking Solution

Parameter	TCLP Stock Solution[1)] mg/L	TCLP Final Solution mg/L
As	100	5
Ba	100	5
Cd	20	1
Cr	100	5
Cu	100	5
Pb	100	5
Se	20	1
Ag	10	0.5

[1)] 10 mL of TCLP Stock Solution added to a sample which is then digested and brought to a final volume of 200 mL gives Final Solution.

TOTAL METALS DIGESTION
FOR AQUEOUS SAMPLES

1. Determine the preparation bin number, and the samples to be included, and record this on a blank digestion log sheet. Assign spikes, dups and spike dups as necessary, maintaining a minimum of 1 spike and 1 dup per bin, or 1 spike and 1 dup for every 20 samples. Check for further requirements that might apply to particular clients before proceeding.

2. Shake the sample bottle well, to homogenize the sample. Transfer 200 mL (measured by graduated cylinder) to a 250 mL Erlenmeyer flask. Record the initial volume measured out on the digestion log sheet, and the sample I.D. on the Erlenmeyer.

3. Add 2 mL of conc. HNO_3 and 10 mL conc. HCl.

4. Cover with a watchglass, and heat for 2 hours, or until the sample is reduced to between 25 and 50 mL in volume, making certain the sample doesn't boil during that time.

5. While the samples are heating, make up labels for the sample digestate storage bottles. Each label should have the sample I.D., the QC designation (if any), the preparation bin number, the prep date, the initial volume of sample, and the final volume of digestate.

6. Cool the digestate to room temperature. Filter the digestate if there seems to be a significant amount of suspended solids in it. (Use GF/F filter paper.) Bring the digestate up to 200 mL final volume (measured in a graduated cylinder). Record the final volume on the digestion log sheet and on the sample digestate bottle. Decant the digestate into the sample digestate bottle.

DRAFT

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS ANALYSIS BY ICPMS (DIGMS)

A. Introduction

1. Applicability: This method is applicable to drinking, surface, and waste waters, and to TCLP/EPTOX extracts.
2. Purpose of Testing: Since many metals are acutely or chronically toxic, it is frequently necessary to characterize the metal content of waters and waste waters. The analyses require that the samples be treated so as to be reasonably certain that the subject metals have been liberated from whatever complexes and/or compounds might be holding them at the time of sample collection. In addition, the regulations governing the analysis of EPTOX and TCLP extracts for metal content call for digestion of the extracts prior to analysis. This method deals with the procedure for treating all these aqueous samples for analysis by ICPMS.
3. Method Detection Limit: N/A
4. Reference Methods: Method 6020-M, Version 7.0
5. Summary of Method: An aliquot of sample is digested in nitric acid in order to release complexed or encapsulated metallic species into solution. The product of the digestion is brought up to a specified volume, using Type II water. It is then ready for analysis for total metals content.
6. Interferences: N/A.
7. Sample Collection and Preservation: Aqueous samples should be collected in 500mL polyethylene bottles and acidified to pH<2 with nitric acid. (EPTOX and TCLP filtrates are also preserved with nitric acid.)
8. Holding Time: 180 days (6 months) from date of sampling to date of analysis.
9. Safety Precautions: Many environmental samples are known or suspected health hazards. EPTOX and TCLP extracts may be relatively acidic and have usually been derived from probable or known hazardous substances. Please use standard lab safety practices when handling samples. Laboratory coats and protective eyewear are required. All digestions must be performed in a fume hood.

B. Apparatus

1. Hotplates.
2. 250mL Erlenmeyer flasks.
3. Watch glasses.
4. GFAA 4.5 micron filter paper, such as Gelman GF/F.
5. Eppendorf calibrated micropipet, 2mL.
6. Vacuum flasks and frits.

7. 250mL graduated cylinders.
8. 250mL polyethylene or glass bottles with tight-fitting caps, for storing the finished digestates.

C. Reagents and Standards

1. Reagents: Reagent grade chemicals shall be used in all analyses.
   a. ASTM Type II water (ASTM d1193-99, 1983), a.k.a. Super Q water.
   b. Concentrated nitric acid (HNO_3): Commercially available.
   c. Hydrogen peroxide (H_2O_2), 30%: Commercially available.
2. Spiking Standards: Multi-element standard solutions are used to prepare matrix spikes at approximately mid-range of ICPMS calibration curves. The usual solutions are compounded from stocks supplied to company specifications by SPEX, but special spiking solutions may be required for particular jobs; the analyst should check whether such requirements apply before setting up spiked aliquots. (Present spiking solution constituents and concentrations are listed in the **Appendix** at the end of this method.)
3. Calibration Verification Source: N/A
4. Spiking Protocol: Using an Eppendorf micropipet, add 1 mL of QC-7 and 1 ml of QC-19. (These are Spex standards.)

D. Method

1. Check the latest preparation bin to determine the numbering of the current preparation bin. Preparation bins are labeled in the format YY-###, where YY are the last two digits of the year and ### is an incrementing sequential number. Record the new preparation bin number on a blank digestion log sheet, and determine which samples are to be included in the digestion set. Record those samples, determining which will be getting spiked and/or duplicated and noting that as well.

2. Shake a sample bottle vigorously, to homogenize the contents. For each sample, spiked sample, duplicate or duplicate spiked sample measure out 100 mL, using a graduated cylinder, and transfer the aliquot into a 250mL Erlenmeyer flask. Record the sample I.D. and QC designation (if any), along with the initial volume on the digestions log sheet. Record the sample I.D. and QC information on the Erlenmeyer.

3. Add 0.5 mL of concentrated HNO_3 and 3 mL of Hydrogen Peroxide to the sample. Cover with a watch glass and heat on the hotplate, making certain that the sample does not boil, for 2 hrs, or until the sample volume is reduced to between 25 and 50 mL.

4. While the samples are being reduced in volume, make up labels for the sample digestate bottles. Each label should include the sample I.D., the QC designation (if any), the preparation bin number, the preparation date, the initial volume of sample used, and the final volume of digestate. Waters' digestates are labeled with white tape; filtrates' digestates are labeled with red tape, TCLP extracts' digestates with orange tape.

5. Cool the sample and inspect it for presence of suspended material which might clog nebulizers. If there appears to be a probability of such interference, filter the sample through Gelman GF/F paper. (Be sure to use thoroughly cleaned equipment, prerinsed with dilute HNO_3, so as to reduce the chance of sample contamination.) Bring the filtrate up to a final volume of 100 mL, using a graduated cylinder, and transfer it to the previously labeled 250mL digestate bottle. At this point the sample is approximately 0.5% (v/v) HNO_3, and is ready for analysis.

E. Calculations N/A

F. Quality Control

1. Preparation Blank (PB): The preparation bin shall include a digestion blank, which is a 100 mL aliquot of Super Q water carried through the entire digestion procedure. The digestate bottle containing this sample is to be labeled with PBYY-###, where YY-### is the code number assigned to the preparation bin.
2. Laboratory Control Sample (LCS): *i.e.*, Preparation Blank Spike. In addition to the PB, the preparation bin will have a 200 mL aliquot of Super Q water to which has been added 1 mL of each spiking standard, before the aliquot is carried through the digestion procedure. The digestate bottle containing this sample is to be labeled PBSYY-###, where YY-### is the code number assigned to the preparation bin.
3. Matrix Spike (#####S): The spiking protocol is to be applied to a minimum of 1 sample/bin or 1 in 20 samples, whichever gives the greater number of spiked samples. Matrix spikes may be required more often than this frequency, depending on the needs of the clients represented in the bin's set of samples. It is up to the analyst to check that all clients' requirements, as well as the default levels described here, are met. Label the spiked sample digestate bottle with the sample I.D. followed immediately by an 'S'. Note on the digestion log sheet the spiking standard used and the volume of standard added.
4. Matrix Duplicate (#####D): One sample/bin or 1 in every 20 samples, whichever generates the greater number of duplicates, is to be carried through the digestion procedure in two replicate aliquots. As with matrix spikes, specific client demands may lead to a greater frequency of duplicates than 1 in 20 samples, and the analyst will have to determine this before starting the digestion procedure. Label the sample duplicate digestate bottle with the sample I.D. followed immediately by D.

5. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked at the same level. It is the analyst's responsibility to find out whether the samples included in the set to be prepared require this level of QC. If so, code the second spiked sample on the sample digestate bottle and in the Digestion Log sheet by placing "SD" immediately after the ENCOTEC identification for the sample.

G. Provenance

This method was written by

_____ Senior Chemist/Technical

It has been reviewed and accepted by

_____ Supervisor/Group Leader

_____ Department Manager

_____ Technical Director

APPENDIX

A. Spex Spiking Solutions

Parameter	QC-19 Stock Solution mg/L	Final Solution ug/L
Sb	100	50
As	100	50
Be	100	50
Cd	100	50
Ca	100	50
Cr	100	50
Co	100	50
Cu	100	50
Fe	100	50
Pb	100	50
Mn	100	50
Mg	100	50
Mo	100	50
Ni	100	50
Se	100	50
Tl	100	50
Ti	100	50
V	100	50
Zn	100	50

Parameter	QC-7 Stock Solution mg/L	Final Solution ug/L
Al	100	50
Ba	100	50
B	100	50
Ag	100	50

PREPARATION OF METALS DIGESTATES FOR ANALYSIS BY HYDRIDE ATOMIC ABSORPTION (HAS,HSE)

A. Introduction

1. Applicability: This method is applicable to all metals digestates, whether prepared for analysis by graphite furnace (GFAA) or by inductively coupled plasma(ICP)/flame atomic absorption(FLAA).
2. Purpose of Testing: The digestates prepared from aqueous, solid, or liquid samples for analysis for other metal parameters will need further conversion to a form suitable for use in the FLAA hydride analysis procedure. This method addresses the operations necessary for the conversion.
3. Method Detection Limit: Please reference **Use of the Hydride Generator in Arsenic and/or Selenium Analysis (AS,SE).**
4. Reference Methods: Varian Techtron Pty Limited, manufacturer (after EPA 600/4-79-020, Method 206.5); SW-846, 3rd Ed., Rev. 0, Method 7061; SW-846, Rev. 0, Method 7741.
5. Summary of Method: Urea and hydrochloric acid (HCl) are added to an aliquot of digested sample and the solution is boiled vigorously. After cooling, the residue is brought up to final volume and divided for Arsenic and Selenium analyses. The aliquots are ready for analysis for Selenium, but will require the addition of potassium iodide just prior to analysis for Arsenic.
6. Interferences: Nitric acid is a major interferant in hydride analysis; addition of urea to the digestate prior to boiling serves to remove this. All organic interferants have been removed and organic forms of the analytes have been converted to inorganic ones in the digestion process.
7. Sample Collection and Preservation: The "samples" here are the metals digestates, kept in preparation bins at room temperature, and preserved with 2.5%-10% HNO_3/5%HCl or with 5% HNO_3 alone.
8. Holding Time: 180 days from date of sample collection to date of analysis.
9. Safety Precaution: Digestates are preserved at 2.5%-10% HNO_3/5% HCl or at 5% HNO_3 alone. In addition, strong acid is required in the procedure. Consequently, take care in handling both the digestates and the reagents used. Gloves are strongly recommended; safety glasses and lab coats must be worn at all times in the laboratory. All Arsenic/Selenium conversions must be carried out in a fume hood.

B. Apparatus

1. Erlenmeyer flasks, 125mL.
2. Calibrated re-pipet, capable of delivering 25 mL of HCl.
3. Measuring spoon, 1/2 tsp (~5 mL).
4. Hotplates.
5. Polyethylene scintillation vials, 25mL.
6. Graduated cylinder, 50mL.
7. Volumetric flasks, 200mL.
8. Class A pipets, 2mL and 5mL.
9. Calibrated Eppendorf pipet, 1mL.

C. Reagents and Standards

1. Reagents: Reagent grade chemicals will be used in all tests:
   a. ASTM Type II Water (ASTM D1193-99(1983)): *i.e.*, Super Q water.
   b. Urea ($(NH_2)_2CO$) crystals: Commercially available.
   c. Concentrated hydrochloric acid (HCl): Commercially available.
2. Spiking Standards:
   a. Arsenic/Selenium Stock Spiking Standard: The usual solution is supplied to company specifications by SPEX, but special spiking solutions may be required for particular applications; the analyst should check whether such requirements apply before setting up spiked aliquots. The usual solution concentration in Arsenic and Selenium is 1000 mg/L. Shelf life is specified by SPEX.
   b. Arsenic/Selenium Intermediate Solution: Using a Class A pipet, measure 2 mL Arsenic/Selenium Stock Spiking Standard into a Class A 200mL volumetric flask. Dilute to the mark with Super Q water. The concentration of this intermediate solution is 10 mg/L in Arsenic and in Selenium. Shelf life is indefinite.
   c. Arsenic/Selenium Spiking Standard: Using an Eppendorf pipet, measure 1 mL Arsenic/Selenium Intermediate Solution into a Class A 200mL volumetric flask. Dilute to the mark with Super Q water. The concentration of this spiking standard is 50 ug/L in Arsenic and in Selenium; the shelf life is indefinite.
3. Calibration Verification Source: N/A
4. Spiking Protocol: Using a Class A pipet, add 5 mL of Arsenic/Selenium Spiking Standard (C. 2. c., above) to the sample aliquot designated as the Arsenic/Selenium conversion spike prior to conversion.

D. Method

1. Fill out a blank Arsenic/Selenium Conversion Log sheet with the date, analyst identification and the client and ENCOTEC identifications for the sample digestates to be converted for hydride analysis. Determine which digestates are to be spiked and duplicated and list the spikes and duplicates as well.

2. Shake a sample digestate bottle vigorously, to homogenize the contents. For each sample, spiked sample, duplicate or duplicate spiked sample measure out 25 ml, using a graduated cylinder, and transfer the aliquot into a 125ml Erlenmeyer flask. Record the amount measured out on the Conversions Log sheet, and label the flask with the client and ENCOTEC identifications and the QC designation (if any). Add Arsenic/Selenium Spiking Solution (see **C. 2. c.**, above) to those aliquots which have been designated as spiked ones.

3. Measure a small amount of urea (~1/2 tsp.) into each Erlenmeyer.

4. Using a calibrated re-pipet, add 25 mL concentrated hydrochloric acid (HCl). Place the flask on a hotplate set at a medium-high setting.

5. Allow all sample digestates to boil vigorously for 15 minutes, taking care to prevent loss of sample by spattering out of the flasks or through boiling to dryness.

6. Cool converted sample digestates and check for the presence of insoluble particles. (If such material is present, vacuum filter the conversion through Gelman GF/F glass fiber filter paper.) Bring the conversions up to a 50 mL final volume, using a graduated cylinder and return the conversions to the Erlenmeyers used to boil them. Record the final volumes on the Conversion Log sheet.

7. Gather as many scintillation vials as there are conversions, and label the cap of each vial with As, one of the sample—ENCOTEC and client identifications and QC designation (if any). Pour off 25 mL of each conversion into each vial and cap it with the properly labeled cap. (The separation is necessary because the analysts will have to add potassium iodide to the vial contents to complete the conversion of the Arsenic from As^{V} to As^{III}; the boiling process has sufficed to convert the Selenium from Se^{VI} to Se^{IV}.) Seal the Erlenmeyers with parafilm.

8. Xerox two copies of the Conversion Log sheet and place one with the Erlenmeyers and the other with the scintillation vials. Place the original Conversion Log sheet in the Arsenic/Selenium Conversion Logbook. Store both Erlenmeyers and scintillation vials on a cart, temporarily. The conversions are now ready for analysis.

E. Calculations N/A

F. Quality Control

1. Preparation Blank (PB): Each conversion set shall have with it a 25 mL aliquot of Super Q water carried through the entire conversion procedure. The conversion is labeled on both the Erlenmeyer and the scintillation vial with As/Se PB and the date of preparation. The designation is also PB in the Conversion Log.
2. Laboratory Control Sample (LCS): Each conversion set shall include a 25 mL aliquot of Super Q water to which has been added 5 mL of the Arsenic/Selenium Spiking Solution. The Erlenmeyer and scintillation vial containing this sample are labeled with As/Se LCS and the date of preparation. The Conversion Log designation is LCS.
3. Matrix Spike (####S): The spiking protocol is to be applied to a minimum of 1 sample/set or 1 in 20 samples, whichever gives the greater number of spiked samples. Matrix spikes may be required more often than this frequency, depending on the needs of the clients represented in the conversion set of samples. It is up to the analyst to check that all clients' requirements, as well as the default levels described here, are met. Label the spiked sample conversion flask and scintillation vial with the ENCOTEC identification followed immediately by an 'S'. Note on the Conversion Log sheet the spiking standard used and the volume of standard added.
4. Matrix Duplicate: One sample/set or 1 in every 20 samples, whichever generates the greater number of duplicates, is to be carried through the conversion procedure in two replicate aliquots. As with matrix spikes, specific client demands may lead to a greater frequency of duplicates than 1 in 20 samples, and the analyst will have to determine this before starting the digestion procedure. Label the sample duplicate Erlenmeyer and scintillation vial with the ENCOTEC identification followed immediately by D. Use the same designation in the Conversion Log.

5. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked at the same level. It is the analyst's responsibility to find out whether the samples included in the set to be prepared require this level of QC. If so, code the second spiked sample on the Conversion Log sheet by placing "SD" immediately after the ENCOTEC identification for the sample.

G. Provenance

This method was written by

Martha Waldrop Frank Senior Chemist/Technical

It has been reviewed and accepted by

Sharon K. Windsor Supervisor/Group Leader

Department Manager

Technical Director

PREPARATION OF DIGESTATES FOR HYDRIDE

1. Fill out a blank Conversions Log sheet with date, analyst identification and client and ENCOTEC sample identifications for those samples scheduled for As/Se hydride analysis. Determine and note QC samples as well.

2. Shake a sample digestate bottle vigorously and pour out 25 mL into a graduated cylinder. Note volume on the Conversion Log sheet for the sample and transfer the aliquot to a 125mL Erlenmeyer flask. Label the flask with the sample identifications (client, ENCOTEC and QC, if applicable).

3. Measure a small amount (~1/2 tsp) into each Erlenmeyer, and, using a calibrated re-pipet, add 25 mL concentrated HCl. Place the flask on a hotplate set at a medium-high setting.

4. Allow all prepared sample digestates to boil vigorously for 15 minutes, taking care that no solution is lost due to spattering out of the flask or through boiling to dryness.

5. Cool conversions and check for presence of insoluble particles, filtering them out through Gelman GF/F glass fiber filter paper. Bring clean conversions up to 50 mL final volume, using a graduated cylinder, and return them to the Erlenmeyers used to boil them. Record final volume on the Log sheet.

6. Gather as many polyethylene scintillation vials as there are conversions and label the cap of each vial with As/Se and the sample identifications (ENCOTEC and QC, if applicable). Pour off 25 mL of each conversion into one of the scintillation vials, capping it with the properly labeled cap.

7. Xerox two copies of the Conversion Log sheet and place one with the Erlenmeyers and the other with the scintillation vials. Temporary storage for both conversion aliquot sets is a cart. Return the original Conversion Log sheet to the Arsenic/Selenium Conversion Logbook.

PREPARATION OF AQUEOUS SAMPLES FOR ANALYSIS FOR MERCURY BY COLD VAPOR (HGP)

A. Introduction

1. Applicability: This method is applicable to all waters and wastewaters for which the determination of mercury content is required.
2. Purpose of Testing: Mercury metal and all of its compounds are toxic and readily absorbed through skin and lung tissues; furthermore, mercury is liquid at room temperature and relatively volatile as well. Since mercury is quite useful in various industrial processes, it is necessary to monitor industrial and municipal waters and wastewaters for the element.
3. Method Detection Limit: Please reference **Analysis for Mercury by Cold Vapor** for method detection limits.
4. Reference Methods: EPA-600/4-79-020, Rev. 3/83, Method 245.1; SW-846, Rev. 0, Method 7470; Standard Methods, Ed. 17, Method 3112B.
5. Summary of Method: A measured aliquot of the water to be analyzed is digested with sulfuric and nitric acids. The digestate is diluted and oxidization is initiated using potassium permanganate and potassium persulfate. After heating in a constant temperature water bath and cooling, the sample is ready for analysis.
6. Interferences: Sulfides' interference is removed by means of the potassium permanganate-driven oxidation. Organic interferences are, for the main part, removed in the digestion procedure. For further discussion of possible interferants see **Analysis for Mercury by Cold Vapor.**
7. Sample Collection and Preservation: Aqueous samples for which total mercury content is to be determined are collected in 500mL glass or polyethylene bottles and preserved at pH<2, using concentrated nitric acid. Aqueous samples for which dissolved mercury content is to be determined are filtered through 0.5 micron filters prior to preservation at pH<2. Samples are stored at room temperature.
8. Holding Time: 28 days from date of sample collection to analysis; preparation must, therefore, be completed in sufficient time to meet this deadline.

9. Safety Precautions: As noted above, mercury is toxic and volatile at room temperature. In addition, solids for which mercury determination is contemplated are likely to be hazardous. Furthermore, the reagents used in preparing samples for mercury determination include concentrated sulfuric acid. Consequently, all steps in preparation of samples for mercury determination take place under a fume hood. Take care in handling both the samples and the reagents used. Gloves are strongly recommended; safety glasses and lab coats must be worn at all times in the laboratory.

B. Apparatus

1. BOD bottles, with ground glass stoppers, 150mL.
2. 4 calibrated re-pipets, two capable of delivering 2 to 5 mL concentrated acid, two capable of delivering 5 to 15 mL oxidizing reagents.
3. Constant temperature water bath, capable of maintaining 95° Celsius for two or more hours.
4. Class A pipets, 25mL, 10mL, 5mL, and 2mL.
5. Eppendorf pipets, 2000uL, 1000uL and 500uL.
6. Class A volumetric flasks, 1000mL, 500mL, 200mL.
7. Graduated cylinder, 100mL.

C. Reagents and Standards

1. Reagents: Unless otherwise specified, reagent-grade chemicals shall be used in all tests.
   a. ASTM Type II water (ASTM 1193-99, 1983): *i.e.*, Super Q water.
   b. Concentrated sulfuric acid, H_2SO_4: Suitable for mercury determination, commercially available.
   c. Concentrated nitric acid, HNO_3: Suitable for mercury determination, commercially available.
   d. Potassium permanganate, $KMnO_4$, crystals: Commercially available.
   e. Potassium permanganate solution, 5% (w/v): Dissolve 50 gm $KMnO_4$ (weighed to the nearest 0.1 gm) in Super Q water in a 1000mL Class A volumetric flask and bring to a final volume of 1 liter.
   f. Potassium persulfate, $K_2S_2O_8$, solution, 5% (w/v): Dissolve 50 gm $K_2S_2O_8$ (weighed to the nearest 0.1 gm) in Super Q water in a 1000mL Class A volumetric flask and bring to a final volume of 1 liter.
2. Standards:
   a. Mercury Stock Standard, 1000mg/L: Commercially available.
   b. Mercury Intermediate Standard, 10 mg/L: Using a Class A pipet, transfer 2 mL of Mercury Stock Standard into a 200mL Class A volumetric flask and dilute to the

mark using Super Q water. Make fresh at the time of preparation and dispose of excess in properly labeled hazardous waste container.

c. Mercury Working Intermediate Standard, 100 ug/L: Using Class A pipet, transfer 10 mL of Mercury Intermediate Standard into a 1000mL Class A volumetric flask and dilute to the mark using Super Q water. Make fresh at the time of preparation and pour excess standard down the drain.

d. Mercury Standards: Using Eppendorfs, Class A pipets, Class A volumetric flasks, and Super Q water throughout, perform the following dilutions:

1) 10.0 ug/L: Dilute 50 mL of the Mercury Working Intermediate Standard to 500 mL.
2) 5.0 ug/l: Dilute 25 mL of the Mercury Working Intermediate Standard to 500 mL.
3) 2.0 ug/L: Dilute 10 mL of the Mercury Working Intermediate Standard to 500 mL.
4) 1.0 ug/L: Dilute 5 mL of the Mercury Working Intermediate Standard to 500 mL.
5) 0.5 ug/L: Using a 2mL Class A pipet and a 500uL calibrated Eppendorf, dilute 2.5 mL of the Mercury Working Intermediate Standard to 500 mL.
6) 0.2 ug/L: Using a 1000uL calibrated Eppendorf, dilute 1.0 mL of the Mercury Working Intermediate Standard to 500 mL.

3. Calibration Verification Source: Supplied to company specifications by SPEX. The concentration of this solution is 1000 mg/L, and it is diluted down to 100 ug/L using the steps outlined for Mercury Intermediate and Mercury Working Intermediate Standards. The concentration used in preparation for analysis is developed as follows:

a. 3.0 ug/L: Using Class A pipets, transfer 15 mL of the 100 ug/L solution to a Class A 500mL volumetric flask and dilute to the mark using Super Q water.

4. Spiking Protocol: Using a calibrated Eppendorf pipet, add 2 mL of the Mercury Working Intermediate Standard (100 ug/L concentration) to 93 mL of the sample to be spiked. The theoretical value for the spike added is

$$\text{spike conc.} = \frac{2.0 \text{ mL spike} * 100 \text{ ug/L conc.}}{(93.0 \text{ mL sample} + 2.0 \text{ mL spike})} = 2.105 \text{ ug/L}$$

and the dilution factor for the sample is

$$df = \frac{93.0 \text{ mL sample}}{(93.0 \text{ mL sample} + 2.0 \text{ mL spike})} = 0.979$$

D. Method

1. Get a Mercury Preparation Log sheet and fill in the date, the analyst identification, and the standards (including the prepared blank) and QC samples, and compile a roster of the aqueous samples to be prepared. For each sample, record the client and ENCOTEC sample identifications. Determine which of the samples are to be spiked and duplicated and note the spikes and duplications on the Mercury Preparation Log sheet.

2. Prepare the Mercury Standards, following the directions in **C.** 2., above. Using a 100mL graduated cylinder, measure 95 mL of each standard and transfer it to a properly cleaned and labeled BOD bottle. Measure out, also, an aliquot of Super Q water, to be used as the standard defining the low-response end of the standards range. (Standards, including this blank, are prepared in BOD bottles labeled with their concentrations.)

3. Prepare the Calibration Verification Sample (see **C.** 3., above) and measure 95 mL of it into a BOD bottle. Prepare the Laboratory Control Sample (see **F.** 2., below) in another BOD bottle.

4. Measure out 95 mL of each aqueous sample and duplicate sample into separate clean BOD bottles. Measure out 93 mL of each sample aliquot to be spiked or duplicate spiked, and add 2 mL of the Working Intermediate Mercury Standard to it in accordance with **C.** 4, above. In all cases, note the BOD bottle code next to the sample identification on the Mercury Preparation Log Sheet as the BOD bottle is filled.

5. Using a re-pipet, add 5 mL concentrated sulfuric acid to each standard, sample, and QC sample and swirl to mix. Then, using another re-pipet, add 2.5 mL concentrated nitric acid and swirl to mix.

6. Using a third re-pipet, add 15 mL of 5% (w/v) potassium permanganate solution and swirl to mix. Let the mixtures stand at room temperature for at least 15 minutes. (If the deep purple color indicating the presence of excess potassium permanganate does not persist for the 15 minute period add crystals of potassium permanganate until the color does persist for 15 minutes.) Start the water bath heating, making sure that it is set to 95° Celsius.

7. When the standards and samples have been oxidized by the $KMnO_4$ for 15 minutes, and the water bath has equilibrated at 95°C, add 8 mL 5% (w/v) potassium persulfate solution to each of the standards and samples, using the fourth re-pipet. Swirl to mix the solution. Securely seat stoppers in the BOD bottles and place the stoppered bottles in the prepared water bath.

8. Process the standards and samples for 2 hours. At the end of that time period, remove the bottles from the water bath and allow them to cool to room temperature.

9. Record the standard and sample final volumes on the Mercury Preparation Log sheet. Place the prepared samples and standards on a cart for temporary storage. Xerox two copies of the Mercury Preparation Log sheet and place them on the cart with the samples. Put the original sheet in the Mercury Preparation Log. The samples are ready for analysis.

E. Calculations N/A

F. Quality Control

1. Calibration Verification Sample (ICV/CCV): *i.e.*, Ampule. This is a 95 mL aliquot of the Calibration Verification Source (see **C.** 3. a., above) which is carried through the standards preparation procedure at the same time the standards are prepared. A Calibration Verification Sample is required with every preparation set. Record the sample on the Log sheet in the row immediately following that for the most concentrated standard, coding the sample ICV/CCV.
2. Laboratory Control Sample (LCS): This is a 93 mL aliquot of Super Q water to which has been added 2.0 mL of the Mercury Working Intermediate Standard prior to preparation. It is prepared with the standards rather than with the samples. An LCS is required with every preparation set. List this QC sample immediately after the ICV/CCV on the Log sheet and code it LCS.

3. Matrix Spike (#####S): The spiking protocol is to be applied to a minimum of 1 sample/bin or 1 in 20 samples, whichever gives the greater number of spiked samples. Matrix spikes may be required more often than this frequency, depending on the needs of the clients represented in the bin's set of samples. It is up to the analyst to check that all clients' requirements, as well as those default levels described here, are met. Note the spiked sample on the Mercury Preparation Log sheet by placing an "S" immediately after the ENCOTEC identification for the sample. Indicate the spiking protocol on the Log sheet also.

4. Matrix Duplicate (#####D): One sample/bin or 1 in every 20 samples, whichever generates the greater number of duplicates, is to be carried through the digestion procedure in two replicate aliquots. Again, specific client demands may lead to a greater frequency of duplicates than this, and the analyst will have to determine this before starting the digestion procedure. Indicate the duplicate sample on the Mercury Preparation Log sheet by placing a "D" immediately after the ENCOTEC identification for the sample.

5. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked at the same level. It is the analyst's responsibility to find out whether the samples included in the set to be prepared require this level of QC. If so, code the second spiked sample on the Mercury Preparation Log sheet by placing "SD" immediately after the ENCOTEC identification for the sample.

G. Provenance

This method was written by

Martha Waldemichaels — Senior Chemist/Technical

It has been reviewed and accepted by

Sharon K. Wendorff — Inorganics Extractions Supervisor

_____ — Department Manager

_____ — Technical Director

PREPARATION OF SOIL/SOLID SAMPLES
FOR ANALYSIS FOR MERCURY

1. Fill out a Mercury Preparation Log sheet with date, analyst i.d., standards and QC samples and ENCOTEC and client i.d.s for the aqueous samples to be included in the preparation set. Determine the samples to be spiked and duplicated and include those aliquots in the set.

2. Prepare the 100 ug/L Working Intermediate Standard, then 0.2 ug/L, 0.5 ug/L, 1.0 ug/L, 2.0 ug/L, 5.0 ug/L, and 10.0 ug/L standards. Using a graduated cylinder, measure out a 95 mL aliquot of each of the last 6 standards into a properly labeled 150mL BOD bottle. Measure out a 95 mL aliquot of Super Q water for the low-range end of the standards' set. Measure out a 95 mL aliquot of the Calibration Verification Source, and a 93 mL aliquot of Super Q water to which is added 2.0 mL of 100 ug/L standard.

3. Measure out a 95 mL aliquot of each sample and duplicate sample into a separate clean BOD bottle. Measure out 93 mL aliquots of the spiked and duplicate spiked samples and add 2.0 mL of 100 ug/L standard to each. Record the BOD bottle code next to the sample identification on the Mercury Preparation Log Sheet as the bottle is filled.

4. Using re-pipets, add 5 mL conc. H_2SO_4 and 2.5 mL HNO_3, swirling to mix reagents after each addition.

5. Using a re-pipet, add 15 mL 5% (w/v) $KMnO_4$ solution to each BOD bottle. Let stand at least 15 minutes. If the deep purple color does not persist for that time period, add crystals of $KMnO_4$ until the color does persist for 15 minutes. Start the water bath heating, making sure it's set at 95° Celsius.

6. When the standards have stood 15 minutes and the water bath has equilibrated, add 8 mL of 5% (w/v) $K_2S_2O_8$ solution, cap the bottles securely, and place in the water bath for 2 hours.

7. Record the final volume of the samples on the Mercury Preparation Log sheet. Place the samples and standards on a cart for temporary storage. Xerox the Log sheet twice and place the copies with the samples. Put the original of the Log sheet in the Mercury Preparation Log.

ANALYSIS OF TOTAL AND DISSOLVED METALS BY THE ARL 3560 SIMULTANEOUS ICP

A. Introduction

1. Applicability: This method is applicable to the analysis of total and dissolved metals. The list of metals that can be analyzed using the ARL 3560 is shown in Table 1. This method outlines the procedures and requirements for any ICP method developed on this instrument. For specific information on the configuration of individual methods (air, water, wastewater, soil, etc...) refer to **APPENDIX I**, at end of this document.
2. Purpose of Testing: Many metals are chronic or acute toxins at certain concentrations. Therefore, control of metal pollution is frequently required in industrial discharges to the environment. Many Superfund (CERCLA) and RCRA sites have known or suspected metals contamination; this requires that samples be analyzed for metals content in order to ascertain the scope of pollution in the environment.
3. Instrument Detection Limit: For complete lists of instrument detection limits, see **APPENDIX I**, Tables 3 and 5.
4. Reference Methods: RCRA SW-846, 3rd edition, method 6010; EPA Contract Laboratory Protocol SOW 3/90.
5. Summary of Method: Digestates and filtrates are exposed to an argon plasma which provides sufficient energy to cause elements to excite and emit radiation. This light is directed into photomultiplier detectors (PMT) with a stationary Rowland Circle configuration. A PMT is located at a factory installed angle to the grating which corresponds to a wavelength. This allows for rapid simultaneous analysis of many elements because the grating does not move to select wavelengths as in a sequential instrument.
6. Interferences:
   a. Physical- Viscosity or high salt content may cause sample transport problems which will result in intensity readings differing from standards in reagent water. Serial dilution will indicate if this interference is present.
   b. Chemical- Due to the high energies involved in ICP, very few chemical interferences are present.
   c. Spectral- There are three types of spectral interference: background shift, spectral background, and spectral overlap. Background shift is caused by self-absorption of various elements at high concentrations. Compensation for background shift is achieved by using background correction points. Spectral background is caused by elements emitting light at wavelengths close to the analyte wavelength. It is only an interference if it occurs on a background correction point or if the interferant's concentration is high enough to cause the

peak to overlap with the background correction point or the analyte peak. Careful attention to background readings is required to ensure that this is not occurring. Direct spectral overlap occurs when an interfering element emits light coincident with the analyte wavelength. This is due to higher order wavelengths. Interelement correction calibration is required to compensate for this interference.

7. Sample Collection and Preservation: Please refer to the digestion methods.
8. Holding Time: 6 months from sampling date to analysis date.
9. Safety Precaution: Many samples which require metals analysis are known or suspected health hazards. Normal lab safety practices should be observed. Lab coat and protective eye-wear are required.

B. Apparatus

a. ARL 3560 ICP with autosampler and peristaltic pump.
b. Class "A" Pipets, various volumes.
c. Calibrated re-pipets, Eppendorf pipets, various volumes.
d. High and low solids nebulizers.

C. Reagents and Standards

1. Reagents: All acids are reagent grade or better.
   a. ASTM Type II water (ASTM 1193-1199(1983)): aka Super-Q water.
   b. Nitric acid (HNO_3), concentrated, ultrex grade: Commercially available.
   c. Nitric acid, 1%: Dilute 20 mL of concentrated nitric acid in Super Q water in a marked and labeled 2L jug. Bring up to the mark with Super Q water. Shelf life is indefinite.
   d. Concentrated hydrochloric acid, HCl: Commercially available.
   e. Hydrochloric acid, HCl, 1% (v/v) solution: Dilute 20 mL concentrated HCl in Super Q water in a marked and labeled 2L jug. Bring up to the mark with Super Q water. Shelf life is indefinite.
2. Standards: Refer to each method (see **APPENDIX I**, Tables 4 and 6) for standard preparation and concentrations.
3. Calibration Verification Source: Spex XENT-2. Refer to each method (see **APPENDIX I**, Tables 4 and 6).
4. Spiking Protocol: For digested matrix spikes refer to the appropriate digestion procedure. For analytical spikes, add 1 mL of the spiking solution listed in Table 4 to 9 mL of sample.

D. Instrument Maintenance

1. Daily:
   a. Change Peristaltic Pump Tubing.
   b. Check and fill the argon wetter vessel, located in the back of the torch box, to the full mark if necessary.
   c. Run an instrument status report. Include a hardcopy in the data package.
   d. Run an instrument profile. Include a hardcopy in the data package.
   e. Empty the waste container.
   f. Clean the torch, if there are visible deposits.
   g. Rinse the nebulizer for five minutes with 1% HNO3.
   h. Record actions in the Daily Maintenance Log. An example sheet is in **APPENDIX II.**
2. Monthly:
   a. Check the coolant water in the front compartment and if necessary replenish with Super Q water to the full mark.
   b. Check and re-calibrate argon gas flows if necessary.
   c. Record actions in the Instrument Maintenance Log. An example sheet is in **APPENDIX II.**
3. Quarterly:
   a. Change the vacuum pump oil. This requires bleeding the optical chamber. It usually takes about three hours to pump the pressure back down within tolerance after the oil is changed.
   c. Record actions in the Instrument Maintenance Log. An example sheet is in **APPENDIX II.**

E. Method

1. Set the instrument up and allow the plasma to run for at least a half-hour before beginning analysis.
2. Perform an instrument status check (Refer to **APPENDIX II**). Include a hardcopy in the data package.
3. Perform an instrument profile in order to verify that the instrument is aligned properly. Include a hardcopy in the data package.
4. Calibrate the instrument using the standards listed in the appropriate method, see **APPENDIX I**, Table 4 or 6. Verify that each curve meets the criteria outlined in **G.**, below.
5. Initiate a run log (refer to **APPENDIX II**). Keep this throughout the analytical run, using it to note any QC problems or special notes that will be helpful to the data reviewer.
6. Analyze the ICV and ICB. Verify that these meet acceptance criteria outlined in **G.**, below, and **APPENDIX I**, Table 3 or 5.
7. Analyze the CRI standard.

8. Analyze the ICSA and ICSAB solution. Verify that these meet acceptance criteria outlined in G., below.
9. Continue analyses following the **ICP Sequence Table**, below. Verify that the various quality control samples meet acceptance criteria outlined in G., below.
10. Following every ten analyses run CCV and CCB solutions. Verify that they meet acceptance criteria outlined in G., below.
11. Every analytical run must terminate with CRI, ICSA, and ICSAB prior to the last CCV/CCB analysis.
12. Include the raw data, instrument status and profile pages, calibration report, and result file report in the data package. Upload the result file onto the network and reduce the data. Save the data values to the DMS system.
13. Mark off, on the schedule, the work that was performed; include any notes about the run.
14. Fill out the Data Cover Page (refer to **APPENDIX II**). Turn the data in to the review bin.

F. Calculations

1. Most calculations are performed by the computer during and after analysis. The computer performs linear regression determinations on the calibration curves. It also calculates mg/Kg values for soil samples based upon weights and volumes entered from the preparation log. A program written by the ENCOTEC MIS Department takes the data file from the instrument and translates it into a Dbase file. It then calculates all spikes, duplicates, serial dilutions, ICV/CCV, and ICSAB recoveries and flags data points accordingly. It also enters acceptable results into the sample database for subsequent report generation after review by data management.

G. Quality Control (see, also, INORGANICS DEPARTMENT, Metals QC Protocol)

1. Initial Calibration Verification (ICV): Analysis of the ICV immediately follows the calibration procedure. The recovery criterion window is 90%-110% of theoretical value.

2. Initial Calibration Blank (ICB): This is analyzed immediately after analysis of the ICV. The absolute value of concentration for any analyte must be less than the instrument detection limit for that analyte, **APPENDIX I**, Table 4 or 6.

3. Continuing Calibration Verification (CCV) - Typically, this solution is the same as the ICV, but it doesn't have to be. The CCV solution is analyzed after ten non-calibration analyses; acceptable recovery is, again, 90%-110% of theoretical value.

4. Continuing Calibration Blank (CCB): The reagent blank solution used in ICB analysis is re-analyzed immediately after each CCV. Unlike the ICB, the acceptable recoveries are less than the absolute value of twice the instrument detection limit.

5. Preparation Blank (PB): Each digestion set should have an aliquot of reagent blank which has been treated as a sample. The bottle is marked PBYY-###, where YY is the last two digits of the current year and ### is a number, assigned in sequence. The absolute value for the concentration of any analyte must be less than twice IDL. Should a PB fail this evaluation, report the poor recoveries to a supervisor and/or data management.

6. Laboratory Control Sample (LCS), aka Preparation Blank Spike (PBS): Every digestion set should have an aliquot of reagent blank to which has been added a known amount of all analytes observed by the ICP before being carried through the digestion procedure. The bottle is labeled LCSYY-###, using the code described in G. 5., above. Recovery of the LCS should be within 80%-120% of the theoretical value for the analytes included. If results fail to meet this criterion, report to a supervisor and/or data management. Flag the data when calculating it, by noting the poor recovery on the cover sheet of the data set.

7. Matrix Spike (#####S): At least one sample in a digestion set and, more commonly, one in every 20 samples, will have a replicate to which has been added the same known amount of all analytes observed by the ICP as was added to the LCS. This replicate is then digested as a sample. The spike recovery should be within a 75%-125% criterion range. If criterion is not met, perform a post-digestion spike (see G. 9.,below) and flag the data when calculating it, with an "N".

8. Matrix Duplicate (#####D): One sample in a digestion set, or one for every 20 samples in the set, whichever is the greater frequency, will have a replicate which is also digested by the same protocol. Should both replicates show concentrations $\geq$ 5X IDL, the relative percent difference between the two replicates should be $\leq$ 20%. Should the RPD be greater than 20%, report to a supervisor and/or data management, and flag the data when calculating it, with a "*". When either the sample or the duplicate shows a concentration $\leq$ 5X IDL, the absolute range between the two replicates should be $\leq$ IDL. If the range is greater than IDL, flag the data when calculating it, again using "*". When either or both replicates recovers at < IDL, report the RPD as "not

calculable" (N/C). The result reported as sample concentration is that for the first replicate, labeled *#####*, rather than the duplicate, labeled *#####*D. Do not report the average of the two replicates as the sample concentration.

Note: The bottles holding samples, standards and QC samples are labeled with color-coded tapes, to indicate matrices. The coding is as follows:

white - aqueous, including wastewaters, but not extractions

yellow - solids, soils, including oils and other non-aqueous matrices; a yellow stripe is added to the top and bottom of the ICP standards used to establish the calibration when a solids digestion set is to be analyzed

orange - TCLP extracts

red - EPTOX extracts

green - added to those digestions prepared for furnace analysis only; do not analyze a green-taped sample by ICP.

pink - added to those bottles holding ICP standards used to calibrate the instrument when an aqueous, TCLP or EPTOX digestion set is to be analyzed

9. Analytical Spike (*#####*A): When a matrix spike result fails to meet criterion, it is necessary for the analyst to prepare and analyze an analytical spike, by adding a known amount of analyte(s) of interest to an aliquot of digested, unspiked sample. Analysis should return a recovery of 75%-125% of theoretical value of the spike added.
Analytical spikes are also required when the frequency of matrix spikes available in a digestion set does not generate an overall spiking frequency of 1 in every 20 samples analyzed in the run. They are also necessary when the concentration of a sample which also has a matrix spike is greater than the linear range of the ICP.

Note: Analytical spikes generally dilute the samples they are made on by as much as the spike volume added. Accordingly, in no case is a sample to be diluted more than 10% by the spiking solution added; that is to say, a sample should be at least 90% of the composite of sample and spike prepared for an analytical spike. The one apparent exception is the case where a sample is off-scale and needs to have a spike analyzed. Here, it is necessary to run an analytical spike on an aliquot of sample which has been diluted with reagent blank to a concentration that will register at approximately mid-range. Dilute a second aliquot to the same level,

including the spiking solution in the diluent; calculate spike recovery on the observed concentration of the diluted sample. In addition, the spiking solutions and the reagent blank should be of acid strength and composition appropriate to the samples being analyzed.

10. Post-digestion Matrix Duplicate, aka Instrument Duplicate (#####I): If there are insufficient duplicates in the analysis set (i.e., less than one in twenty, or one per analytical set, whichever is the greater frequency), a sample or samples should be selected for re-analysis, to bring the total number of duplicate analyses up to the correct frequency. The control limits and calculations are the same as for Matrix Duplicates.

11. Serial Dilution (####L): One sample in every twenty (or one sample per analytical set, whichever is the greater frequency), is to be diluted to 1:4 (i.e., one part sample and 4 parts reagent blank) and re-analyzed. Should any concentration in the undiluted sample be $\geq$ 50X IDL, then the relative percent difference between the sample's concentration and that of the dilution should be $\leq$ 10%. Should the RPD fail the criterion, flag the data when calculating it, with an "E".

12. Linear Range Analysis (LRA): The linear range of the instrument for each element is established quarterly. This is a means of extending the range of concentrations that can be considered on-scale. The analytes contained in the LRA sample must recover within 95%-105% of their theoretical values in order for the sample concentrations to be reported up to the theoretical values of the LRA analytes.

13. Interference Check Sample (ICSA and ICSAB): A two-part analysis to check whether interference corrections are still properly calibrated. The ICSA sample is composed of interferants only; the ICSAB sample is a combination of interferants and analytes. Recoveries must be within 80%-120% of analyte theoretical values. Concentrations for both samples are listed in **APPENDIX I**, Tables 4 and 6.
The two samples are analyzed at the beginning and again at the end of each analysis set, or once every 8 hours, whichever is more frequent. Should criterion be unmet at the beginning of the analytical set, the problem must be found and rectified, the calibration redefined, and the ICSA/ICSAB analyzed successfully before analysis can proceed to samples. Should the criterion be unmet for subsequent ICSA/ICSAB analyses in the analytical set, all those samples in the set for which analytes of interest are affected by the interferants will have to be reanalyzed after the problem has been corrected.

14. Company Required Detection Limit Standard (CRI): A standard composed of all ICP analytes at concentrations 3-5 times IDL. Recovery control limits are 70%-130% of theoretical values. If the analysis recovers out of control limits, flag the data when calculating it, by noting the poor recovery on the cover sheet of the data set and report the problem to your supervisor. If the analysis does recover outside of criterion then the supervisor or data reviewer must make a decision about the quality of the data. The sample is analyzed once at the beginning and again at the end of the analytical run.

NOTE: This is an interim protocol. When enough data is produced to ascertain the performance, more definite criteria will be established.

15. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked with the analyte(s) of interest, at the same level. Both spiked replicates get spike recovery calculation, using Matrix Spike criterion range, and the two spiked replicates also are subject to calculation of relative percent difference, with Matrix Duplicate criterion range. Should any of the three calculations show lack of control, a supervisor and/or data management should be notified immediately, and the data should be flagged when calculated, with the flags specified for Matrix Spikes and/or Matrix Duplicates.

16. Interelement Correction Factors: In the case of direct spectral overlap, correction factors must be applied in order to eliminate false positive signal due to the interfering element. These correction factors are determined by analyzing pure standards of the suspected element at a concentration of 200-500 mg/L. The resulting positive value for the interfered element is then divided by the value of the interferant to produce a correction factor. For example, if 500 mg/L of cobalt produces a false positive value of 1.0 mg/L aluminum, then the correction factor would be 0.002 mg/L false Al per mg/L cobalt. These correction factors are then entered into the database on the ARL computer until they are to be recalibrated.
When calibration of an interfering element is lost during a run, those elements with which it interferes may not be accepted unless the concentration of the interfering element is low enough to not make a contribution above detection limit. For example, iron interferes on manganese, but it only produces a false positive reading above the 0.005 mg/L detection limit for manganese at a concentration of 38 mg/L.

If calibration is lost for iron during an analytical run, then values for manganese may be accepted only when iron concentration is less than 38 mg/L for those samples. Refer to **APPENDIX I**, Table 2 for the most recent interference correction factors and the concentrations above which the interfering elements will have positive results greater than detection limits for the interfered-with elements.

H. Method Performance

Please refer to the individual methods listed in **APPENDIX I** for description of any method performance study.

I. Provenance

This method was written by

_____ Department Manager

It has been reviewed and accepted by

_____ Metals Analysis Supervisor

_____ Department Manager

_____ Technical Director

_____ Laboratory Manager

SEQUENCE TABLE

S0 (Calibration Blank)
S1
S2
S3
S4
ICV
ICB
  Check calibration for precision and accuracy
LRA
CRA(I)
ICSA
ICSAB
PB
LCS
CCV1
CCB1
  Check calibration for precision and accuracy
  Check QC samples for compliance with criteria
#####
#####
#####
#####
#####S
#####SD
#####
#####
#####
#####D
CCV2
CCB2
  Check calibration for precision and accuracy
  Check QC samples for compliance with criteria
  |
  Repeat 10 non-calibration samples and **CCV#**, **CCB#** pattern until final samples have been analyzed, then end with
  |
CCVn-1
CCBn-1
#####L1 **(One serial dilution for every 20 samples analyzed)**
  |
CRA(I)
ICSA
ICSAB
CCVn
CCBn

Table 1
ARL ICP Model 3560
Available Elements

Element	Symbol	Wavelength (nm)
Aluminum	Al	308.220
Antimony	Sb	206.840
Arsenic	As	189.040
Barium	Ba	455.400
Beryllium	Be	313.040
Cadmium	Cd	226.500
Calcium	Ca	317.930
Chromium	Cr	267.720
Cobalt	Co	228.620
Copper	Cu	324.750
Iron	Fe	259.940
Lead	Pb	220.350
Magnesium	Mg	279.080
Manganese	Mn	257.610
Mercury	Hg	184.950
Molybdenum	Mo	202.030
Nickel	Ni	231.600
Potassium	K	766.490
Scandium	Sc	361.380
Selenium	Se	203.980
Silicon	Si	288.160
Silver	Ag	328.070
Sodium	Na	589.590
Sulfur	S	180.730
Thallium	Tl	190.860
Tin	Sn	189.990
Titanium	Ti	337.280
Vanadium	V	292.400
Zinc	Zn	213.860

Table 2
ARL ICP Interference Correction Windows

Interference	MDL mg/L	Interference Correction	Maximum Concentration (mg/L)
MN ON NI	0.02	6.416428-03	3.0
SB ON SB	0.1	1.103048-01	0.9
V ON AL	0.2	2.181238-02	9.0
V ON BE	0.005	2.391058-03	2.0
CR ON SB	0.2	3.141708-03	63.0
CR ON SB	0.1	1.177468-01	0.8
FE ON CD	0.02	2.377358-04	84.0
FE ON MN	0.005	1.351028-04	37.0
FE ON ZN	0.02	1.304258-04	153.0
CO ON NI	0.02	3.535098-03	5.5
CO ON TL	0.05	5.821468-03	8.5

MDL IS DETECTION LIMIT OF INTERFERED ANALYTE

MAX CONCENTRATION IS MAXIMUM CONCENTRATION BELOW WHICH THE INTERFERANT DOES NOT AFFECT THE INTERFERED-WITH CONCENTRATION.

APPENDIX I
Methods Section

ARL MODEL 3560
Air Method

A. Instrument Specifications

1. Pre-Integration Wash: 25 seconds.
2. On-Peak Integrations: 3 readings.
3. Off-Peak Integrations: 1 reading.
4. Integration Time: 10 seconds per reading.
5. Forward Power: 650 watts
6. Nebulizer: ARL VMDSN Model 135, high dissolved solids nebulizer.
7. Carrier Gas Flow: 25 psi.
8. Plasma Gas Flow: 42 psi.
9. Coolant Gas Flow: 30 psi.

B. Task File

1. Task File: SCANH2O
2. Analytical Lines: Refer to Table 3 for the analytical lines and background points selected.
3. Interelement Correction Factors: Refer to Table 2 for the interelement correction factors.

C. Sequence File

1. Sequence File: SCANH2O
2. Standards: Refer to Table 4 for the standards used in the sequence file.

D. Method Performance

1. An evaluation of the EPM 2000 air sampling filters (Whatman Laboratory Products) required for use in this method per the Air Sampling Protocol was undertaken in order to establish a realistic Limit of Quantification (LOQ) for each individual element. It was anticipated that Barium and Zinc would be present at significant levels as a result of the manufacturing process for glass fiber filters. This was confirmed by the study.
As a consequence, additional flags have been added to the data reporting forms to reflect this. The LOQs were not raised to reflect the background levels because of possible lot to lot variations in filters (this was beyond the scope of the evaluation) and of the standard practice of not blank correcting data.

2. Mercury presents a special problem in that elemental Mercury and organomercuric compounds with significant vapor pressures cannot be analyzed and reported with the approved sampling procedure. Both Arsenic and Selenium were analyzed by Hydride AA in order to achieve lower reporting limits

(relative to analysis by ICP).

3. Analyses of seven filters randomly selected from a lot of 100 were performed in order to determine background levels of the Appendix IX metals in the EPM 2000 Hi-Vol filters. Listed in Table 3 on the following page are the average of the seven replicate analyses in ug, the range of the individual data points, and the reporting limit defined as the LOQ or Limit of Quantification. The LOQs for Barium and Zinc are based on the instrument detection limit (IDL).

4. According to the manufacturer of the air filters, the use of Ultra-pure QM-A Quartz filters would significantly reduce background levels. The particle retention, however, is different and must be considered if it is to be substituted. Such a substitution would require a similar evaluation as has been undertaken for the EPM 2000 filters.

Table 3

LOQ Evaluation of EPM 2000 Air Sampling Filters

Element	Average ug per 1/2 filter	Range found	LOQ
Antimony	< 40	39-40	40
Arsenic	< 0.40	-	0.40
Barium	112	106-122	4.0
Beryllium	< 1.0	0.99-1.01	1.0
Cadmium	< 1.0	0.99-1.01	1.0
Chromium	< 4.0	-	4.0
Cobalt	< 4.0	-	4.0
Copper	< 4.0	-	4.0
Lead	< 4.0	-	4.0
Mercury	< 0.1	0.02-0.1	0.1
Nickel	< 4.0	-	4.0
Selenium	< 0.4	-	0.4
Silver	< 2.0	-	2.0
Thallium	< 10	-	10
Tin	< 40	-	40
Vanadium	< 4.0	-	4.0
Zinc	56	53-64	4.0

ARL MODEL 3560
Water/Wastewater Method

A. Instrument Specifications

1. Pre-Integration Wash: 25 seconds.
2. On-Peak Integrations: 3 readings.
3. Off-Peak Integrations: 1 reading.
4. Integration Time: 10 seconds per reading.
5. Forward Power: 650 watts
6. Nebulizer: ARL VMDSN Model 135, high dissolved solids nebulizer.
7. Carrier Gas Flow: 25 psi.
8. Plasma Gas Flow: 42 psi.
9. Coolant Gas Flow: 30 psi.

B. Task File

1. Task File: SCANH2O
2. Analytical Lines: Refer to Table 3 for the analytical lines and background points selected.
3. Interelement Correction Factors: Refer to Table 2 for the interelement correction factors.

C. Sequence File

1. Sequence File: SCANH2O
2. Standards: Refer to Table 4 for the standards used in the sequence file.

Table 4
ARL ICP MODEL 3560
WATER/WASTEWATER METHOD
ANALYTICAL LINES

TASK FILE: SCANH2O
SEQUENCE FILE: SCANH2O

ELEMENT	SYMBOL	WAVELENGTH (NM)	BG1	BG2	IDL (UG/L)	REMARKS
Beryllium	Be	313.040	-60	60	5.0	
Sodium	Na	589.590	-60	60	200	
Magnesium	Mg	279.080	-60	60	200	
Aluminum	Al	308.220	0	60	200	
Potassium	K	766.490	-60	60	200	
Calcium	Ca	317.930	-60	60	200	
Vanadium	V	292.40	-60	0	20	
Chromium	Cr	267.720	0	60	20	
Manganese	Mn	257.610	-60	0	5	
Iron	Fe	259.940	-60	60	20	
Cobalt	Co	228.620	-60	0	20	
Nickel	Ni	231.600	-60	60	20	
Copper	Cu	324.750	-60	0	20	
Zinc	Zn	213.860	-60	60	20	
Arsenic	As	189.040	0	60	100	
Selenium	Se	203.980	0	60	100	
Silver	Ag	328.070	-50	0	10	
Cadmium	Cd	226.500	-50	0	5	
Antimony	Sb	206.840	-43	0	200	
Barium	Ba	455.400	-60	60	20	
Thallium	Tl	190.860	0	60	50	
Lead	Pb	220.350	-60	60	40	

BG1 & BG2 are motor steps from analyte peak.
IDLs are determined quarterly.

Table 5
Instructions for Solutions
for SEQUENCE FILE: SCANH2O

SPEX STOCK SOLUTION CONCENTRATIONS IN MG/L

	XENT-25	XENT-26	XENT-4	XENT-6	XENT-3	XENT-24	INT-A1	INT-B1	
Ba		[100]	[1000]					[50]	
Tl		[100]		[400]					
V		[100]	[1000]					[50]	
Sb		[100]		[400]					
Zn		[100]	[1000]					[100]	
Cu		[100]	[1000]					[50]	
Pb		[100]	[1000]					[100]	
Co		[100]	[1000]					[50]	
Ni		[100]	[1000]					[100]	
Cr		[100]	[1000]					[50]	
Se		[200]			[1000]				
As		[200]			[1000]				
Fe	[500]					[500]	[2000]		
Mg	[5000]					[5000]	[5000]		
Na	[5000]					[2500]			
K	[5000]					[2500]			
Ca	[5000]					[5000]	[5000]		
Al	[5000]					[5000]	[5000]		
Be		[20]	[200]					[50]	
Cd		[20]	[200]					[100]	
Ag		[50]		[100]				[100]	
Mn		[20]	[200]					[50]	

STDS, LRA, QC, and ICV/CCV for SCANH2O and SCANSOIL

```
STD  1      10ml STD 2 ----> 1000ml
STD  2      10ml XENT-4 ---> 1000ml
STD  3      10ml STD 4 ---->  500ml
STD  4      10ml XENT-3 ---> 1000ml
STD  5       1ml STD 6 ---->  500ml
STD  6      10ml XENT-24 --> per 100ml
STD  7      25ml STD 8 ---->  500ml
STD  8      10ml XENT-6 ---> 1000ml
```

```
ICV/CCV   10ml XENT-25 + 10ml XENT-26 -->1000ml
LRA       10ml XENT-4 + 10ml XENT-6   --> 200ml

ICS-A     10ml INT-A1  ------------>   per 100ml
ICS-AB    10ml INT-A1 + 1ml INT-B1 -> per 100ml


Spking soln 1ml each XENT-25 & XENT-26
                          ----> per 100ml
```

For SCANH2O: ALL SOLUTIONS are in 1% HNO3
and 5% HCl (10ml & 50ml ->1000ml)

ARL MODEL 3560
Soil/Non-Aqueous Method

A. Instrument Specifications

1. Pre-Integration Wash: 25 seconds.
2. On-Peak Integrations: 3 readings.
3. Off-Peak Integrations: 1 reading.
4. Integration Time: 10 seconds per reading.
5. Forward Power: 650 watts
6. Nebulizer: ARL VMDSN Model 135, high dissolved solids nebulizer.
7. Carrier Gas Flow: 25 psi.
8. Plasma Gas Flow: 42 psi.
9. Coolant Gas Flow: 30 psi.

B. Task File

1. Task File: SCANSOIL
2. Analytical Lines: Refer to Table 5 for the analytical lines and background points selected.
3. Interelement Correction Factors: Refer to Table 2 for the interelement correction factors.

C. Sequence File

1. Sequence File: SCANSOIL
2. Standards: Refer to Table 6 for the standards used in the sequence file.

Table 6
ARL ICP MODEL 3560
SOIL/NON-AQUEOUS METHOD
ANALYTICAL LINES

TASK FILE: SCANSOIL
SEQUENCE FILE: SCANSOIL

ELEMENT	SYMBOL	WAVELENGTH (NM)	BG1	BG2	IDL (UG/L)	IDL (MG/KG) *
Beryllium	Be	313.040	-60	60	5.0	0.25
Sodium	Na	589.590	-60	60	200	10
Magnesium	Mg	279.080	-60	60	200	10
Aluminum	Al	308.220	0	60	200	10
Potassium	K	766.490	-60	60	200	10
Calcium	Ca	317.930	-60	60	200	10
Vanadium	V	292.40	-60	0	20	1.0
Chromium	Cr	267.720	0	60	20	1.0
Manganese	Mn	257.610	-60	0	5	0.25
Iron	Fe	259.940	-60	60	20	1.0
Cobalt	Co	228.620	-60	0	20	1.0
Nickel	Ni	231.600	-60	60	20	1.0
Copper	Cu	324.750	-60	0	20	1.0
Zinc	Zn	213.860	-60	60	20	1.0
Arsenic	As	189.040	0	60	100	5.0
Selenium	Se	203.980	0	60	100	5.0
Silver	Ag	328.070	-50	0	10	0.5
Cadmium	Cd	226.500	-50	0	5	0.25
Antimony	Sb	206.840	-43	0	200	10
Barium	Ba	455.400	-60	60	20	1.0
Thallium	Tl	190.860	0	60	50	2.5
Lead	Pb	220.350	-60	60	40	2.0

BG1 & BG2 are motor steps from analyte peak.
IDLs are determined quarterly.
* Assumes a 4g--> 200mL digestion and 100% solids.

Table 7
Instructions for Solutions
for SEQUENCE FILE: SCANSOIL

SPEX STOCK SOLUTION CONCENTRATIONS IN MG/L

	XENT-25	XENT-26	XENT-4	XENT-6	XENT-3	XENT-24	INT-A1	INT-B1	
Ba		[100]	[1000]					[50]	
Tl		[100]		[400]					
V		[100]	[1000]					[50]	
Sb		[100]		[400]					
Zn		[100]	[1000]					[100]	
Cu		[100]	[1000]					[50]	
Pb		[100]	[1000]					[100]	
Co		[100]	[1000]					[50]	
Ni		[100]	[1000]					[100]	
Cr		[100]	[1000]					[50]	
Se		[200]			[1000]				
As		[200]			[1000]				
Fe	[500]					[500]	[2000]		
Mg	[5000]					[5000]	[5000]		
Na	[5000]					[2500]			
K	[5000]					[2500]			
Ca	[5000]					[5000]	[5000]		
Al	[5000]					[5000]	[5000]		
Be		[20]	[200]					[50]	
Cd		[20]	[200]					[100]	
Ag		[50]		[100]				[100]	
Mn		[20]	[200]					[50]	

STDS, LRA, QC, and ICV/CCV for SCANH2O and SCANSOIL

```
STD  1      10ml STD 2 ----> 1000ml
STD  2      10ml XENT-4 ---> 1000ml
STD  3      10ml STD 4 ---->  500ml
STD  4      10ml XENT-3 ---> 1000ml
STD  5       1ml STD 6 ---->  500ml
STD  6      10ml XENT-24 --> per 100ml
STD  7      25ml STD 8 ---->  500ml
STD  8      10ml XENT-6 ---> 1000ml

ICV/CCV   10ml XENT-25 + 10ml XENT-26 -->1000ml
LRA       10ml XENT-4 + 10ml XENT-6   --> 200ml

ICS-A     10ml INT-A1  ----------->   per 100ml
ICS-AB    10ml INT-A1 + 1ml INT-B1 -> per 100ml


Spking soln 1ml each XENT-25 & XENT-26
                          ----> per 100ml
```

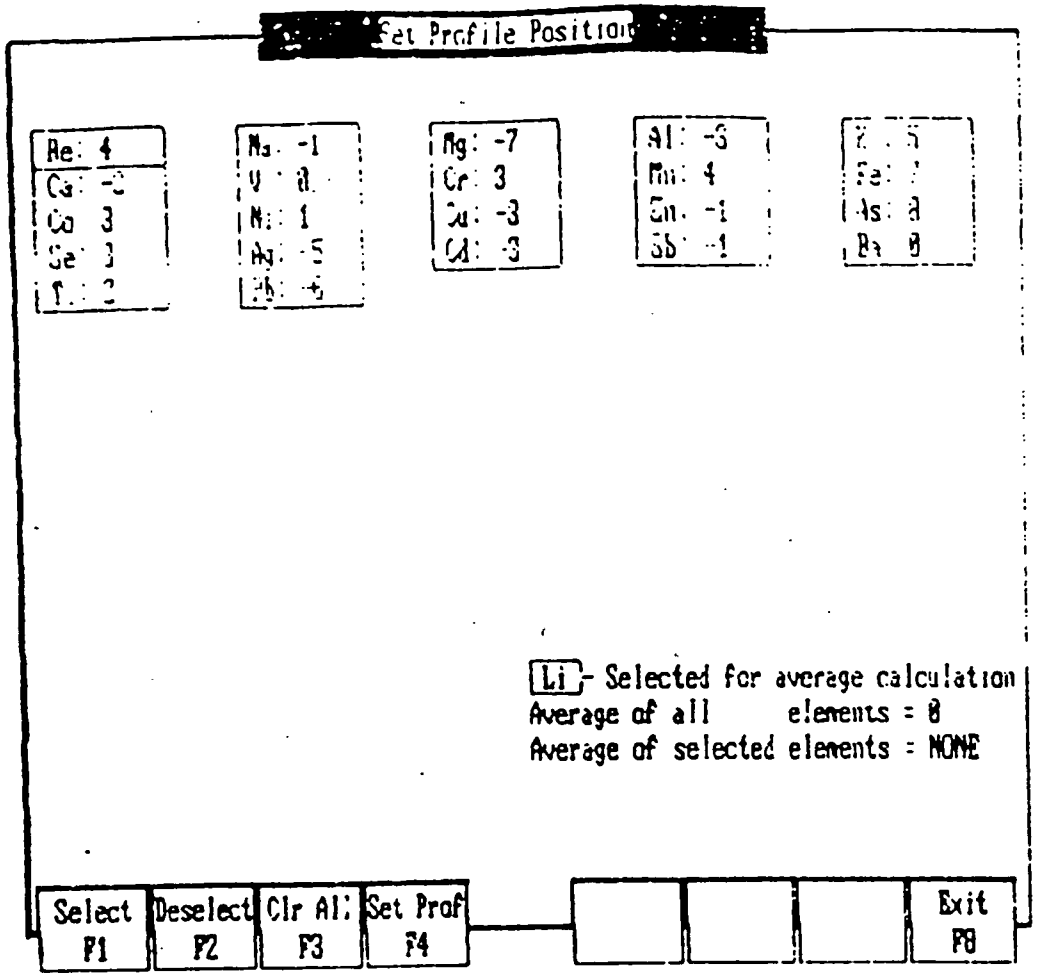
For SCANSOIL: ALL SOLUTIONS are in 10% HNO3 and 5% HCl.

APPENDIX II
Documentation

Instrument Status

Status	Range			Measured
Vacuum	(5.00	....	50.00)	9.37
Setsap	(35.00	....	40.00)	38.45
Mains	(210.00	....	254.00)	236.6
- 1000 Volt Supply	(-1050.00	....	-950.00)	-999.6
Cabinet Temperature	(24.00	....	40.00)	25.75
+ 5 Volt Supply	(4.75	....	5.25)	5.09
+ 12 Volt Supply	(11.70	....	12.30)	12.07
- 12 Volt Supply	(-12.30	....	-11.70)	-11.94
+ 24 Volt Supply	(22.50	....	26.50)	24.56
-100 Volt Supply	(-102.00	....	-98.00)	-100.1

Plate current _____
PA Filament _____
PA Volt _____
PA Grid _____


Set Profile Position
Re: 4
Ca: -2
Co: 3
Se: 3
Ti: 2
Na: -1
V: 0
Ni: 1
Ag: -5
Pb: -6
Mg: -7
Cr: 3
Cu: -3
Cd: -3
Al: -6
Mn: 4
Zn: -1
Sb: -1
Li - Selected for average calculation
Average of all elements = 0
Average of selected elements = NONE
Select F1
Deselect F2
Clr All F3
Set Prof F4
Exit F8

ARL ICP 3560 DAILY INSTRUMENT MAINTENANCE LOGBOOK

INST.: ICP-001 PAGE:_____

PUMP TUBING	ARGON WETTER	RINSED NEBULIZER	INSTRUMENT PROFILE	INSTRUMENT STATUS	EMPTY WASTE	CLEANED TORCH	INITIAL	DATE

INORGANICS DEPARTMENT

PAGE ONE - ANALYTICAL REPORT, COVER SHEET

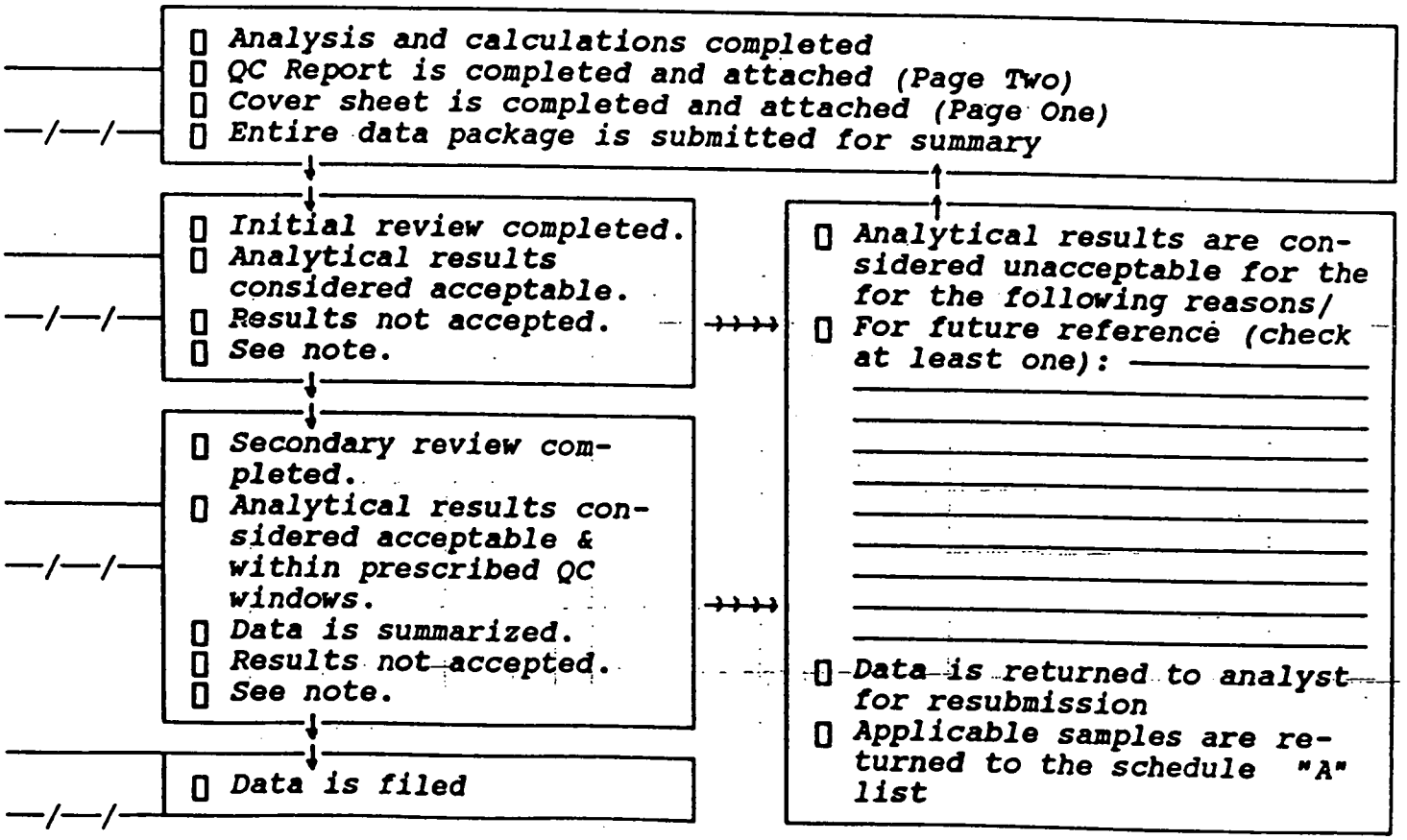
DATE OF ANALYSIS: ___/___/__

PARAMETER(S)
_____
_____
_____

ANALYST: _____

Clients included in this data set:

	name	job #		name	job #
1.	_____	_____	5.	_____	_____
2.	_____	_____	6.	_____	_____
3.	_____	_____	7.	_____	_____
4.	_____	_____	8.	_____	_____



ARL file # : ________ STD Batch #: 91-______ Analyst: ______________
Date: ____/____/______

Sample id	Bin		Matrix	Dil Fctr	Parameters	Comments side:____

INSTRUMENT REPAIR LOG

INST_____ DATE_____ TIME_____ CHEMIST_____

PROBLEM: _____

METHOD OF CORRECTION: _____

INST_____ DATE_____ TIME_____ CHEMIST_____

PROBLEM: _____

METHOD OF CORRECTION: _____

INST_____ DATE_____ TIME_____ CHEMIST_____

PROBLEM: _____

METHOD OF CORRECTION: _____

ANALYSIS OF TOTAL AND DISSOLVED METALS BY THE PERKIN-ELMER ELAN 5000 ICP/MS

1.0 SCOPE AND APPLICATION

This method is applicable to the analysis of total aqueous and non-aqueous and dissolved metals and is based on USEPA Methods 6020 and 200.8. The document outlines the procedures and requirements for any ICP/MS method developed using the Perkin-Elmer ELAN 5000 ICP/MS.

2.0 SUMMARY OF METHOD

2.1 Digestates and filtrates are exposed to an argon plasma which provides sufficient energy to atomize and ionize elements. These atoms and ions are directed into a quadrupole mass spectrometer which repetitively scans the stream's mass spectrum over a range of 5-270 amu. This allows for very low level, yet fast, multi-element analysis of samples.

2.2 Table 1, below, lists the elements determined by this method and provides Practical Quantitation Limits (PQLs) for each in both aqueous and solid matrices.

3.0 SAFETY PRECAUTIONS

Many samples which require metals analysis are known or suspected health hazards. Normal lab safety practices should be observed. Wearing a lab coat and protective eye-wear is required.

4.0 INTERFERENCES

4.1 Physical: Viscosity or high salt content may cause sample transport problems which will result in intensity readings differing from standards in reagent water. Serial dilution will indicate if this interference is present.

4.2 Chemical: Due to the high energies involved in ICP/MS, very few chemical interferences are present.

4.3 Isobaric Elemental: An isotope of one element can have the same mass/charge ratio as the isotope of a different

element. For example, ^{80}Se has an interference from ^{80}Kr. Some isobaric elemental interferences can come from charged species, as in the case of $^{48}Ca^{+2}$ interfering with ^{24}Mg. The analytical system corrects for the concentration of the interferents by means of evaluation of the concentration of other isotopes of the elements of interest. Most elements have at least one isotope free from this type of interference.

4.4 Abundance Sensitivity: This is a measure of the degree of resolution of masses in the quadrupole. This kind of interference most often occurs when a small peak is next to a large one.

4.5 Isobaric Polyatomic Ion: Polyatomic ions are formed in the plasma and can form mass/charge ratios that are the same as isotopes of interest. For example, an argon-argon ion, $Ar\text{-}Ar^{+1}$, has the same mass/charge ratio as ^{80}Se. Interference by these ions is subject to the same techniques as are used in correcting for interference by isobaric elements.

5.0 APPARATUS AND MATERIALS

5.1 Perkin-Elmer ELAN 5000 ICP/MS with autosampler, peristaltic pump.

5.2 High and low solids nebulizers.

5.3 Class "A" Pipets, various volumes.

5.4 Calibrated re-pipets, Eppendorf pipets, various volumes.

5.5 Class "A" volumetric flasks, various volumes.

6.0 REAGENTS

6.1 ASTM Type II water (ASTM 1193-1199(1983)): aka Super-Q water.

6.2 Concentrated nitric acid, HNO_3, ultrex grade: Commercially available.

6.3 Nitric acid, HNO_3, 1% (v/v): Dilute 20 mL of concentrated nitric acid *ultrex?* in Super Q water in a marked and labeled 2L jug. Bring up to the mark with

Super Q water. Shelf life is indefinite.

6.4 Concentrated hydrochloric acid, HCl: Commercially available.

6.5 Hydrochloric acid, HCl, 1% (v/v): Dilute 20 mL concentrated HCl in Super Q water in a marked and labeled 2L jug. Bring up to the mark with Super Q water. Shelf life is indefinite.

6.6 Standards

6.6.1 Stock Standards: Stock standards for all elements listed in Table 1 are supplied to ENCOTEC specifications by manufacturers which certify the standards as traceable to EPA reference materials. Shelf life is specified by the manufacturer.

6.6.2 Calibration Standards: Dilute stock standards to the following final concentrations, using Class A volumetric flasks and pipettes for the procedures. Use, as diluent, the mixture of 1% nitric acid and 1% hydrochloric acid that will match the acid concentrations in the samples to be analyzed. Shelf life is indefinite.

0.100 ug/L
0.050 ug/L
0.010 ug/L

6.7 Calibration Verification Source: Calibration verification sources are supplied by SPEX, to ENCOTEC specifications. Combine the supplied sources and dilute to a final concentration of 0.040 mg/L for each element listed in Table 1.

6.8 Spiking Protocol: Matrix spikes using stock spiking solutions provided by commericial manufacturers to ENCOTEC specifications are generated in the digestion procedure. For post-digestion analytical spikes, add the appropriate spiking solution to a sample digestate or filtrate in an amount to provide the fortification levels listed in Table 2. See, also, Section 11.10.1 through 11.10.4, below.

6.9 Tuning Solution: Contains 0.010 mg/L of Mg, Cu, In, Tb, and Pb. Commercially available.

6.10 Internal Standard Solution: Contains 0.500 mg/L of Sc, Y, In, Tb, and Bi. Commercially available.

6.11 Company-required detection limit sample (CRI): Prepare a solution from the stock standards with a concentration equal to 3-5X the PQLs for all the elements listed in Table 1.

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to **Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by ICPMS (DIGMS)** and **Acid Digestion of Soils and/or Solids for Total Metals Analysis by ICPMS (DIGMS)** for sample preservation and handling requirements. Sample extracts are stored at room temperature. Sample analysis must be completed within 6 months of sampling date.

8.0 PROCEDURE

Instrument conditions

8.1 Set up the instrument according to the parameters specified in Table 3. Allow the plasma to run for at least a half-hour before beginning analysis.

8.2 Optimize the signal produced with the tuning solution (Section 6.9, above). Run an Intensity Check verifying instrument stability. Include a printout of the results in the data package.

Calibration

8.3 Perform an instrument tuning evaluation by analyzing the tuning solution at least four times. The relative standard deviations for the elements in the four replicate analyses must be less than 10%. Include a printout of the evaluation in the data package.

8.4 Run a Scan on the tuning solution and verify the mass calibration and resolution. The mass calibration must be within ± 0.1 amu of the theoretical values for the elements in the tuning solution. The resolution must be less than 1.0 amu full width at 10% peak height.

8.5 Calibrate the instrument using the standards listed in the appropriate method (see **APPENDIX I**, Table 4 or 6).

8.6 Analyze the Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) samples. Verify that these meet acceptance criteria outlined in Section 11.1 through 11.3, below, and **APPENDIX I**, Table 3 or 5.

8.7 Analyze the Company-Required Detection Limit sample (CRI).

Sample analysis

8.8 Continue analysis following the **Analysis Sequence Table**, below. Verify that the various quality control samples meet acceptance criteria outlined in Section 11.0, below.

1. S0 (Calibration Blank)
2. S1
3. S2
4. S3
5. Initial Calibration Verification (ICV).
6. Initial Calibration Blank (ICB).
   Check calibration for precision and accuracy.
7. Company-Required Detection Limit sample (CRI).
8. Method Blank.
9. Laboratory Control Sample.
10. Continuing Calibration Verification (CCV) 1.
11. Continuing Calibration Blank (CCB) 1.
    Check calibration for precision and accuracy.
    Check QC samples for compliance with criteria.

12 - 21. Samples and QC Samples for 10 non-calibration analyses.

22. CCV2
23. CCB2
    Check calibration for precision and accuracy.
    Check QC samples for compliance with criteria.

24 - 33. Repeat 10 non-calibration samples and CCV#, CCB# pattern until final samples have been analyzed.

34. CCVn-1
35. CCBn-1
36. One serial dilution for every 20 samples analyzed (See Section 11.12, below).
37. CRI
38. CCVn
39. CCBn

8.9 Dilute those samples for which results are greater than linear range and reanalyze.

Calibration verification

8.10 Following every ten analyses run CCV and CCB solutions. Verify that they meet acceptance criteria outlined in Section 11.1 and Sections 11.3 and 11.4, below.

8.11 Be certain to end each analytical run with analysis of the CRI prior to the last CCV/CCB analysis.

8.12 Include the run log, the raw data, the instrument tuning, mass calibration, and resolution pages, the calibration report, and the result file report in the data package. Save the data values to the DMS system.

8.13 Indicate, on the group schedule, the work that was performed; include any notes about the run.

8.14 Fill out the Data Cover Page (refer to **APPENDIX II**). Place the data in the review bin.

9.0 MAINTENANCE PROCEDURES

Daily procedures

9.1 Change the peristaltic pump tubing.

9.2 Inspect the sampler and skimmer cones for cleanliness. Clean, if necessary, using instrument manufacturer procedures.

9.3 Check the vacuum system and record both the base and operating vacuum levels on the printout of the daily Intensity Check that will be included in the analytical run data package.

9.4 Record settings for the torch assembly's argon gas flows and for the ion optics on the printout of the daily Intensity Check.

9.5 Rinse the nebulizer for five minutes with 1% HNO3 (see Section 6.3, above).

9.6 Make a copy of the Intensity Check sheet with the notations for the vacuum system, argon flows, and ion optics and insert the copy in the Maintenance Log. (The original of the sheet will be included in the data package.)

Weekly

9.7 Check the coolant water level in the recirculation cooling unit and if necessary replenish with Super Q water to the appropriate level. Record the check and replenishing activity in the Maintenance Log.

9.8 Check vacuum pump oil level and visually inspect the oil for signs of abnormal wear. Record the check in the Maintenance Log.

Monthly

9.9 Change the vacuum pump oil. This requires bleeding the vacuum chamber. It usually takes about two hours to pump the pressure back down within tolerance after the oil is changed. Record the operation in the Maintenance Log.

10.0 CALCULATIONS

11.0 QUALITY CONTROL

11.1 Internal Standard: Monitor internal standards for all analyses. If the intensity of any internal standard is not 50-150% of the intensity of that standard in the Calibration Blank (see Section 8.6, above) take the following corrective action.

11.1.1 If the out-of-window result occurs in a sample dilute the sample 1/5 (that is to say, one part sample and four parts diluent) using 1% nitric acid and reanalyze. Repeat this procedure for the sample until the internal standard intensities are within criterion.

11.1.2 If the out-of-window result occurs in a CCV or CCB, stop analysis and correct the problem. When the problem is corrected, initiate a new analytical run, analyzing those samples analyzed after the last satisfactory CCV or CCB first.

11.2 Initial Calibration Verification (ICV): Analyze the ICV immediately after completing the calibration procedure. The recovery criterion window is 90%-110% of theoretical value.

11.3 Initial Calibration Blank (ICB): Analyze this immediately after analysis of the ICV. The absolute value of concentration for any analyte must be less than the PQL reported for that analyte in Table 1.

11.4 Continuing Calibration Verification (CCV) - Typically, this solution is the same as the ICV, but it doesn't have to be. Analyze the CCV solution after ten non-calibration analyses; acceptable recovery is, again, 90%-110% of theoretical value.

11.5 Continuing Calibration Blank (CCB): Re-analyze the reagent blank solution used in ICB analysis immediately after each CCV. Unlike the ICB, acceptable recoveries are less than the absolute value of three times the PQL.

11.6 Method Blank (MB): Each digestion set should have an aliquot of reagent blank which has been treated as a sample. The absolute value for the concentration of any analyte must be less than three times PQL. Should a MB fail this evaluation, report the poor recoveries to a supervisor and/or data management.

11.7 Laboratory Control Sample (LCS): Every digestion set should have an aliquot of reagent blank to which has been added a known amount of all analytes observed by the ICP/MS before being carried through the digestion procedure. Recovery of the LCS should be within 80%-120% of the theoretical value for the analytes included. If results fail to meet this criterion, report to a supervisor and/or data management. Flag the data when evaluating it, by noting the poor recovery on the cover sheet of the data set.

11.8 Matrix Spike: At least one sample in a digestion set and, more commonly, one in every 20 samples, will have a replicate to which has been added the same known amount of all analytes observed by the ICP as was added to the LCS. This replicate is then digested as a sample. The spike recovery should be within a 75%-125% criterion range. If criterion is not met, perform a post-digestion analytical spike (see 11.10, below) and flag the data when evaluating it, with an "N".

11.9 Matrix Duplicate: One sample in a digestion set, or one for every 20 samples in the set, whichever is the greater frequency, will have a replicate which is also digested by the same protocol. Should both replicates show concentrations $\geq$ 5X PQL, the relative percent

difference between the two replicates should be ≤ 20%. Should the RPD be greater than 20%, report to a supervisor and/or data management, and flag the data when evaluating it, with a "*". When either the sample or the duplicate shows a concentration ≤ 5X PQL, the absolute range between the two replicates should be ≤ PQL. If the range is greater than PQL, flag the data when calculating it, again using "*". When either or both replicates recovers at < PQL, report the RPD as "not calculable" (N/C). The result reported as sample concentration is that for the first replicate, rather than the duplicate. Do not report the average of the two replicates as the sample concentration.

11.10 Analytical Spike: When a matrix spike result fails to meet criterion, prepare and analyze an analytical spike, by adding a known amount of analyte(s) of interest to an aliquot of digested, unspiked sample. Analysis should return a recovery of 75%-125% of theoretical value of the spike added.

11.10.1 Analytical spikes are also required when the concentration of a sample which also has a matrix spike is greater than the linear range of the ICP/MS.

11.10.2 The spiking solution should be of acid strength and composition appropriate to the samples being analyzed.

11.10.3 Analytical spikes generally dilute the samples on which they are made by as much as the spike volume added. Accordingly, in no case dilute a sample more than 10% with the spiking solution added; that is to say, a sample should be at least 90% of the composite of sample and spike prepared for an analytical spike.

11.10.4 When a sample is off-scale and needs to have a spike analyzed run an analytical spike on an aliquot of sample which has been diluted with reagent blank to a concentration that will register at approximately mid-range. Dilute a second aliquot to the same level, including the spiking solution in the diluent; calculate spike recovery on the observed concentration of the diluted sample.

11.11 Post-digestion Matrix Duplicate: If there are insufficient duplicates in the analysis set (i.e., less than one in twenty, or one per analytical set, whichever is the greater frequency), a sample or samples should be selected for re-analysis, to bring the total number of duplicate analyses up to the correct frequency. The control limits and calculations are the same as for Matrix Duplicates.

11.12 Serial Dilution: One sample in every twenty (or one sample per analytical set, whichever is the greater frequency), is to be diluted to 1/5 (i.e., one part sample and 4 parts reagent blank) and re-analyzed. Should any concentration in the undiluted sample be $\geq$ 50X PQL, then the relative percent difference between the sample's concentration and that of the dilution should be < 10%. Should the RPD fail the criterion, flag the data when evaluating it, with an "E".

11.13 Linear Range Analysis (LRA): Establish the linear range of the instrument for each element quarterly. (This is a means of extending the range of concentrations that can be considered on-scale.) The analytes contained in the LRA sample must recover within 95%-105% of their theoretical values in order for sample concentrations to be reported up to the theoretical values of the LRA analytes.

11.14 Company Required Detection Limit Standard (CRI): A standard composed of all ICP/MS analytes at concentrations 3-5 times PQL. Analyze the sample once at the beginning and again at the end of the analytical run. Recovery control limits are 70%-130% of theoretical values. If the analysis recovers out of control limits, flag the data when evaluating it, by noting the poor recovery on the cover sheet of the data set and report the problem to your supervisor. If the analysis does recover outside of criterion then the supervisor or data reviewer must make a decision about the quality of the data.

> NOTE: This is an interim protocol. When enough data is produced to ascertain the performance, more definite criteria will be established.

11.15 Matrix Spike Duplicate: Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked with the analyte(s) of interest, at the same level. Both spiked replicates get spike

recovery calculation, using Matrix Spike criterion range, and the two spiked replicates also are subject to calculation of relative percent difference, with Matrix Duplicate criterion range. Should any of the three calculations show lack of control, notify your supervisor and/or data management immediately, and flag the data when evaluating it , with the flags specified for Matrix Spikes and/or Matrix Duplicates.

12.0 METHOD PERFORMANCE

A set of MDL studies is presented at the end of this procedure. The Method Detection Limits were determined by spiking a known concentration of the analytes into laboratory reagent water and carrying the mixture through the extraction and analysis procedures used for samples. See, also, **Standard Operating Procedure for the Determination of the Method Detection Limit and/or Instrument Detection Limit.**

13.0 REFERENCES

13.1 Test Methods for Evaluation of Solid Waste, SW-846, Method 6020, Rev. 0, Nov., 1990.

13.2 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 200.8, Rev. 0,

13.3 USEPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, Document Number ILM03.0,

14.0 PROVENANCE

This method has been written by

_____ (job title, first author)

_____ Technical Documentation Officer

It has been read and approved by

_____ Technical Documentation Officer

_____ Group Leader, Metals

_____ Inorganics Department Manager

_____ Technical Director

USE OF THE HYDRIDE GENERATOR IN ARSENIC AND/OR SELENIUM ANALYSIS (AS, SE)

A. Introduction

1. Applicability: This method is applicable to determination of arsenic and/or selenium in any suitably prepared sample. It is not applicable to samples which have not been subjected to acid digestion by the general nitric or nitric/hydrochloric and the concentrated hydrochloric procedures.
2. Purpose of Testing: Both arsenic and selenium are highly toxic cumulative poisons, as are many of their compounds. They occur commonly in soils and are frequently found as byproducts of various industrial processes. These considerations lead to the inclusion of both of these elements in various monitoring lists, such as the RCRA metals list, or the Priority Pollutants list.
3. Detection Limit: The default detection limit is 0.001 mg/L, unless otherwise specified by the client. Since samples are diluted to 1/2 the concentration found in the digestates, the reporting limit is 0.002 mg/L. The instrument working range is 0.0005 mg/L to 0.025 mg/L.
4. Reference Methods: Varian, manufacturer; after EPA SW-846, Method 7041 and 7741, Rev. 0 and Standard Methods for the Analysis of Water and Wastewater, 17th Ed., Method 3114 B and C.
5. Summary of Method: Converted arsenic sample digestates are combined with potassium iodide, to insure reduction of all As^{V} to As^{III}. Analysis for either Arsenic(III) or Selenium(IV) proceeds by combining prepared sample digestates with sodium borohydride under acidic conditions. A volatile hydride is formed and is purged into a heated quartz cell atomizer on an atomic absorption spectrophotometer (FLAA). The high temperature results in dissociation of the hydride species into elemental form. The FLAA is used to determine the element concentrations.
6. Interferences: Free chlorine present in the concentrated hydrochloric acid may oxidize the hydride and can contaminate the generating equipment. Standard Methods recommends purging any fresh source of HCl with helium for 3 hours, to remove the chlorine, which will be present in varying amounts in different lots of acid. Nitrite can greatly reduce recovery of the selenium hydride, but this interferant is removed by using urea in conversion of digestates for hydride-based analysis. High iodide concentrations, which will be likely in Arsenic determinations can interfere with Selenium determination; be certain not to use equipment designated for Arsenic determination in analysis for Selenium.

Concentrations of noble metals (*e.g.*, Silver, Gold, Platinum, Palladium, etc., at ~0.100mg/L), concentrations of copper, nickel, and lead greater than 1.0 mg/L, and concentrations of other hydride-forming metals (*e.g.*, Bismuth, Antimony, Tin and Tellurium at 0.1 to 1.0 mg/L) may suppress response for Arsenic and Selenim hydrides. Presence of Arsenic or Selenium in the other metal's analysis can cause similar suppression.

7. Sample Collection and Preservation: The "samples" in this procedure are the result of As/Se conversions, prepared ≤ 48 hours prior to analysis. These are stored at room temperature and preserved in 50% HCl.

8. Holding Time: The holding time for the As/Se conversions is 48 hours. The holding time between sample collection and analysis for Arsenic and/or Selenium is 180 days.

9. Safety Precaution: Arsenic, selenium, and their hydrides are highly toxic, and strong acids are used in the conversion procedure. Therefore, gloves are strongly recommended. Lab coats and glasses are required.

B. Apparatus

1. Class A pipets, 25mL, 10mL, 9mL, 8mL, 4mL, and 2mL.
2. Calibrated Eppendorf pipets, 1000uL and 500uL.
3. Class A volumetric flasks, 1000mL and 200mL.
4. Calibrated re-pipets, one capable of delivering 1.0 mL, the other capable of delivering 100 mL.
5. Varian SpectraAA 20 atomic absorption unit.
6. Varian VGA-76 hydride-generating peristaltic pump.
7. Gas/liquid separator.
8. Quartz absorption cell.
9. Hollow cathode lamps, suitable for Arsenic and/or Selenium determination.

C. Reagents and Standards

1. Reagents: Reagent grade chemicals will be used in all tests.

   a. ASTM Type II water (ASTM 1193-99, 1983): *i.e.*, Super Q water.

   b. Concentrated hydrochloric acid, HCl: Commercially available.

   c. Hydrochloric acid, HCl, 1% (v/v) solution: Dilute 20 mL concentrated HCl in Super Q water in a marked and labeled 2L jug. Bring up to the mark with Super Q water. Cool to room temperature before using in hydride generation and analysis. Shelf life is indefinite.

   d. Calibration Blank water, a.k.a. Dilution water: Dilute 100 mL of concentrated HCl in ~50 mL of Super Q water in a 200mL volumetric flask. Add 4.0 g urea, rinse the crystals down with Super Q water and allow to cool overnight. Bring up to volume with Super Q water.

d. Potassium Iodide, KI, 1% (w/v) solution: Weigh to the nearest 0.01 g 2.00 g of potassium iodide and transfer to a 200mL Class "A" volumetric flask. Dilute to the mark using Super Q water. Shelf life is indefinite.

e. Sodium Borohydride ($NaBH_4$) Reagent: Combine 3.0 g $NaBH_4$ and 2.5 g NaOH (both weighed to the nearest 0.1 g) in a 500mL Class "A" volumetric flask. Dilute to the mark with Super Q water. Store at $\leq$ 4° Celsius. Shelf life is approximately 2 days. The reagent must be at room temperature for use in hydride analysis.

2. Standards:

a. Arsenic and Selenium Stock Standards, 1000 mg/L: Commercially available.

b. Arsenic or Selenium Intermediate Solution, 10 mg/L: Using a Class "A" pipet, measure 2 mL of either of the Stock Standards into a Class "A" 200mL volumetric flask. Dilute to the mark with Super Q water. Shelf life is indefinite.

c. Arsenic or Selenium Working Intermediate Solution, 100ug/L: Add ~50 mL of Super Q water to a 200mL volumetric flask and, using a re-pipet, add 100 mL concentrated HCl to it. Add 4.0 g urea, rinse the crystals down with Super Q water and allow the flask to cool overnight. Using a Class "A" pipet, measure 2 mL of the Intermediate Solution into the solution. Dilute to the mark with Super Q water.

d. Standards: When preparing the 50% HCl mixture for the Working Intermediate Solution, prepare a 200mL volumetric flask for each of the following Arsenic and Selenium Standards. That is to say, place ~50 mL Super Q water in each flask and, using a re-pipet, add 100 mL concentrated HCl, then add 4.0 g urea (rinsing the crystals down with Super Q water) and allow to cool overnight. Using Eppendorfs, Class "A" pipets, and Super Q water throughout, perform the following dilutions:

Arsenic Standards

1) 9.0 ug/L: Add 18 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

2) ~~7.0 ug/L~~; Add 14 mL of ~~the~~ Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

3) 4.0 ug/L: Add 8 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

4) 2.0 ug/L: Add 4 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

5) 1.0 ug/L: Add 2.0 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
6) 0.5 ug/L: Add 1.0 mL (1000 uL) of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

Selenium Standards

1) 12.0 ug/L: Add 24 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
2) 9.0 ug/L: Add 18 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
3) 5.0 ug/L: Add 10 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
4) 3.0 ug/L: Add 6 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
5) 1.0 ug/L: Add 2.0 mL of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.
6) 0.5 ug/L: Add 1.0 mL (1000 uL) of the Working Intermediate Solution to a prepared flask and dilute to the mark with Super Q water.

e. Arsenic/Selenium Spiking Standard, 250 ug/L: Using a Class "A" pipet, measure 25 mL of the Intermediate Solution (10mg/L) into a 1000mL Class "A" volumetric flask and dilute to the mark using 1% HCl solution.

3. Calibration Verification Source: This solution is supplied to company specifications by SPEX and contains both Arsenic and Selenium. The standard is used to generate Intermediate, 10mg/L, and Working Intermediate, 100ug/L, Solutions, from which an Initial/Continuing Calibration Verification solution at 4.0 ug/L concentration is prepared. (Working Intermediate and Initial/Continuing Calibration Verification solutions are prepared in 50% HCl (v/v), fortified with urea.)

4. Spiking Protocol: Using a Class "A" pipet and an Eppendorf pipet, combine 9.9 mL of sample with 100 uL of Arsenic/Selenium Spiking Standard (SS). The theoretical spike concentration is

$$\text{spike conc.} = \frac{100\ \text{uL SS} * 250\ \text{ug/L SS conc}}{(9900\ \text{uL sample} + 100\ \text{uL spike})} = 2.5\ \text{ug/L}$$

The dilution factor for the sample is

$$df = \frac{\text{9900 uL sample}}{\text{(9900 uL sample + 100 uL spike)}} = 0.99$$

D. Instrument Maintenance

1. Daily
   a. Empty the waste vessel.
   b. Check the supply of inert gas, and replace if necessary.
   c. Check both the absorption cell and the liquid/gas separator for cracks or flaws. Should the latter show damage, check with the supervisor as to whether it can or should be repaired.
   d. Change the peristaltic pump tubing.
   e. Adjust the pump flow rates, see **E.** 11, below.
   f. Adjust the oxidant and acetylene gas flows in the SpectraAA 20.
   g. Record pump flow, oxidant, and acetylene gas adjustments in the Daily Instrument Maintenance Logbook, located next to the instrument used.
2. Bi-weekly
   a. Replace the 1% HCl in which the liquid\gas separator and the absorption cell are soaked when not in use.
   b. Check that the knurled screws for the pump beds are not worn, and that they function to tighten the pump beds over the pump tubes.
   c. Clean the SpectrAA 20 burner head, and record the action in the Daily Instrument Maintenance Logbook.

E. Method

1. Remove $NaBH_4$ reagent pump bottle from cold storage and make certain there is a supply in the bottle sufficient for the analysis set to be run. Place the $NaBH_4$ bottle in a warm water bath to bring it to room temperature more quickly. Remove the concentrated HCl pump bottle from storage and make certain there is a supply in the bottle sufficient for the analysis set to be run. Check also that the supply of 1% (v/v) HCl will last for the analysis set.

Note: Minimum volumes of $NaBH_4$ and concentrated HCl needed to analyze a set of 40 samples are approximately 450-500 mL. The pump bottles are 500mL-sized Nalgene bottles with uptake tube-sized holes drilled into their caps.

2. Remove the gas/liquid separator and the absorption cells from their 1% (v/v) HCl solution soaking baths and allow them to drain. Settle the gas/liquid separator in its carriage, located on the instrument side of the VGA-76 hydride generator. (See figure 1 for the absorption cell, and figure 2 for the location of the gas/liquid separator on the VGA-76.) Secure the gas/liquid separator with the O-ring provided.

3. Take a Flame/Hydride Analysis Bench Sheet and fill in the date, the analyst's identification, and the particular element, either Arsenic or Selenium, to be analyzed. Insert the flame backup disk into the disk port on the SpectrAA 20 and close the port toggle. Turn the SpectrAA 20 on and select the hydride program for the element to be analyzed.

4. Using the "Method","Instrument Parameters", and "Optimization" pages in the computer software, fill out the rest of the information requested at the top of the Bench Sheet, *i.e.*, the measurement type, the wavelength, the slit width, the integration time, etc.

5. At the same time, set the slit width and wavelength on the SpectrAA 20. Insert the correct hollow cathode lamp (either Arsenic or Selenium) in the turret specified on "Instrument Parameters" and rotate the turret to the operating position. The "Optimization" page is used to optimize both the adjustment of the monochrometer and the position of the lamp in the turret; it provides a color-bar gauge whereby the analyst can determine the amount of light detected by the instrument.

> Note: When the color bar has extended the full length of the gauge, use the "re-scale" soft key to bring it back down into a more sensitive area of the gauge.

6. When both monochrometer and lamp position are adjusted to provide a maximum light detection range for the instrument without the absorption cell in place, carefully insert the absorption cell into the cell carriage, and place the cell carriage on the mounting hooks attached to the burner ~~in the~~ SpectrAA 20 (see figure 1). Rock the cell carriage back and down, so that the absorption cell is in the light path. Now, adjust the horizontal and vertical placement of the burner so that the light detected by the instrument is again at a maximum (see figure 3 for the placement of the cell carriage assembly on the burner).

7. When the hollow cathode lamp has been adjusted to provide as strong a signal as possible, adjust the deuterium lamp to the optimum balance with the hollow cathode lamp, using horizontal and vertical adjustment knobs and possibly the shutter as well. (The deuterium lamp assembly is located at the right front of the lamp-side of the instrument.)

8. Attach the inert gas supply line and the liquid drain tube to the separator (again, see figure 2). Make sure the liquid drain runs into an empty, stable vessel.

9. Get the set of pump tubes designated for the element to be analyzed (either Arsenic or Selenium), and fit it onto the hydride generator. Figure 4 shows how the pump tubes run from the sample, acid, and $NaBH_4$ capillary nipples down over the peristaltic pump to the tee piece assembly where tube contents meet together with the inert gas that carries the new-made mixture through the reaction coil (where the hydride is actually generated) to the gas/liquid separator. Figure 2 shows where to fasten the reaction coil outlet to the gas/liquid separator, *i.e.*, to the side of the thinner column of the separator. Figure 2 also shows where to couple the separator to the absorption cell.

10. Open the inert gas cylinder outlet and the fuel gas cylinder. Make certain that the flow gauges read the following:

VGA nitrogen supply: 45 psi
FLAA air supply (house air): 60 psi
FLAA acetylene supply: 10 psi

11. Lock the pump beds over the pump tubes, keeping the $NaBH_4$ and HCl tubes under the wider, inner bed and the sample tube under the narrower, outer bed (the pump beds are in the locked position in Figure 3). Start the pump and adjust the three flows, using distilled H_2O and a 10-ml graduated cylinder. Adjustment is made by turning the knurled knobs on the backs of the pump beds. Flow rates should be

sample: 7.5 ml/min
~~HCl & $NaBH_4$~~: 1.2 ml/min

When flow rates are adjusted, turn the pump off.

12. Rotate the absorption cell out of the light path and start the flame, then set the air and acetylene flows to the rates specified by the "Instrument Parameters" page of the software. Lower the cell into the flame and let it heat and dry for about 20 minutes before attempting any measurements.

13. Insert the HCl and NBH_4 uptake tubes in the proper pump bottles. Insert the sample uptake tube into an Erlenmeyer flask containing a supply of 1% HCl solution. (Refer to Figures 3 and 4.)

14. Gather together the samples to be analyzed and the standards to be used to set up a calibration curve. As/Se digestions are carried out on hot plates in Erlenmeyer flasks, and digestions personnel usually indicate spike, duplicate, dilution and soil data on the flask as well as on the As/Se Conversions Log sheet copy provided with the analysis set.

> Note: Remember, hydride generation needs to be carried out at room temperature; the pump tube delivery rates are temperature sensitive. As/Se samples must be at room temperature before being analyzed.

15. Turn the hydride pump back on. Go to the "Instrument Parameters" page in the computer software and change the read delay to 0 sec. Then go to the "Calibration" page in the software, press the "instrument zero" hard key, and read the 1% HCl to check stability and to re-zero the instrument. Return to the "Instrument Parameters" page, to change the read delay from 0 to 45 sec.

16. First analyze the Calibration Blank water as the lowest standard in the calibration, then analyze the standards listed in **C. 2. d.**, above, in order from the lowest to the highest concentration.

> Note: An analysis consists of three readings of the absorbance of the analyte, preceded and followed by three readings of the 1% HCl solution, which is treated as background monitor. Each set of three readings is averaged by the software and the average is reported as well as the individual readings. The analyst will record all readings and averages as they are generated. Background readings are noted in the upper half of a bench sheet row, while sample or standard readings are recorded in the lower half. ~~Absorbances~~ used in calculations are values obtained by subtracting the average of the background readings taken before and after the sample or standard from the average absorbance recorded for the sample or standard. Record the corrected absorbance values on the bench sheet as well as the observed values.

The calibration curve is obtained by performing a linear regression on the standards, including the Calibration Blank solution read at the beginning of the run. Concentration is defined as the independent, "x-" variable and absorbance is defined as the dependent, "y-" variable. Check that the correlation coefficient for this regression is $\geq$0.995 and that using the recorded absorbance values in the inverse of the regression function (see **F.**, below) gives concentration values within 80%-120% of theoretical values. When these constraints have been met, start analyzing samples.

17. The first samples to be analyzed are the Initial Calibration Verification and the Initial Calibration Blank, see **G.** 1 and 2, below. These two QC samples must meet criterion or analysis is halted until the problem is corrected, a matter that may require re-analyzing the calibration standards. The criterion window for the ICV is 80%-120% of theoretical value, while the ICB must show an absolute value of absorbance less than the default detection limit.

18. Arsenic samples are in polyethylene scintillation vials while Selenium samples are in Erlenmeyer flasks. For Arsenic samples, add 200 uL of 1% (w/v) KI solution (see **C.** d., above), using a calibrated Eppendorf, to the scintillation vial prior to analysis. Let the sample stand 3-5 minutes before starting analysis. Selenium samples do not need pre-treatment.

19. Following every ten analytical samples, analyze the Calibration Verification source (CCV) and the Calibration Blank solution (CCB). The recovery of the former must fall within 80%-120% of the theoretical value and the absolute value of the latter must be less than default detection limit for analysis to proceed. See **G.**, below, for further discussion of calibration constraints.

20. When the last sample has been read, check through the bench sheets for off-scale readings, for Matrix Spikes that recovered out of control, and for samples listed on the As/Se Conversion Log sheet which are not listed on the bench sheets. Off-scale readings require dilution and re-analysis, using Dilution water as diluent. Failed Matrix Spikes require analysis of an Analytical Spike, **G.** 8., below, using the spike protocol described in **C.** 4., above. All samples listed on the As/Se Conversion Log sheet should be analyzed; if a sample listed on the sheet is not available for analysis, find out the nature of the discrepancy and note it on the bench sheets.

21. When all samples have been analyzed, read the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) one last time, follow with a final background reading, then turn the flame off. Leave the pump running and insert all uptake tubes into a source of distilled water. Let the pump cycle the water through the system for ~5 minutes, then remove the tubes from the water and let the pump cycle to drain them. When the tubes are drained, shut the pump off and unhook the tubes.

22. Disassembly order is as follows:
uncouple absorption cell and gas/liquid separator.
turn off inert gas supply.
unhook inert gas inlet, liquid drain, and reaction coil inlets from gas/liquid separator, release the O-ring holding the separator in place.
drain the separator, rinse it in distilled H_2O, and put it to soak in 1% HCl.
open the pump beds, remove the pump tubes and reaction coil; place the reaction coil in a properly labeled bag and discard the pump tubes.
cover the tops of the HCl(conc) and $NaBH_4$ reagent bottles with parafilm and put the $NaBH_4$ bottle in the refrigerator.
rotate the absorption cell carriage out of the light path, lift it off the mounting spigots, and carefully slip the cell out of the mounting clips.
put the As/Se cell in 1% HCl to soak.

F. Calculations

1. The linear regression developed in E. 16., above, is of the form

$$abs = (m * conc, ug/L) + b$$

where abs = the absorbance of the sample or standard analyzed
conc = the concentration of the sample or standard analyzed
m = the slope of the regression equation (usually denoted with a "b" on calculators)
b = the y-intercept of the regression equation (usually denoted with an "a" on calculators)

The inverse of this equation is used to determine the observed concentration of a sample or standard from the absorbance

$$conc, ug/L = \frac{(abs - b)}{m}$$

However, the sample is diluted in conversion, so that the reported concentration is

reported conc = conc, ug/L * df

where df = the dilution factor, indicated on the Conversion Log sheet (usually this is 2, but frequently the sample dilution may be 5 or 10)

2. For those samples that are solid matrix, the analyst is required to convert the concentration from mg/L to mg/Kg

$$\text{reported conc} = \frac{\text{conc, ug/L} * \text{df} * \text{digestate volume, mL} * 10^{-3}\text{L/mL}}{\text{initial sample weight, g} * 10^{-3}\text{Kg/g} * 10^{3}\text{ug/mg}}$$

where digestate volume = the final volume of the nitric acid or nitric acid/hydrochloric acid digestion procedure.

G. Quality Control

1. Initial Calibration Verification (ICV): Analysis of the ICV immediately follows the calibration procedure. The recovery criterion window is 80%-120% of theoretical value.

2. Initial Calibration Blank (ICB): The ICB is analyzed immediately after analysis of the ICV. The solution used is the Calibration Blank solution, (50% HCl, 50% H_2O (v/v), fortified with urea). The absolute value of concentration for Arsenic or Selenium must be less than the default detection limit for that analyte.

3. Continuing Calibration Verification (CCV) - Typically, this solution is the same as the ICV, but it doesn't have to be. The CCV solution is analyzed after ten non-calibration analyses; acceptable recovery is, again, 80%-120% of theoretical value.

4. Continuing Calibration Blank (CCB): The Calibration Blank solution used in ICB analysis is re-analyzed immediately after each CCV. Again, the acceptable recoveries are less than the absolute value of the instrument detection limit.

5. Preparation Blank (PB): Each preparation set should have at least one aliquot of reagent blank which has been treated as a sample. The flask is coded PBYY-###, where YY is the last two digits of the current year and ### is a number, assigned to the preparation bin for the nitric acid or nitric acid/hydrochloric acid digestion procedure. The results of

analysis of the PB should show absolute values for the concentration of Arsenic or Selenium at less than IDL. Should a PB fail this evaluation, report the poor recoveries to a supervisor and/or data management and be certain the cover sheet for the data set includes this information. In the situation where a PB recovers at an absolute value greater than the detection limit, it is permissible to accept as satisfactory **only** those results which recover at a concentration greater than 10X the recovery value of the PB. Samples prepared with a preparation blank that recovers at a level greater than detection limit which themselves recover at less than 10X the level of the PB must be re-prepared and re-analyzed.

6. Laboratory Control Sample (LCS), *i.e.*, Preparation Blank Spike (PBS): Every preparation set should have an aliquot of reagent blank to which has been added known amounts of Arsenic and Selenium before being carried through the conversion procedure. The flask is coded PBSYY-###, using the code described in **G.** 5., above. Code the analysis LCS.
Recovery of the LCS should be within 80%-120% of the theoretical value for the Arsenic or Selenium included. If results fail to meet this criterion, report to a supervisor and/or data management. Flag the data when calculating it, by noting the poor recovery on the cover sheet of the data set.

7. Matrix Spike (#####S): At least one sample in a preparation set and, more commonly, one in every 20 samples, will have a replicate to which has been added the same known amounts of Arsenic and Selenium as were added to the LCS. This replicate is then digested as a sample. The spike recovery should be within a 75%-125% criterion range . If criterion is not met, perform a post-preparation spike (see **F.** 8.,below) and flag the data when calculating it, with an "N".

8. Analytical Spike (#####A): An analytical spike is an aliquot of digested, unspiked sample to which has been added a known amount of Arsenic or Selenium after conversion. The spiking solution used should be of the same acid composition and concentration(s) as the sample being spiked. Analysis should return a recovery of 75%-125% of theoretical value of the spike added.
When a matrix spike result fails to meet criterion, it is necessary for the analyst to make up and analyze an analytical spike. Analytical spikes are also required when the frequency of matrix spikes available in a preparation set does not generate an overall spiking frequency of 1 in every 20 samples analyzed in the run. They are also necessary when the sample concentration is greater than the calibration range

established for the analytical set.

Note: Analytical spikes generally dilute the samples they are made on by as much as the spike volume added. Accordingly, in no case is a sample to be diluted more than 10% by the spiking solution added; that is to say, a sample should be at least 90% of the composite of sample and spike prepared for an analytical spike. The one apparent exception is the case where a sample is off-scale and needs to have a spike analyzed. Here, it is necessary to run an analytical spike on an aliquot of sample which has been diluted with reagent blank to a concentration that will register at approximately mid-range. Dilute a second aliquot to the same level, including the spiking solution in the diluent; calculate spike recovery on the observed concentration of the diluted sample. In addition, the spiking solutions and the diluent should be of acid strength and composition appropriate to the samples being analyzed.

9. Matrix Duplicate (#####D): One sample in a preparation set, or one for every 20 samples in the set, whichever is the greater frequency, will have a replicate which is also digested by the same protocol. Should both replicates show concentrations $\geq$ 5X IDL, the relative percent difference between the two replicates should be $\leq$ 20%. Should the RPD be greater than 20%, report to a supervisor and/or data management, and flag the data when calculating it, with a "*". When either the sample or the duplicate shows a concentration $\leq$ 5X IDL, the absolute range between the two replicates should be $\leq$ IDL. If the range is greater than IDL, flag the data when calculating it, again using "*". When either or both replicates recovers at < IDL, report the RPD as "not calculable" (N/C). The result reported as sample concentration is that for the first replicate, labeled #####, rather than the duplicate, labeled #####D. Do not report the average of the two replicates as the sample concentration.

10. Post-preparation Matrix Duplicate, *i.e.*, Instrument Duplicate (#####I): If there are insufficient duplicates in the analysis set (*i.e.*, less than one in twenty, or one per analytical set), a sample or samples should be selected for re-analysis, to bring the total number of duplicate analyses up to the correct frequency. The control limits and calculations are the same as for Matrix Duplicates.

11. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked with the analyte(s) of interest, at the same level. Both spiked replicates get spike recovery calculation, using Matrix Spike criterion range, and the two spiked replicates also are subject to calculation of relative percent difference, with Matrix Duplicate criterion range. Should any of the three calculations show lack of control, a supervisor and/or data management should be notified immediately, and the data should be flagged when calculated, with the flags specified for Matrix Spikes and/or Matrix Duplicates.

H. Provenance

This method was written by

Martha Stoddard Frank Senior Chemist/Technical

It has been reviewed and accepted by

Steven W. Schneider Group Leader, Inorganics Department

Department Manager, Inorganics Department

Technical Director

SEQUENCE TABLE

S0 (Calibration Blank)
S0.5
S1.0
S2.0
S5.0
S9.0
S12.0
ICV
ICB
Check calibration for precision and accuracy
PB
LCS
|
Analyze the first 7 samples
|
CCV1
CCB1
Check calibration for precision and accuracy
|
Repeat 10 non-calibration samples and **CCV#, CCB#** pattern until all the samples have been analyzed, then end with
|
CCVn
CCBn

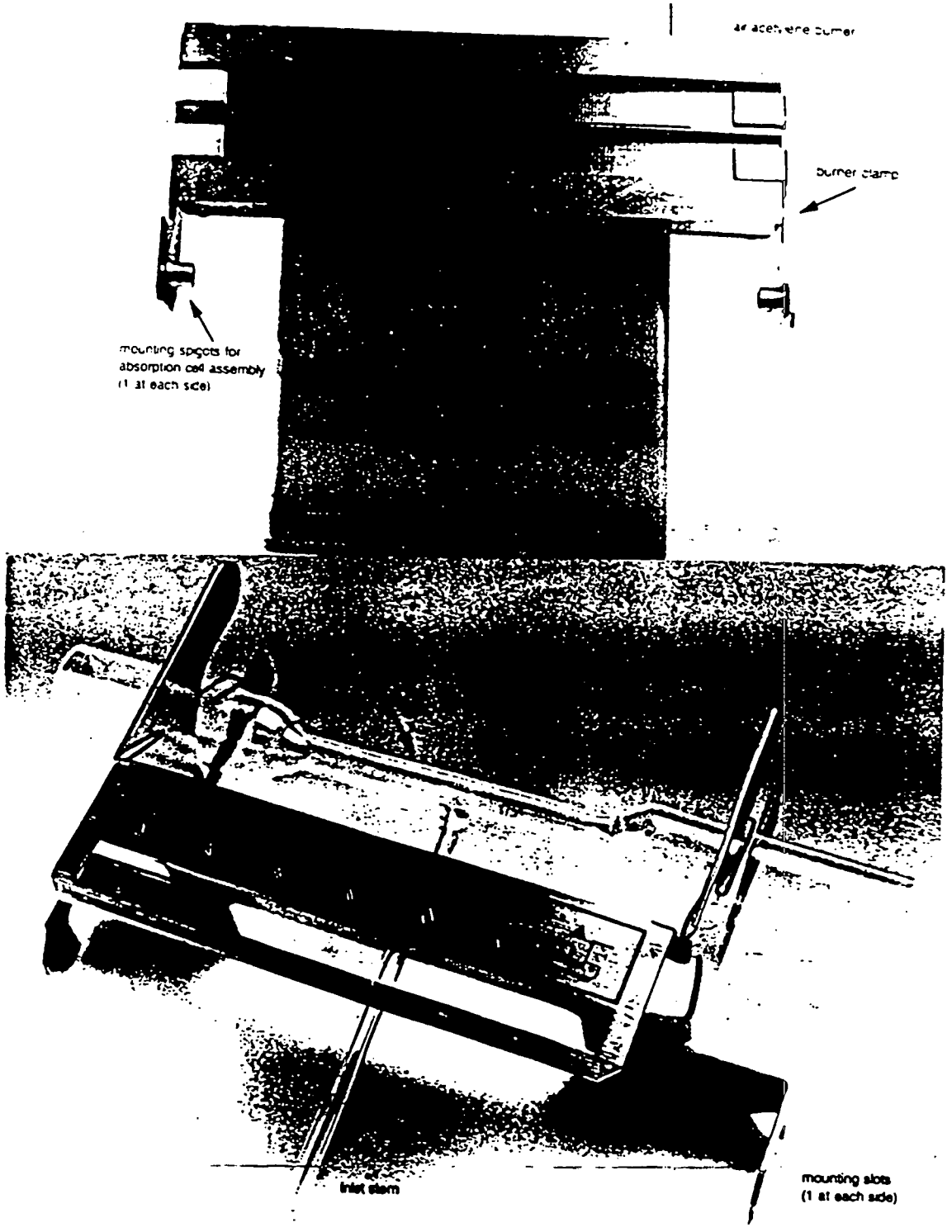


Figure 1: Absorption cell and cell carriage mounting assembly (after Varian).

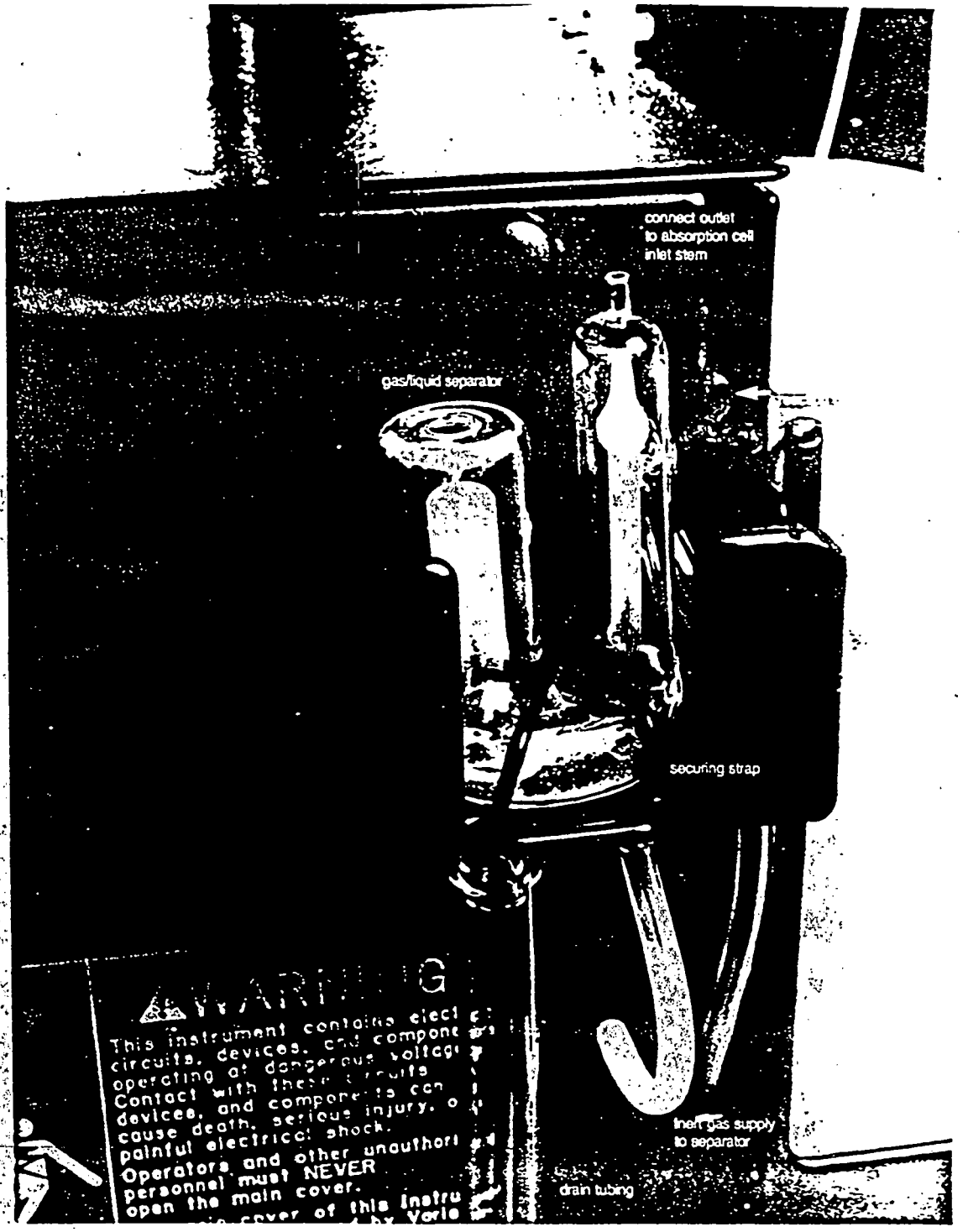


Figure 2: Gas/liquid separator in position on the VGA-76 (after Varian).

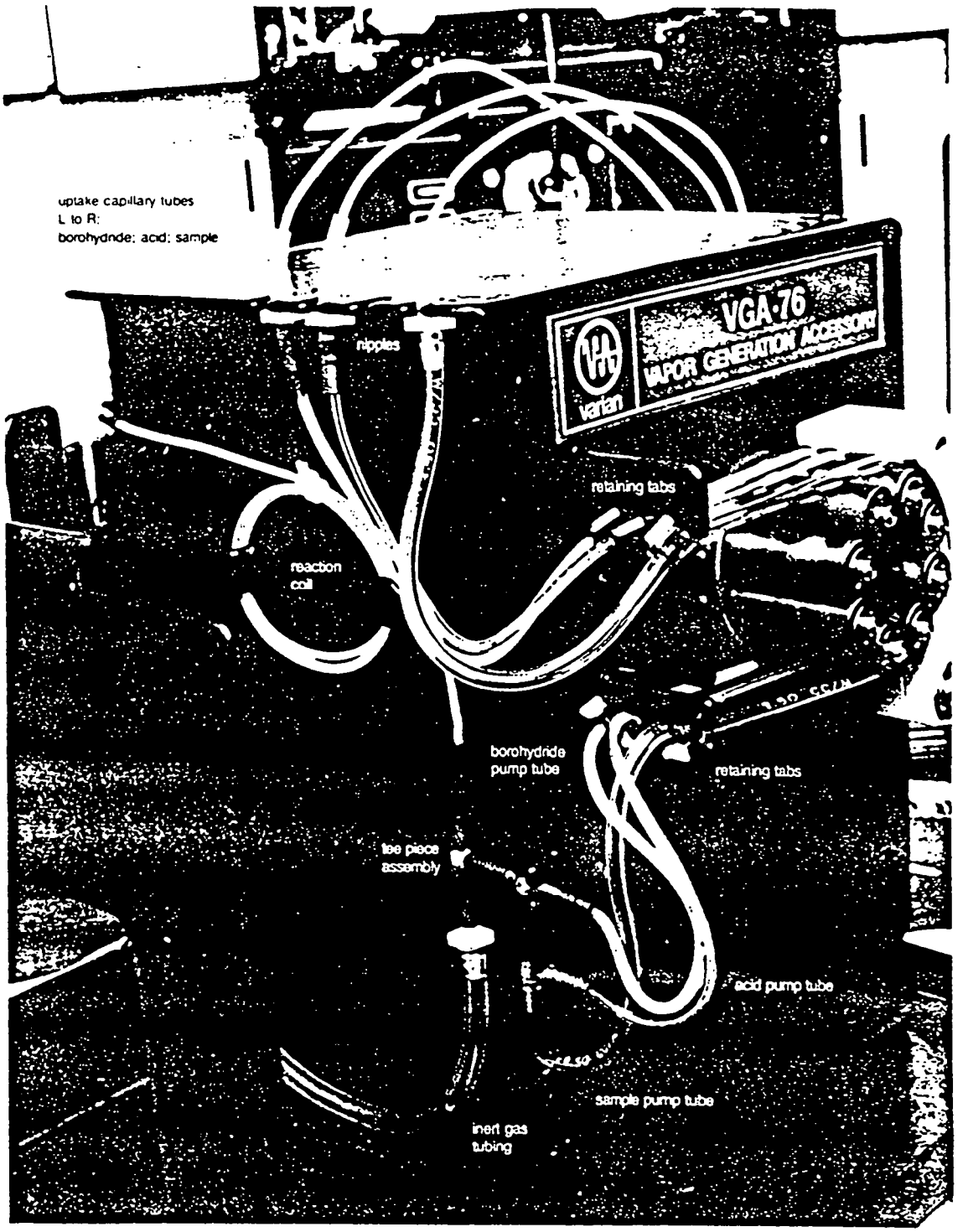


Figure 4: Capillary uptake tubes shown in position ready for analysis (after Varian).

ANALYSIS FOR MERCURY BY COLD VAPOR (HG)

A. Introduction

1. Applicability: This method is applicable to determination of mercury concentration in any sample prepared following the **Preparation of Soil/Solid Samples for Analysis for Mercury by Cold Vapor (HGP)** or the **Preparation of Aqueous Samples for Analysis for Mercury by Cold Vapor (HGP)**.
2. Purpose of Testing: Mercury is a highly toxic cumulative poison, as are most of its compounds. Both the element and its compounds are frequently found as byproducts of various industrial processes. These considerations lead to the inclusion of this element in various monitoring lists, such as the RCRA metals list, or the Priority Pollutants list.
3. Detection Limit: The default detection limit is the lowest standard used in calibration, 0.0002 mg/L, as is the reporting limit. The instrument working range is 0.0002 mg/L to 0.010 mg/L.
4. Reference Methods: Varian, manufacturer; after EPA SW-846, method 7471, Rev. 0, and Standard Methods for the Analysis of Water and Wastewater, 17th Ed., Method 3112B and C.
5. Summary of Method: The prepared samples are combined in a reaction coil with tin(II)chloride and strong acid. A volatile hydride is generated and is purged into an unheated quartz cell atomizer on an atomic absorption spectrophotometer (FLAA). The hydride breaks down into elemental form and the FLAA is used to determine Mercury concentration.
6. Interferences: Sulfide and most organic interferences are removed in the digestion procedure.
7. Sample Collection and Preservation: The "samples" in this procedure are the Mercury digestions, prepared $\leq$ 24 hours prior to analysis. These are stored at room temperature and preserved in sulfuric acid.
8. Holding Time: The holding time for the Hg preparations is 24 hours. The time between sample collection and analysis for Mercury is 26 days.
9. Safety Precaution: Mercury and its hydride are highly toxic, and strong acids are used in the digestion procedure. Therefore, gloves are strongly recommended. Lab coats and glasses are required.

B. Apparatus

1. Class "A" volumetric flasks, 1000mL and 250mL.
2. Class "A" pipet, 9mL.
3. Calibrated Eppendorf pipet, 1000uL.
4. Calibrated re-pipet, capable of delivering 1.0 mL.
5. Varian SpectrAA 20 atomic absorption unit.
6. Varian VGA-76 vapor-generating peristaltic pump.
7. Gas/liquid separator.
8. Quartz absorption cell.
9. Hollow cathode lamp, suitable for Mercury determination.

C. Reagents and Standards

1. Reagents: Reagent grade chemicals will be used in all tests.

   a. ASTM Type II water (ASTM 1193-99, 1983): i.e., Super Q water.

   b. Concentrated nitric acid, HNO_3: Commercially available.

   c. Nitric acid, HNO_3, 1% (v/v) solution: Dilute 20 mL concentrated HNO_3 in Super Q water in a marked and labeled 2L jug. Bring up to the mark with Super Q water. Cool to room temperature before using in cold vapor generation and analysis. Shelf life is indefinite.

   d. Hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$: Commercially available.

   e. Sodium chloride-Hydroxylamine hydrochloride solution, $NaCl$-$NH_2OH{\cdot}HCl$,: Weigh out, to the nearest 0.1 g, 120 g NaCl and 120 g $NH_2OH{\cdot}HCl$ and quantitatively transfer to a 1L Class "A" volumetric flask, using Super Q water. Dilute to volume with Super Q water. Store at room temperature. Shelf life is approximately 2 weeks.

   f. Tin(II)chloride ($SnCl_2$) solution: Combine 30 mL of Super Q water with 50 mL concentrated hydrochloric acid in a 250mL Class "A" volumetric flask. Add 50 mg $SnCl_2$, weighed to the nearest 0.1 g and rinsed into the flask with Super Q water. Bring up to volume with Super Q water. Store at $\leq$ 4° Celsius; shelf life is approximately 2 days. The reagent must be cooled or warmed to room temperature before using in cold vapor generation and analysis.

2. Standards: Standards are digested with the samples in the preparation set. The copies of the Mercury Preparation Log sheet provided with the preparation set list the concentrations of these standards.

3. Calibration Verification Source: The source is supplied to company specifications by SPEX. The calibration verification solution is also included in the preparation set. Its final concentration is 3.0 ug/L.

4. Spiking Protocol: Using a Class "A" pipet and an Eppendorf pipet, combine 9 mL of converted sample with 1 mL of the highest standard (HS) in the preparation set. The theoretical spike concentration is

$$\text{spike conc.} = \frac{1.0 \text{ mL HS} * 10 \text{ ug/L HS conc}}{(9.0 \text{ mL sample} + 1.0 \text{ mL HS})} = 1.0 \text{ ug/L}$$

The dilution factor for the sample is

$$df = \frac{9.0 \text{ mL sample}}{(9.0 \text{ mL sample} + 1.0 \text{ mL HS})} = 0.90$$

D. Instrument Maintenance

1. Daily
   a. Empty the waste vessel.
   b. Check the supply of inert gas, and replace if necessary.
   c. Check both the absorption cell and the liquid/gas separator for cracks or flaws. Should the latter show damage, check with the supervisor as to whether it can or should be repaired.
   d. Change the peristaltic pump tubing.
   e. Adjust the pump flow rates, see E. 11, below.
   f. Record pump flow adjustment in the Daily Instrument Maintenance Logbook, located next to the instrument used.
2. Bi-weekly
   a. Replace the 1% HCl in which the liquid\gas separator is soaked when not in use.
   b. Check that the knurled screws for the pump beds are not worn, and that they function to tighten the pump beds over the pump tubes.

E. Method

1. Remove the $SnCl_2$ reagent pump bottle from cold storage and make certain there is a supply in the bottle sufficient for the analysis set to be run. Place the $SnCl_2$ bottle in a warm water bath to bring it to room temperature more quickly. Make certain there is a supply of Super Q in the other reagent pump bottle sufficient for the analysis set to be run. Check also that the supply of 1% (v/v) HNO_3 will last for the analysis set.

   Note: Minimum volumes of $SnCl_2$ and Super Q needed to analyze a set of 25 samples are approximately 250-300 mL. The pump bottles are 500mL-sized Nalgene bottles with uptake tube-sized holes drilled into their caps.

2. Remove the gas/liquid separator from its 1% (v/v) HNO_3 solution soaking bath and allow it to drain. Settle the gas/liquid separator in its carriage, located on the instrument side of the VGA-76 hydride generator. (See figure 2 for the location of the gas/liquid separator on the VGA-76.) Secure the gas/liquid separator with the O-ring provided.

3. Take a Flame/Hydride Analysis Bench Sheet and fill in the date, the analyst's identification, and the particular element to be analyzed, in this case Mercury. Insert the flame backup disk into the disk port on the SpectrAA 20 and close the port toggle. Turn the SpectrAA 20 on and select the hydride program for the element to be analyzed.

4. Using the "Method","Instrument Parameters", and "Optimization" pages in the computer software, fill out the rest of the information requested at the top of the Bench Sheet, *i.e.*, the measurement type, the wavelength, the slit width, the integration time, etc.

5. At the same time, set the slit width and wavelength on the SpectrAA 20. Insert the Mercury hollow cathode lamp in the turret specified on "Instrument Parameters" and rotate the turret to the operating position. The "Optimization" page is used to optimize both the adjustment of the monochronometer and the position of the lamp in the turret; it provides a color-bar gauge whereby the analyst can determine the amount of light detected by the instrument.

> Note: When the color bar has extended the full length of the gauge, use the "re-scale" soft key to bring it back down into a more sensitive area of the gauge.

6. When both monochrometer and lamp position are adjusted to provide a maximum range of light detection for the instrument without the absorption cell in place, get the absorption cell from the desiccator located in the Instruments Lab. Carefully insert the absorption cell into the cell carriage, and place the cell carriage on the mounting hooks attached to the burner in the SpectrAA 20 (see figure 1). Rock the cell carriage back and down, so that the absorption cell is in the light path. Now, adjust the horizontal and vertical placement of the burner so that the light detected by the instrument is again at a maximum.

7. When the hollow cathode lamp has been adjusted to provide as strong a signal as possible, adjust the deuterium lamp to balance the hollow cathode lamp, using horizontal and vertical

adjustment knobs and possibly the shutter as well. (The deuterium lamp assembly is located at the right front of the lamp-side of the instrument.)

8. Attach the inert gas supply line and the liquid drain tube to the separator (again, see figure 2). Make sure the liquid drain runs into an empty, stable vessel.

9. Get the set of pump tubes designated for Mercury and fit it onto the hydride generator. Figure 3 shows how the pump tubes run from the sample, acid, and $SnCl_2$ capillary nipples down over the peristaltic pump to the tee piece assembly where tube contents meet together with the inert gas that carries the new-made mixture through the reaction coil (where the hydride is actually generated) to the gas/liquid separator. Figure 2 shows where to fasten the reaction coil outlet to the gas/liquid separator, *i.e.*, to the inlet located on the side of the thinner column of the separator. Figure 2 also shows where to couple the separator to the absorption cell,*i.e.*, to the top of the thinner column of the separator.

10. Open the inert gas cylinder outlet and make certain that the flow gauge reads 45 psi.

11. Lock the pump beds over the pump tubes, keeping the $SnCl_2$ and Super Q water tubes under the wider, inner bed and the sample tube under the narrower, outer bed. Start the pump and adjust the three flows, using distilled H_2O and a 10-ml graduated cylinder. Adjustment is made by turning the knurled knobs on the backs of the pump beds. Flow rates should be

sample: 7.5 ml/min
Super Q water & $SnCl_2$: 1.2 ml/min.

When flow rates are adjusted, turn the pump off.

12. Insert the Super Q water and $SnCl_2$ uptake tubes in the proper pump bottles. Insert the sample uptake tube into an Erlenmeyer flask containing a supply of 1% HNO_3 solution. (Refer to Figures 3 and 4.)

14. Gather together the samples to be analyzed and the standards to be used to set up a calibration curve. The Hg bottles are not labeled with client names or Encotec sample numbers; rather, they have semipermanent codes attached and the Mercury Preparation Log sheet copies provided with the preparation set give the correspondence between bottle code and identity of contents. Refer to a copy frequently, because it will not only tell which Hg bottle has which sample, it will also indicate which of the bottles are duplicates,

digested spikes (along with spiking levels) and/or, if soils, the mass of soil weighed out.

> Note: Remember, hydride needs to be carried out at room temperature; the pump tube delivery rates are temperature sensitive. Mercury preparations must be at room temperature before being analyzed.

15. Turn the hydride pump back on. Go to the "Instrument Parameters" page in the computer software and change the read delay to 0 sec. Then go to the "Calibration" page or the "Analytical Results" page in the software, press the "instrument zero" hard key, and read the 1% HCl solution to check stability and to re-zero the instrument. Return to the "Instrument Parameters" page, to change the read delay from 0 to 60 sec.

16. Prior to analyzing the prepared blank and standards, add 10 mL of Hydroxylamine hydrochloride solution to each of the standards bottles to remove the excess potassium permanganate present. Swirl each bottle to mix the reagents and wait until the deep purple color dissipates before proceeding with analysis.

17. First analyze the prepared blank as the lowest standard in the calibration, then analyze the standards included in the preparation set in order from the lowest to the highest concentration.

> Note: An analysis consists of three readings of the absorbance of the analyte, preceded and followed by three readings of the 1% HNO_3 solution, which is treated as a reagent blank. Because the reading is of peak height rather than peak area, the software requires that the "read" hard key be pressed to generate each absorbance value in a set of three, but the software will average the set and the average is reported as well as the individual readings. The analyst will record all readings and averages as they are generated. Reagent blank readings are noted in the upper half of a bench sheet row, while sample or standard readings are recorded in the lower half. Absorbances used in calculations are values obtained by subtracting the average of the blank readings taken before and after the sample or standard from the average absorbance recorded for the sample or standard. Record the corrected absorbance values on the bench sheet as well as the observed values.

The calibration curve is obtained by performing a linear regression on the standards, including the prepared blank read at the beginning of the run. Concentration is defined as the independent, "x-" variable and absorbance is defined as the dependent, "y-" variable. Check that the correlation coefficient for this regression is $\geq$0.995 and that using the recorded absorbance values in the inverse of the regression function (see **F.**, below) gives concentration values within 90%-110% of theoretical values. When these constraints have been met, start analyzing samples, treating them first with the hydroxylamine hydrochloride solution, see **E.** 16, above.

18. The first samples to be analyzed are the Initial Calibration Verification and the Initial Calibration Blank. The Initial Calibration Blank is the blank prepared at the beginning of the preparation set, also used in the standards calibration set. These two QC samples must meet criterion or analysis is halted until the problem is corrected, a matter that may require re-analyzing the calibration standards. The criterion window for the ICV is 80%-120% of theoretical value, while the ICB must show an <u>absolute</u> value of absorbance less than the instrument detection limit.

19. Following every ten non-calibration analyses, analyze the Calibration Verification source (CCV) and the preparation blank solution (CCB). The recovery of the former must fall within 80%-120% of the theoretical value and the <u>absolute</u> value of the latter must be less than instrument detection limit for analysis to proceed. See **G.**, below, for further discussion of calibration constraints.

20. When the last sample has been read, check through the bench sheets for off-scale readings, for Matrix Spikes that recovered out of control, and for samples listed on the Mercury Preparation Log sheet which are not listed on the bench sheets. Off-scale readings require dilution and re-analysis, using the preparation blank solution as diluent. Failed Matrix Spikes require analysis of an Analytical Spike, **G.** 8., below, using the spike protocol described in **C.** 4., above. All samples listed on the Mercury Preparation Log sheet should be analyzed; if a sample listed on the sheet is not available for analysis, find out the nature of the discrepancy and note it on the bench sheets.

21. When all samples have been analyzed, read the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) one last time, followed by a final 3 readings of the 1% HNO_3 solution. Leave the pump running and insert all

uptake tubes into a source of distilled water. Let the pump cycle the water through the system for ~5 minutes, then remove the tubes from the water and let the pump continue cycling to drain them. When the tubes are drained, shut the pump off and unhook the tubes.

22. Disassembly order is as follows:
uncouple absorption cell and gas/liquid separator.
turn off inert gas supply.
unhook inert gas inlet, liquid drain, and reaction coil inlets from gas/liquid separator, release the O-ring holding the separator in place.
drain the separator, rinse it in distilled H2O, and put it to soak in 1% HCl.
open the pump beds, remove the pump tubes and reaction coil; place the reaction coil in the properly labeled bag and discard the pump tubes in a proper container.
cover the top of the $SnCl_2$ reagent pump bottle with parafilm and place in the refrigerator.
rotate the absorption cell carriage out of the light path, lift it off the mounting spigots, and carefully slip the cell out of the mounting clips.
put the Hg cell in the desiccator to keep dry.

F. Calculations

1. The linear regression developed in E. 16., above, is of the form

$$abs = (m * conc, ug/L) + b$$

where abs = the absorbance of the sample or standard analyzed
conc = the concentration of the sample or standard analyzed
m = the slope of the regression equation (usually denoted with a "b" on calculators)
b = the y-intercept of the regression equation (usually denoted with an "a" on calculators)

The inverse of this equation ~~is used to~~ determine ~~the~~ observed concentration of a sample or standard from the absorbance

$$conc, ug/L = \frac{(abs - b)}{m}$$

2. For those samples that are solid matrix, the analyst is required to convert the concentration from mg/L to mg/Kg

$$\text{reported conc} = \frac{\text{conc, ug/L} * \text{preparation volume, mL} * 10^{-3}\text{L/mL}}{\text{initial sample weight, g} * 10^{-3}\text{Kg/g} * 10^{3}\text{ug/mg}}$$

G. Quality Control

1. Initial Calibration Verification (ICV): Analysis of the ICV immediately follows the calibration procedure. The recovery criterion window is 80%-120% of theoretical value.

2. Initial Calibration Blank (ICB): For cold vapor analysis, the preparation blank (see G. 5., below) is also used as the S0 standard in calibration and as the ICB, and the CCB (see G. 4., below). When operated as ICB, the sample is analyzed immediately after analysis of the ICV. The absolute value of concentration for Mercury must be less than the instrument detection limit.

3. Continuing Calibration Verification (CCV) - Typically, this solution is the same as the ICV, but it doesn't have to be. The CCV solution is analyzed after ten non-calibration analyses; acceptable recovery is, again, 80%-120% of theoretical value.

4. Continuing Calibration Blank (CCB): The reagent blank solution used in ICB analysis is re-analyzed immediately after each CCV. Again, the acceptable recovery is less than the absolute value of the instrument detection limit.

5. Preparation Blank (PB): Each preparation set should have an aliquot of reagent blank which has been treated as a sample. The results of analysis of the PB should show absolute values for the concentration of Mercury at less than IDL. Should a PB fail this evaluation, report the poor recoveries to a supervisor and/or data management and be certain the cover sheet for the data set includes this information. In the situation where a PB recovers at an absolute value greater than the detection limit, it is permissible to accept as satisfactory **only** those results which recover at a concentration greater than 10X the recovery value of the PB. Samples prepared with a preparation blank that recovers at a level greater than detection limit which themselves recover at less than 10X the level of the PB must be re-prepared and re-analyzed.

6. Laboratory Control Sample (LCS), *i.e.*, Preparation Blank Spike (PBS): Every preparation set should have an aliquot of reagent blank to which has been added a known amount of Mercury before being carried through the preparation procedure. The flask is coded PBS or LCS. Code the analysis LCS. Recovery of the LCS should be within 80%-120% of the theoretical value for the Mercury included. If results fail to meet this criterion, report to a supervisor and/or data management. Flag the data when calculating it, by noting the poor recovery on the cover sheet of the data set.

7. Matrix Spike (#####S): At least one sample in a preparation set and, more commonly, one in every 20 samples, will have a replicate to which has been added the same known amounts of Mercury as was added to the LCS. This replicate is then digested as a sample. The spike recovery should be within a 75%-125% criterion range . If criterion is not met, perform an analytical spike (see G. 8.,below) and flag the data when calculating it, with an "N".

8. Analytical Spike (#####A): An analytical spike is an aliquot of digested, unspiked sample to which has been added a known amount of Mercury after preparation. Analysis should return a recovery of 75%-125% of theoretical value of the spike added. When a matrix spike result fails to meet criterion, it is necessary for the analyst to make up and analyze an analytical spike. Analytical spikes are also required when the frequency of matrix spikes available in a preparation set does not generate an overall spiking frequency of 1 in every 20 samples analyzed in the run. They are also necessary when the sample concentration is greater than the calibration range established for the analytical set.

> Note: Analytical spikes generally dilute the samples they are made on by as much as the spike volume added. Accordingly, in no case is a sample to be diluted more than 10% by the spiking solution added; that is to say, a sample should be at least 90% of the composite of sample and spike prepared for an analytical spike. The one apparent exception is the case where a sample is off-scale and needs to have a spike analyzed. Here, it is necessary to run an analytical spike on an aliquot of sample which has been diluted with reagent blank to a concentration that will register at approximately mid-range. Dilute a second aliquot to the same level, including the spiking solution in the diluent; calculate spike recovery on the observed concentration of the diluted sample. In addition, the spiking solution and the diluent should be part of the

preparation set, *i.e.*, the spiking solution is the highest standard and the diluent is the preparation blank.

9. Matrix Duplicate (#####D): One sample in a preparation set, or one for every 20 samples in the set, whichever is the greater frequency, will have a replicate which is also digested by the same protocol. Should both replicates show concentrations $\geq$ 5X IDL, the relative percent difference between the two replicates should be $\leq$ 20%. Should the RPD be greater than 20%, report to a supervisor and/or data management, and flag the data when calculating it, with a "*". When either the sample or the duplicate shows a concentration $\leq$ 5X IDL, the absolute range between the two replicates should be $\leq$ IDL. If the range is greater than IDL, flag the data when calculating it, again using "*". When either or both replicates recovers at < IDL, report the RPD as "not calculable" (N/C). The result reported as sample concentration is that for the first replicate, labeled #####, rather than the duplicate, labeled #####D. Do not report the average of the two replicates as the sample concentration.

10. Post-preparation Matrix Duplicate, *i.e.*, Instrument Duplicate (#####I): If there are insufficient duplicates in the analysis set (*i.e.*, less than one in twenty, or one per analytical set), a sample or samples should be selected for re-analysis, to bring the total number of duplicate analyses up to the correct frequency. The control limits and calculations are the same as for Matrix Duplicates.

11. Matrix Spike Duplicate (#####SD): Some clients request that one sample of the set sent in should be analyzed with two replicates, each spiked with the analyte(s) of interest, at the same level. Both spiked replicates get spike recovery calculation, using Matrix Spike criterion range, and the two spiked replicates also are subject to calculation of relative percent difference, with Matrix Duplicate criterion range. Should any of the three calculations show lack of control, a supervisor and/or data management should be notified immediately, and the data should be flagged when calculated, with the flags specified for Matrix Spikes and/or Matrix Duplicates.

G. Provenance

This method was written by

Martha Goldwin Hawk — Senior Chemist/Technical

It has been reviewed and accepted by

Steven W. Schneider — Group Leader, Inorganics Department

R. L. Mitchell — Inorganics Department Manager

Walter Rund — Technical Director

SEQUENCE TABLE

S0 (Preparation Blank)
S0.2
S0.5
S1.0
S2.0
S5.0
S10.0
ICV
ICB (Preparation Blank)
Check calibration for precision and accuracy
PB
LCS
|
Analyze the first 7 samples
|
CCV1
CCB1 (Preparation Blank)
Check calibration for precision and accuracy
|
Repeat 10 non-calibration samples and **CCV#, CCB#** pattern until all but the last 1-9 samples have been analyzed, then end with
|
CCVn-1
CCBn-1 (Preparation Blank)
Check calibration for precision and accuracy
|
Analyze the last 1-9 samples
|
CCVn
CCBn (Preparation Blank)

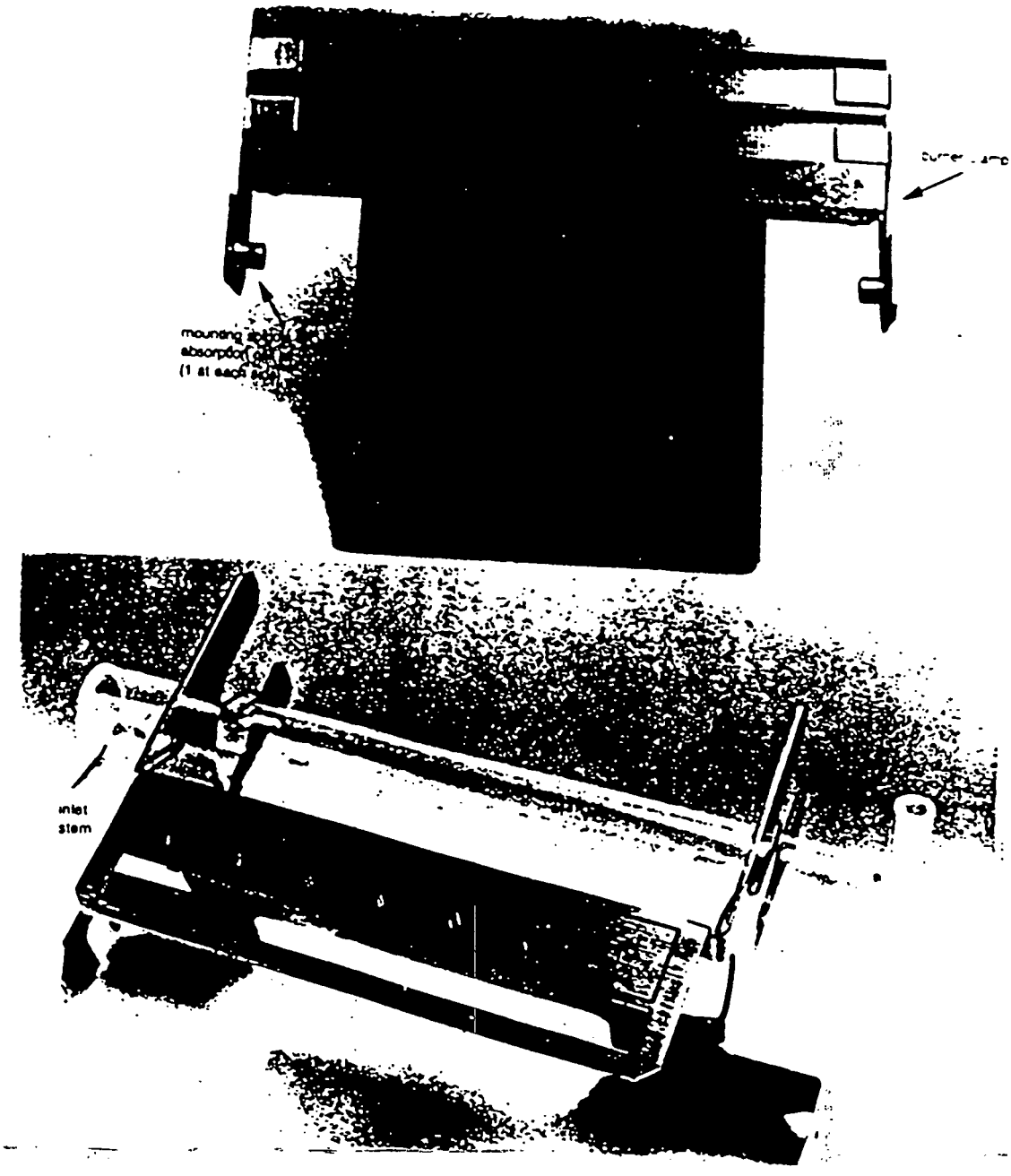


Figure 1: Absorption cell and cell carriage mounting assembly (after Varian).

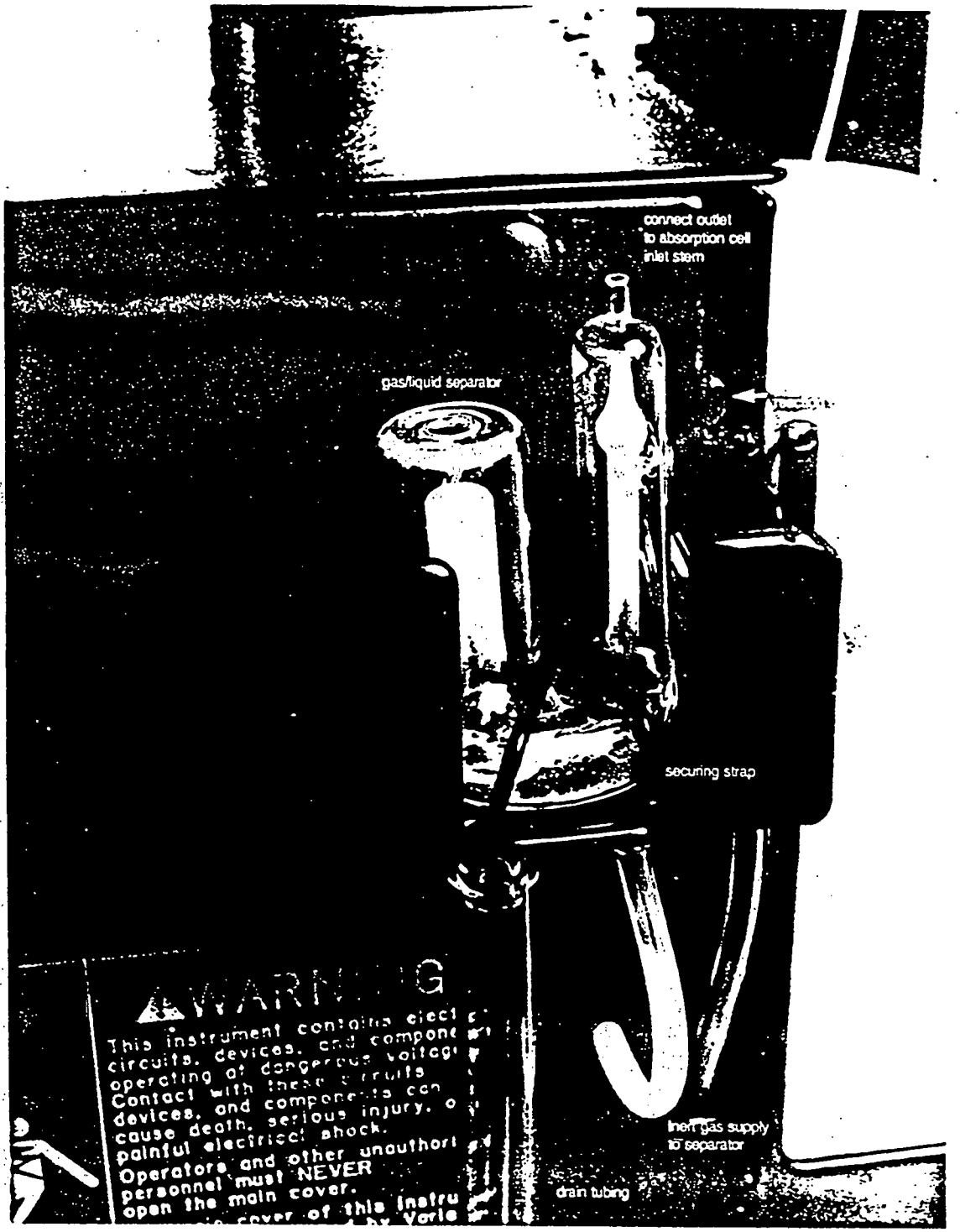


Figure 2: Gas/liquid separator in position on the VGA-76 (after Varian).

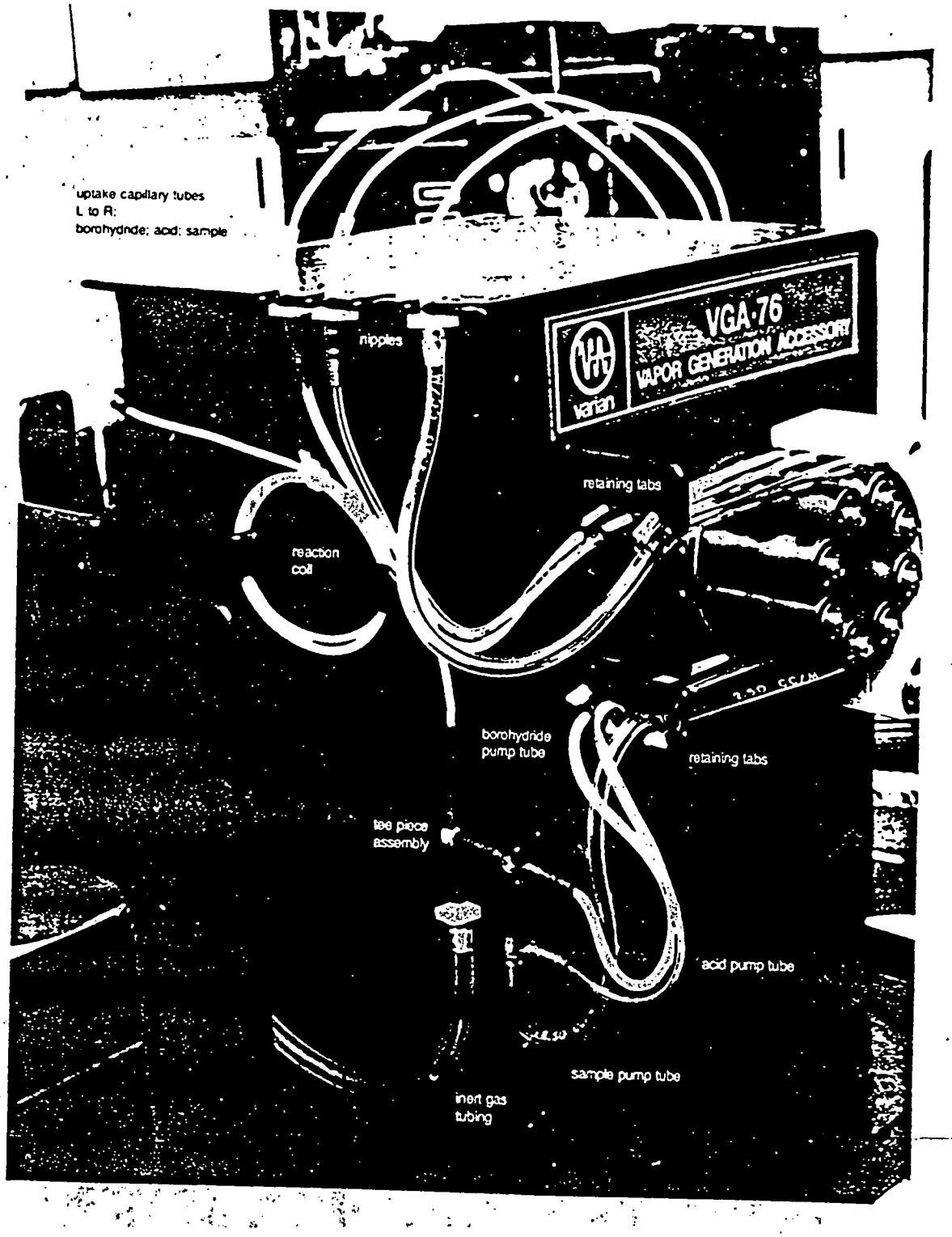


Figure 3: Capillary uptake tubes shown in position ready for analysis (after Varian).

Figure 4: VGA-76 set up to show absorption cell mounted on burner and reagent bottles set in place (after Varian).

FIELD S.O.P. NO. 1
PROCEDURES FOR MEASURING pH

1.0 CALIBRATION PROCEDURE

The pH meter will be calibrated daily.

1. Switch on instrument.

2. Connect electrode to meter via the BNC connector and remove protective cap from electrode.

3. Rinse end of electrode in distilled/deionized water.

4. Measure and record temperature of buffer solutions.

5. Immerse pH electrode in pH buffer 7.00, set the temperature adjust dial to that of the buffer 7.00, and allow sufficient time for the electrode to stabilize. Adjust the calibration dial for the correct readout.

6. Remove electrode from buffer and rinse with distilled/deionized water.

7. Immerse pH electrode in buffer 4.00, set the temperature control to that of the buffer 4.00, and allow sufficient time for the electrode to stabilize. Adjust the Slope Control for the correct readout.

8. Rinse electrode with distilled/deionized water. The meter is calibrated and ready for use.

2.0 OPERATION PROCEDURE

1. Calibrate pH meter.

2. Rinse probe in distilled/deionized water.

3. Fill two 100-milliliter plastic disposable beakers with water from the sample.

4. Measure and record temperature of sample. Adjust temperature dial for ambient water temperature.

5. Insert probe into one sample beaker and obtain a reading. The meter will read between 0 and 14, in 0.01 increments.

6. Rinse probe off in distilled/deionized water.

7. Repeat Step 4, 5, and 6 in other beaker.

8. Log results in field notebook and the average will be the actual result.

3.0 MAINTENANCE PROCEDURE

1. Replace batteries on a regular basis.

2. Store electrode in protective casing when not in use.

3. Keep records of usage, maintenance, calibration, problems, and repairs.

4. After use, the meter will be inspected and the inspection recorded in the field notebook.

5. A replacement meter will be available onsite or ready for overnight shipment.

6. pH meter will be sent back to manufacturer for service when needed.

FIELD S.O.P. NO. 2
PROCEDURES FOR MEASURING CONDUCTIVITY

Conductivity is the ability of a solution to pass an electric current. This current is carried by inorganic dissolved solids. The measure of conductivity is useful to relate the chemical purity of the water and the amount of dissolved solids in a solution.

1.0 CALIBRATION PROCEDURE

The conductivity meter will be calibrated daily.

1. Be sure the probe is clean.
2. Soak the probe in distilled/deionized water for at least 30 minutes.
3. Remove the probe from the water and fling out drops clinging inside.
4. Immerse the probe to or beyond the vent holes in a beaker containing a 1,000 mg/L sodium Chloride Standard Solution. Agitate vertically to remove entrapped air.
5. Repeat Steps 3 and 4 at least once more.
6. Press the Power key and CND key. Verify that the LO BAT indication does not appear.
7. Press the 2 milliSiemens per centimeter (mS/cm) range key.
8. Check the reading on the display. It should be 1.990 mS/cm. If adjustment is needed, use a small screwdriver to adjust the CAL control next to the display. Counter clockwise adjustment increased the reading.

2.0 OPERATION PROCEDURE

1. Calibrate the conductivity meter.
2. Rinse probe in distilled/deionized water.
3. Fill two 100-milliliter plastic disposable beakers with water from the sample.

4. Turn meter on to the 2 mS/cm scale.

5. Insert probe into sample beaker and obtain a reading. The meter will read between 0 and 2.0 mS/cm in 0.001 increments.

6. Repeat Step 5 with other beaker.

7. Record both results in the field notebook and average.

8. Rinse probe off in distilled/deionized water.

9. If the electrodes become coated with foreign compounds, the probe should be cleaned with a detergent solution and then rinsed with distilled/deionized water.

3.0 MAINTENANCE PROCEDURE

1. Replace batteries on a regular basis.

2. Store electrode in protective casing when not in use.

3. Keep records of usage, maintenance, calibration, and of any problems and repair.

4. After use, the meter will be inspected and the inspection recorded in the log book..

5. A replacement meter will be available on-site or ready for overnight shipment.

6. Conductivity meter will be sent back to manufacturer for service when needed.

FIELD S.O.P. NO. 3
PROCEDURES FOR MEASURING TEMPERATURE

Temperature readings will be taken at each water sampling location to assist in pH and conductivity measurement. It will also assist in chemical and biological interpretations. A thermometer may be part of a pH/conductivity meter or separate.

1.0 OPERATION PROCEDURE

1. Rinse thermometer in distilled/deionized water.

2. Immerse thermometer in the water sample and read it to the nearest degree Celsius (°C).

3. Record reading in the field notebook or relevant log.

2.0 PREVENTATIVE MAINTENANCE

1. Use of a Teflon^{R} coated thermometer lends extra strength and shock resistance to guard against accidental breakage.

2. Store in protective casing when not in use.

FIELD S.O.P. NO. 4
PROCEDURES FOR MEASURING DISSOLVED OXYGEN

1.0 CALIBRATION PROCEDURE

The dissolved oxygen meter will be calibrated daily, using the air calibration method.

1. Prepare the probe with a thin Teflon^R membrane stretched over the sensor.
2. Perform a battery check and obtain a barometric pressure reading from a daily weather report.
3. With the unit off, adjust the meter pointer to zero with the screw in the center of the meter panel.
4. Switch dial to ZERO and adjust pointer using the ZERO knob.
5. Switch dial to FULL SCALE and adjust pointer using the FULL SCALE knob. Check batteries if pointer cannot reach full scale.
6. Attach probe to unit and tighten.
7. Turn unit on.
8. Allow 15 minutes for optimum probe stabilization and polarization.
9. Switch dial to CALIB O_2.
10. Hold probe in the air for 10 minutes or until reading is stable.
11. Using the CALIB knob, set the pointer to the mark associated with the local barometric pressure and ambient air temperature. If barometric pressure is unknown, a correction value of 97 percent should be used.

2.0 OPERATION PROCEDURE

1. Calibrate the DO meter.
2. Perform the battery check.
3. Set mode switch to operate and the operation switch to the desired range.

4. Place probe into water sample.

5. Take a water temperature measurement and adjust temperature dial.

6. Switch to DO content measurement and allow reading to stabilize.

7. Record water temperature and DO on appropriate form or in the field notebook.

3.0 MAINTENANCE PROCEDURE

1. Replace batteries on a regular basis, at a suggested interval of every six months or every 1,000 hours of operation.

2. Store electrode in protective casing when not in use.

3. Keep records of usage, maintenance, calibration, and of any problems and repair.

4. A replacement DO meter will be ready for overnight shipment.

5. DO meter will be sent back to manufacturer for service when needed.

FIELD S.O.P. NO. 5
PROCEDURES FOR MEASURING TURBIDITY

1.0 STANDARDIZATION PROCEDURE

Standardization will be performed before each set of tests to ensure consistently accurate results.

1. Turn the instrument off and check the mechanical zero setting. Adjust to a zero NTU reading if necessary.

2. Turn power switch on and perform a battery check.

3. Place the focusing template into the cell holder. This will block all the light from reaching the detector and allow the instrument to be zeroed electronically in Steps 4 and 5.

4. Press the 1.0 range switch and adjust the Zero Control for a reading of zero NTU.

5. Press the 10.0 range switch to verify that the meter still indicates zero NTU. Readjust the Zero Control if necessary.

6. Remove the focusing template and place the appropriate Gelex secondary standard for the turbidity range to be used into the cell holder. Use the index mark on the standard to orient the vial in the same position each time, thereby eliminating variation due to rotation.

7. Place the light shield over the turbidity standard and allow the meter to stabilize.

8. Adjust the span control for a meter reading equal to the value of the Gelex standard in the cell holder. Remove the light shield and turbidity standard. The instrument is now ready for use.

2.0 CALIBRATION PROCEDURE

Each range is calibrated at the factory but should be checked from time to time against fresh Formazin turbidity standard dilutions. Three trimmer potentiometers on the amplifier circuit board provide an adjustment for each range. Check each range as described in the following procedure and make the appropriate adjustments when necessary, using the procedures described in Range Calibration.

1. With the instrument turned off, check the mechanical zero adjustment on the meter face. Adjust for a zero reading if necessary.

2. Turn the instrument on and perform a battery check. change battery if needed.

3. Place the focusing template into the cell holder, press the 1.0 range switch, and adjust the Zero Control to obtain a zero NTU reading.

4. Remove the focusing template and insert a 0.75 NTU turbidity standard. Adjust the SPAN control for a corrected 0.75 NTU reading.

5. Remove the 0.75 NTU standard and replace it with a 10 NTU standard. Press the 10.0 range switch. The meter should indicate 10 ($\pm$0.2) NTU. If it does not, the 10.0 range potentiometer needs adjustment as described in the Range Calibration procedure. Adjust the SPAN control for a reading of exactly 10 NTU.

6. Remove the 10 NTU standard and replace it with the cell riser and 100 NTU standard. Press the 100 range switch. The meter should indicate 100 ($\pm$2) NTU. If it does not, the 100 range potentiometer needs adjustment as described in the Range Calibration procedure.

7. Remove the 100 NTU standard and cell riser and insert the 10 NTU standard. Press the 10.0 NTU range switch. Adjust the SPAN control for a reading of exactly 10 NTU.

8. Remove the 10 NTU standard and replace it with a 0.75 NTU standard. Press the 1.0 range switch. The meter should indicate the corrected value for the 0.75 NTU standard ($\pm$0.02). If it does not, the 1.0 range potentiometer needs adjustment as described in the Range Calibration procedure.

3.0 RANGE CALIBRATION PROCEDURE

In the event the range adjustment potentiometers on the amplifier circuit board require adjustment, remove the instrument from its case and proceed as follows:

1. With the instrument turned off, check the meter's mechanical zero adjustment. Adjust for a zero reading if necessary.

2. Turn on power and perform a battery check.

3. Place the focusing template into the cell holder, press the 1.0 range switch, and adjust the SPAN control fully counterclockwise.

4. Adjust the Zero Control clockwise to obtain a 0.05 NTU reading on the 1.0 scale.

5. Adjust the SPAN control clockwise to obtain a reading of 0.15 NTU on the 1.0 scale. Do not alter the SPAN control setting for the remainder of this procedure.

6. Press the 100 range switch and adjust the Zero Control for a zero reading.

7. Remove the focusing template and insert the cell riser and 100 NTU Formazin turbidity standard. Cover the standard with the light shield and allow the meter to stabilize. Adjust the 100 range adjustment potentiometer to obtain a full-scale reading.

8. Remove the 100 NTU standard and cell riser and insert the focusing template into the cell holder.

9. Press the 10.0 range switch and adjust the Zero Control for a zero reading.

10. Remove the focusing template and substitute the 10 NTU Formazin standard. Cover with the light shield and allow the meter to stabilize. Adjust the 10.0 range adjustment potentiometer to obtain a full-scale reading.

11. Remove the 10 NTU standard and insert the focusing template.

12. Press the 1.0 range switch and adjust the Zero Control for a zero reading.

13. Remove the focusing template and insert the 0.75 NTU Formazin turbidity standard. Cover with the light shield and allow the meter to stabilize. Adjust the 1.0 range adjustment potentiometer to obtain a reading equal to the corrected NTU value determined when addition the turbidity of the dilution water to the nominal value of the standard.

4.0 MEASUREMENT PROCEDURE

1. Turn power switch on and perform a battery check.

2. Press the appropriate range switch: 0-1, 0-10, 0-100 NTU.

3. Place the focusing template into the cell holder and adjust the Zero Control for a reading of zero NTU. Remove focusing template.

4. Fill a clean sample cell to the white line with the sample to be measured and place it into the cell holder. Use the white dot on the sample cell to orient the cell in the same position each time. Cover sample with light shield and allow meter to stabilize.

5. Read and record the turbidity of the sample.

6. Perform a duplicate sample every 10 or set of samples, whichever is more frequent.

5.0 MAINTENANCE PROCEDURE

1. Recharge battery on a regular basis.

2. Store in protective casing when not in use.

3. Keep records of usage, maintenance, calibration, and of any problems and repair.

4. After use the meter will be inspected and the inspection recorded in the field notebook.

5. A replacement meter will be ready for overnight shipment.

6. Keep nephelometric sample tubes clean both inside and out. Replace them when they become scratched or etched. Do not handle the tubes in the region where the light beam enters them.

7. Clean lens periodically.

8. Nephelometer will be sent back to the manufacturer for service when needed.

FIELD S.O.P. NO. 6
PROCEDURES FOR MEASURING OXIDATION REDUCTION POTENTIAL (ORP)

1.0 CALIBRATION PROCEDURE

The ORP meter will be calibrated daily.

1. Switch on instrument.
2. Set the function switch to mV.
3. Connect the shorting cup to the mV input jack.
4. Check the display, zero if necessary.
5. Attach ORP probe to the mV input jack and the temperature probe to the TEMP input jack.
6. Rinse probes with distilled water.
7. Rinse probes with ZoBell solution.
8. Half fill a 50 ml sample cup with ZoBell solution.
9. Immerse the probes in the ZoBell solution and allow to equilibrate.
10. Read the display.
11. Correct mV valve to 25°C by subtracting 1.3 mV/°C for temperatures below 25°C and adding 1.3 mV/°C for temperatures above 25°C.
12. If calculated mV valve is within range of 231 $\pm$ 10 mV, instrument is calibrated. If not, adjust instrument to within 231 $\pm$ 10 mV

2.0 OPERATION PROCEDURE

1. Switch instrument on.
2. Set the function switch to mV.
3. Attach the ORP electrode to the mV input jack.

4. Fill the sample chamber with the solution to the be tested.

5. Immerse the ORP electrode in the solution to be tested.

6. Read the display.

7. Turn power switch to off when done.

3.0 MAINTENANCE PROCEDURE

1. Replace batteries on a regular basis.

2. Store probes in protective casing when not in use.

3. Keep records of usage, maintenance, calibrator, problems and repairs.

4. A replacement ORP meter will be ready for overnight shipping.

5. ORP meter will be sent back to manufacturer for service when needed.

FIELD S.O.P. NO. 7
FOR HNu PHOTOIONIZATION DETECTOR

1.0 OPERATING PROCEDURE

The following procedures are to be used in operating the analyzer:

1. Unclamp the cover from the main readout assembly.

2. Remove the inner lid from the cover by pulling out the two fasteners.

3. Remove the probe, handle and cable from the cover. Attach the handle to the front part of the probe.

4. Connect the probe cable plug to the 12 pin keyed socket on the readout assembly panel. Carefully match the alignment slot in the plug to the key in the connector. Screw down the probe connector until a distinct snap and lock is felt.

5. Screw the probe extension into the probe end cap. The probe may be used without the extension if desired.

6. Set the SPAN control for the probe being used (10.2, 9.5, or 11.7eV) as specified by the initial factory calibration or by subsequent calibrations.

7. Turn the function switch to the BATT (battery check) position. The needle on the meter will go to the green zone if the battery is fully charged. If the needle is below the green arc, or if the Low Battery Indicator comes on, the battery must be recharged before the analyzer is used.

8. Set SPAN pot to the desired value based on the gas to be used.

9. Turn the function switch to the STANDBY position. Turn the zero adjustment until the meter needle is at zero.

10. Calibrate the instrument daily as described in Section 3. Calibration on the selected operating range is desirable.

11. If equipped with optional alarm, set or check the alarm setting at the level desired. Turn the function switch to the desired range, turn the zero adjustment control so the meter needle moves upscale through the desired value. This simulates real conditions. Observe the reading when the alarm sounds. Adjust the ALARM SET, if required, with a screw driver. Turn the function switch to the STANDBY position and reset the zero position

(paragraph 8. above). If the range is to be changed, the alarm must be reset on that range.

12. To operate with option recorder, add the recorder bracket. Remove the plug in the analyzer case and insert power cord into the recorder. Then connect the signal leads to the appropriate jacks in the control module. The recorder is now operational.

    NOTE: Ranges must be marked on the chart as the recorder prints the meter display as % of Full Scale.

13. Turn the function switch to the appropriate operating position. Start with the 0-2000 position and then switch to the more sensitive ranges. The UV light source should be on, confirmed by briefly looking into the probe to observe a purple glow from the lamp.

14. The analyzer is now operational.

15. Hold the probe so that the extension is at the point where the measurement is to be made. The instrument measures the concentration by drawing the gas in at the end of the extension, through the ionization chamber, and out the handle end of the probe.

16. Take the reading or readings as desired taking into account that air currents or drafts in the vicinity of the probe tip may cause fluctuations in readings. Change the ranges as required.

17. Check battery condition as required. If the Low Battery Indicator comes on, turn analyzer off and recharge.

18. After completion of use, check battery condition as described in Paragraph 7.

19. Turn function switch to OFF position.

20. When not operating, leave analyzer in assembled condition, and connected to battery charger.

21. When transporting, disassemble probe and extension from readout assembly and return equipment to its stored condition.

22. In case of emergency, turn function switch to OFF position.

2.0 CALIBRATION OF HNu

HNu calibration checks will be done daily in the field prior to the commencement of field activities. Daily calibration checks will be performed in accordance with the following procedures:

1. Connect the probe to the readout assembly. Screw the probe extension with the probe seed cap. Connect the extension probe to the regulator and cylinder. The calibration gas in the cylinder consists of a mixture of isobutylene and zero air. Isobutylene is non toxic and safe to use in confined areas. There are no listed exposure levels at any concentration.

2. With the SPAN setting and the function switch at the same positions as listed in the Application Data Sheet or Calibration Report, open the valve on the cylinder until a steady reading is obtained.

3. If the reading is the same as the recorded data, the analyzer calibration for the original species of interest is still correct.

4. If the reading has changed, adjust the SPAN setting until the reading is the same.

5. Shut off the cylinder as soon as the reading is established.

6. Record and maintain this new SPAN setting.

3.0 MAINTENANCE PROCEDURE

1. Recharge battery on a regular basis.

2. Store in protective casing when not in use.

3. Keep records of usage, maintenance, calibration, and of any problems and repair.

4. After use the meter will be inspected and the inspection recorded in the field notebook.

5. A replacement meter will be ready for overnight shipment.

6. HNu will be sent back to the manufacturer for service when needed.

FIELD S.O.P. NO. 8
FOR COLORIMETRIC INDICATOR TUBES

1.0 CALIBRATION PROCEDURE

The sealed indicator tubes are pre-calibrated by the manufacturer. No calibration is required.

2.0 OPERATION PROCEDURE

1. Break off ends of sealed glass tube.
2. Place the tube into the hand held pump receptacle.
3. Connect the sample port to the open end of the tube with flexible plastic tube.
4. Pump the required amount of air through the tube in time intervals as indicated by the manufacturer.
5. Remove the tube from the sample port and pump and read the concentration off the tube.
6. Log the results.

3.0 MAINTENANCE PROCEDURE

1. Used tubes are to be disposed of after use when contamination is detected. If no contaminant is detected, the ends may be sealed with an air tight seal. The tube may be reused.
2. The pump will be checked for air leakage and pump volume per stroke. Repairs will be made if leakage or incorrect pump volume is discovered.
3. The pump will be stored in a case and the tube will be stored in a box to prevent breakage.

ATTACHMENT D

CURRENT LABORATORY CONTROL LIMITS

ENVIROSCAN CORP.
INORGANIC QUALITY CONTROL LIMITS

ANALYSIS	CHECK STANDARD-PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL	DUPLICATES - PERCENT DIFFERENCE UCL	UWL	AVG	MATRIX SPIKE-PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL
Alkalinity	not applicable					9.06	6.86	2.47	not applicable				
Ammonia - Auto Analyzer	110.*	108.4	98.8	93.3*	90.0*	12.6	9.55	2.74	116.5	111.5	101.6	91.68	86.72
Ammonia - low level(<10mg/l)	110.*	108.4	98.8	93.3*	90.0*	22.0	16.5	5.37	116.5	111.5	101.6	91.68	86.72
Ammonia - TRAACS	108.7	105.4	96.94	93.3*	90.0*	26.0	20.0	7.94	126.0	117.9	101.8	85.66	77.38
Ammonia - Distillation	110.*	107.7*	100.*	93.3*	90.0*	9.96	7.45	2.42	116.5	108.9	93.55	78.23	70.57
Biomass	not applicable					25.0*	16.7*	0.0*	not applicable				
Bromide - IC	106.4	103.8	98.45	93.15	90.50	25.0*	16.7*	0.0*	122.0	115.7	102.9	90.14	83.75
BOD (5 day)	114.2		100.0		83.75	13.2	10.0	3.66	not applicable				
CBOD (5 day)	114.2		100.0		83.75	15.3	11.6	4.36	not applicable				
Carbon - NPOC (<10mg/l)	110.*	107.7	98.96	90.18	90.*	12.54	9.56	3.59	124.9	119.6	109.1	98.55	93.28
Carbon - NPOC	107.7	105.0	99.78	94.52	91.88	6.90	5.29	2.08	124.9	119.6	109.1	98.55	93.28
Carbon - DIC	not applicable					25.0*	16.7*	0.0*	not applicable				
Carbon - POC	107.7	105.0	99.78	94.52	91.88	19.3	14.7	5.56	(high) not applicable				
Chloride - IC	109.9	106.7	100.1	93.56	90.28	5.22	3.93	1.35	127.2	120.5	107.0	93.53	86.80
Chloride - Auto Analyzer	110.*	108.4	101.8	95.17	91.85	7.16	5.33	1.68	121.4	115.2	102.9	90.6	84.4
Chlorophyll a	110.*	107.*	100.*	93.3*	90.0*	25.0*	16.7*	0.0*	not applicable				
COD - Macro	106.3	103.6	98.2	92.8	90.0*	9.8	7.5	2.99	121.1	111.3	91.5	71.7	61.9
COD - Macro low level(<1g/l)	106.3	103.6	98.2	92.8	90.0*	11.3	8.79	3.84	121.1	111.3	91.5	71.7	61.9
COD - Mini	108.4	105.4	99.3	93.2	90.0	10.7	7.82	2.14	146.6	130.2	97.56	64.88	48.54
COD - Mini low level(<150 mg/l)	108.4	105.4	99.3	93.2	90.0	28.5	21.3	6.95	146.6	130.2	97.56	64.88	48.54
Color	102.6	101.9	100.5	99.13	98.44	8.26	6.02	1.54	not applicable				
Conductivity	110.*	107.*	100.*	93.3*	90.0*	25.0*	16.7*	0.0*	not applicable				
Cyanide, Total	110.*	108.5	101.2	93.9	90.2	8.9	6.8	2.4	132.6	117.8	88.2	58.5	43.7
Cyanide, Reactive	150.*	133.*	100.*	66.7*	50.0*	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Cyanide, Free	110.*	107.*	100.*	93.3*	90.0*	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Cyanide, Amenable	110.*	107.*	100.*	93.3*	90.0*	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Fluoride - Auto Analyzer	108.2	105.0	98.7	92.4	90.0*	27.5	20.5	7.0	119.9	114.3	103.1	91.87	86.26
Ignitability	not applicable					25.0*	16.7*	0.0*	not applicable				
Nitrite - IC	110.*	107.2	101.4	95.59	92.68	25.0*	16.7*	0.0*	117.0	112.4	103.3	94.19	89.63
Nitrite - Auto Analyzer	110.*	107.1	100.1	93.12	90.0*	25.0*	16.7*	0.0*	114.0	109.7	101.1	92.52	88.24
Nitrite + Nitrate-Auto Analyzer	109.6	106.8	101.4	95.96	93.24	7.06	5.37	1.99	126.2	119.1	104.9	90.70	83.61
Nitrate - IC	106.0	103.0	97.00	90.97	90.0*	4.92	3.67	1.18	115.8	110.3	99.31	88.29	82.77
Nitrate - Auto Analyzer	109.6	106.8	101.4	95.96	93.24	7.06	5.37	1.99	126.2	119.1	104.9	90.70	83.61
Orthophosphate - Auto Analyzer	110.0	106.8	100.0	93.8	90.0	11.1	8.61	3.64	126.8	115.9	94.05	72.23	61.32
Orthophosphate - TRAACS	110.*	108.2	99.62	91.07	90.0*	23.1	17.3	5.56	118.3	109.4	91.76	74.09	65.26
pH	+0.05 pH*				-0.05 pH*	+/-0.1 pH			not applicable				
Phenols - Auto Analyzer	106.9	104.1	98.4	92.7	90.0*	8.1	6.5	3.1	127.1	118.2	100.4	82.6	73.7
Phosphorus - Auto Analyzer	110.*	108.1	101.9	95.81	92.74	14.6	11.2	4.64	128.5	120.1	103.3	86.49	78.09
Phosphorus - TRAACS	110.*	108.5	100.2	91.92	90.0*	26.5	20.5	8.60	133.4	121.3	97.18	73.04	60.97
Solids, Settleable	not applicable					25.0*	16.7*	0.0*	not applicable				

ENVIROSCAN CORP.
METALS BY GFAAS AND MERCURY QUALITY CONTROL LIMITS

ANALYSIS	CHECK STANDARD - PERCENT RECOVERY					DUPLICATE PERCENT DIFFERENCE			SPIKE - PERCENT RECOVERY				
	UCL	UWL	AVG	LWL	LCL	UCL	UWL	AVG	UCL	UWL	AVG	LWL	LCL
Antimony	110.	107.	100.0	93.3	90.0	12.5	9.76	4.22	130.2	120.5	101.4	82.2	72.5
Arsenic	110.	107.	100.0	93.3	90.0	20.6	16.2	7.36	113.0	107.8	98.1	88.4	83.6
Cadmium	110.	107.	100.0	93.3	90.0	12.5	9.63	3.95	121.9	114.6	100.0	85.4	78.0
Copper	110.	107.	100.0	93.3	90.0	18.5	14.2	5.43	123.1	115.8	101.1	86.4	79.1
Chromium	110.	107.	100.0	93.3	90.0	29.6	22.2	7.38	124.5	117.3	103.0	88.7	81.6
Lead	110.	107.	100.0	93.3	90.0	36.1	27.2	9.44	118.6	111.9	98.5	85.1	78.4
Mercury	110.	107.	100.0	93.3	90.0	71.8	51.3	10.3	125.6	116.4	98.1	79.7	70.5
Selenium	110.	107.	100.0	93.3	90.0	34.5	26.1	8.84	114.0	108.7	98.3	87.7	82.5
Silver	110.	107.	100.0	93.3	90.0	21.9	16.8	6.62	127.4	118.8	101.8	84.8	76.3
Thallium	110.	107.	100.0	93.3	90.0	25.0*	16.7*	0.0*	125.8	117.1	99.8	82.5	73.8
Hexavalent Chromium	110.	107.	100.0	93.3	90.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*

* default limit

January 6, 1993

ENVIROSCAN CORP.
METALS BY ICP QUALITY CONTROL LIMITS

ANALYSES	CHECK STANDARD - PERCENT RECOVERY					DUPLICATE PERCENT DEVIATION			SPIKE PERCENT RECOVERY				
	UCL	UWL	AVG	LWL	LCL	UCL	UWL	AVG	UCL	UWL	AVG	LWL	LCL
Aluminum	105.	103.3	100.	96.7	95.0	15.1	11.4	3.87	109.2	106.1	100.	93.8	90.7
Aluminum-low level(<10mg/l)	105.	103.3	100.	96.7	95.0	22.5	16.8	5.54	109.2	106.1	100.	93.8	90.7
Antimony	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	113.2	108.6	99.1	89.6	84.9
Arsenic	105.	103.3	100.	96.7	95.0	51.0	38.4	13.1	112.6	108.4	100.2	91.9	87.8
Barium	105.	103.3	100.	96.7	95.0	18.3	13.4	3.68	108.3	105.7	100.6	95.4	92.9
Beryllium	105.	103.3	100.	96.7	95.0	25.9	18.9	5.10	114.7	108.1	94.8	81.6	75.0
Boron	105.	103.3	100.	96.7	95.0	9.38	7.34	3.27	117.0	110.5	96.3	82.0	74.9
Cadmium	105.	103.3	100.	96.7	95.0	29.3	21.9	7.10	108.3	106.0	101.4	96.9	94.6
Calcium	105.	103.3	100.	96.7	95.0	3.46	2.73	1.25	108.8	106.4	101.7	97.0	94.6
Chromium	105.	103.3	100.	96.7	95.0	19.9	15.3	6.00	109.9	106.9	100.8	94.8	91.7
Cobalt	105.	103.3	100.	96.7	95.0	13.1	9.98	3.70	125.*	117.*	100.*	83.3*	75.0*
Copper	105.	103.3	100.	96.7	95.0	7.84	5.98	2.26	109.6	106.7	100.9	95.1	92.1
Iron	105.	103.3	100.	96.7	95.0	17.3	12.9	4.06	108.4	106.0	101.0	96.0	93.5
Iron-low level(<10mg/l)	105.	103.3	100.	96.7	95.0	44.5	33.0	10.1	108.4	106.0	101.0	96.0	93.5
Lead	105.	103.3	100.	96.7	95.0	30.2	23.2	9.15	110.7	107.5	101.0	94.4	91.2
Magnesium	105.	103.3	100.	96.7	95.0	8.77	6.40	2.94	111.2	107.8	101.2	94.5	91.2
Manganese	105.	103.3	100.	96.7	95.0	10.4	7.60	2.01	109.6	105.3	96.8	88.2	84.0
Molybdenum	105.	103.3	100.	96.7	95.0	40.4	30.8	7.53	116.3	111.2	101.1	91.0	86.0
Nickel	105.	103.3	100.	96.7	95.0	36.1	27.9	11.4	109.4	106.4	100.3	94.3	91.2
Phosphorus	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Potassium	105.	103.3	100.	96.7	95.0	21.4	17.1	8.45	113.4	108.6	99.1	89.6	84.9
Selenium	105.	103.3	100.	96.7	95.0	22.5	15.8	2.42	115.9	110.6	100.2	89.7	84.5
Silicon	105.	103.3	100.	96.7	95.0	8.77	6.40	1.64	110.5	107.2	100.5	93.9	90.6
Silver	105.	103.3	100.	96.7	95.0	77.7	57.9	18.3	109.2	105.3	97.5	89.7	85.8
Sodium	105.	103.3	100.	96.7	95.0	5.74	4.44	1.85	109.4	106.2	99.8	93.4	90.1
Sulfur	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Thallium	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Tin	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Titanium	105.	103.3	100.	96.7	95.0	30.6	22.8	5.21	125.*	117.*	100.*	83.3*	75.0*
Vandium	105.	103.3	100.	96.7	95.0	25.0*	16.7*	0.0*	125.*	117.*	100.*	83.3*	75.0*
Zinc	105.	103.3	100.	96.7	95.0	15.7	11.7	3.79	107.8	105.6	101.3	97.0	94.8

* Default Limit

December 22, 1992

ENVIROSCAN CORP.
PESTICIDE/PCB QUALITY CONTROL LIMITS
WATER MATRIX

	CHECK STANDARD					DUPLICATES/WATER			SPIKES/WATER				
ANALYSIS	UCL	UWL	AVG	LWL	LCL	UCL	UWL	AVG	UCL	UWL	AVG	LWL	LCL
Aldrin	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	135.	115.	73.6	32.6	12.1
a-BHC	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	145.	125.	85.0	44.7	24.6
b-BHC	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	141.	120.	78.4	37.0	16.3
Heptachlor	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	163.	137.	85.2	33.7	7.89
d-BHC	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	152.	133.	94.3	55.6	36.2
Lindane	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	170.	142.	85.0	28.4	0.12
Heptachlor Epoxide	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	172.	151.	110.	68.6	47.9
Endosulfan I	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	192.	163.	107.	50.4	22.1
4,4-DDE	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	196.	166.	106.	45.9	15.8
Dieldrin	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	177.	154.	109.	63.5	40.8
Endrin	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	193.	169.	121.	73.9	50.1
4,4-DDD	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	202.	178.	130.	81.3	57.2
Endosulfan II	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	172.	151.	108.	64.8	43.3
4,4-DDT	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	189.	167.	122.	77.8	55.5
Endrin Aldehyde	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	184.	164.	124.	84.9	65.1
Endosulfan Sulfate	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	171.	152.	113.	74.2	54.8
Chlordane	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	121.8*		81.6*		41.4*
Methoxychlor	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Toxaphene	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	134.7*		88.7*		42.7*
PCB 1016	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	128.5*		86.0*		43.5*
PCB 1221	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	174.9*		102.5*		30.1*
PCB 1232	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	215.*		-		10.0*
PCB 1242	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	188.3*		100.0*		11.7*
PCB 1248	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	164.2*		107.6*		51.0*
PCB 1254	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	172.6*		96.7*		20.8*
PCB 1260	115.	110.	100.	90.0	85.0	25.0*	16.7*	0.0*	127.*		-		8.0*

SURROGATES:	UCL	UWL	AVG	LWL	LCL
Tetra-m-xylene	140.	117.6	72.7	27.8	5.41
Decachlorobiphenyl	164.	138.8	87.8	36.8	11.3

* default limit

December 22, 1992

Default limits for spikes were established using Table 4 from USEPA method 608 as listed in Part 136 of CFR 40, 1991 and Table 4 from USEPA method 8080 as listed in SW-846, September 1986. Calculation of limits for several compounds did not yield usable limits therefore the range for Pi and Ps from Table 3 of the corresponding sources were used. The compounds using the defaults Pi and Ps do not list an average recovery.

ENVIROSCAN CORP.
VOLATILES BY GC/MS QUALITY CONTROL LIMITS
MATRIX: SOIL/SOLID

ANALYSIS	INITIAL CALIBRATION % RSD	CONTINUING CALIBRATION % RD FROM AVG.	DUPLICATE - % DIFFERENCE UCL	UWL	AVG	MATRIX SPIKE - PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL
Benzene	<30	<20	25.0*	16.7*	0.0*	151*				37*
Bromodichloromethane	<30	<20	25.0*	16.7*	0.0*	155*				35*
Bromoform	<30	<20	25.0*	16.7*	0.0*	169*				45*
Bromomethane	<30	<20	25.0*	16.7*	0.0*	242*				D
Carbon Tetrachloride	<30	<20	25.0*	16.7*	0.0*	140*				70*
Chlorobenzene	<30	<20	25.0*	16.7*	0.0*	160*				37*
2-Chlorovinyl ether	<30	<20	25.0*	16.7*	0.0*	305*				D
Chloroform	<30	<20	25.0*	16.7*	0.0*	138*				51*
Chloromethane	<30	<20	25.0*	16.7*	0.0*	273*				D
Dibromochloromethane	<30	<20	25.0*	16.7*	0.0*	149*				53*
1,2-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	190*				18*
1,3-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	156*				59*
1,4-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	190*				18*
1,1-Dichloroethane	<30	<20	25.0*	16.7*	0.0*	155*				59*
1,2-Dichloroethane	<30	<20	25.0*	16.7*	0.0*	155*				49*
1,1-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	234*				D
trans-1,2-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	156*				54*
cis-1,2-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	150*				50*
1,2-Dichloropropane	<30	<20	25.0*	16.7*	0.0*	210*				D
cis-1,3-Dichloropropene	<30	<20	25.0*	16.7*	0.0*	227*				D
trans-1,3-Dichloropropene	<30	<20	25.0*	16.7*	0.0*	183*				17*
Ethyl Benzene	<30	<20	25.0*	16.7*	0.0*	162*				37*
Methylene Chloride	<30	<20	25.0*	16.7*	0.0*	221*				D
1,1,2,2-Tetrachloroethane	<30	<20	25.0*	16.7*	0.0*	157*				46*
Tetrachloroethene	<30	<20	25.0*	16.7*	0.0*	148*				64*
Toluene	<30	<20	25.0*	16.7*	0.0*	150*				47*
1,1,1-Trichloroethane	<30	<20	25.0*	16.7*	0.0*	162*				52*
1,1,2-Trichloroethane	<30	<20	25.0*	16.7*	0.0*	150*				52*
Trichloroethene	<30	<20	25.0*	16.7*	0.0*	157*				71*
Trichlorofluoromethane	<30	<20	25.0*	16.7*	0.0*	181*				17*
Vinyl Chloride	<30	<20	25.0*	16.7*	0.0*	251*				D
Xylenes	<30	<20	25.0*	16.7*	0.0*	150*				50*

SURROGATES:	UCL	LCL
1,2-Dichloroethane	80.0	120.
Toluene-d8	80.0	120.
4-Bromofluorobenzene	80.0	120.

D = Detection Limit

* = Default Limit

Default limits for most of the spikes were established using Table 6 from USEPA method 8240 as listed in SW-846, September 1986. If no limit was listed there, laboratory default limits were applied.

All limits for this method are defaults due to the fact that a new GC/MS was purchased and was operational late in the Fall of 1992.

ENVIROSCAN CORP.
VOLATILES BY GC/MS QUALITY CONTROL LIMITS
MATRIX: WATER

ANALYSIS	INITIAL CALIBRATION % RSD	CONTINUING CALIBRATION % RD FROM AVG.	DUPLICATE - % DIFFERENCE UCL	UWL	AVG	MATRIX SPIKE - PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL
Benzene	<30	<20	25.0*	16.7*	0.0*	151*				37*
Bromodichloromethane	<30	<20	25.0*	16.7*	0.0*	155*				35*
Bromoform	<30	<20	25.0*	16.7*	0.0*	169*				45*
Bromomethane	<30	<20	25.0*	16.7*	0.0*	242*				D
Carbon Tetrachloride	<30	<20	25.0*	16.7*	0.0*	140*				70*
Chlorobenzene	<30	<20	25.0*	16.7*	0.0*	160*				37*
2-Chlorovinyl ether	<30	<20	25.0*	16.7*	0.0*	305*				D
Chloroform	<30	<20	25.0*	16.7*	0.0*	138*				51*
Chloromethane	<30	<20	25.0*	16.7*	0.0*	273*				D
Dibromochloromethane	<30	<20	25.0*	16.7*	0.0*	149*				53*
1,2-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	190*				18*
1,3-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	156*				59*
1,4-Dichlorobenzene	<30	<20	25.0*	16.7*	0.0*	190*				18*
1,1-Dichloroethane	<30	<20	25.0*	16.7*	0.0*	155*				59*
1,2-Dichloroethane	<30	<20	25.0*	16.7*	0.0*	155*				49*
1,1-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	234*				D
trans-1,2-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	156*				54*
cis-1,2-Dichloroethene	<30	<20	25.0*	16.7*	0.0*	150*				50*
1,2-Dichloropropane	<30	<20	25.0*	16.7*	0.0*	210*				D
cis-1,3-Dichloropropene	<30	<20	25.0*	16.7*	0.0*	227*				D
trans-1,3-Dichloropropene	<30	<20	25.0*	16.7*	0.0*	183*				17*
Ethyl Benzene	<30	<20	25.0*	16.7*	0.0*	162*				37*
Methylene Chloride	<30	<20	25.0*	16.7*	0.0*	221*				D
1,1,2,2-Tetrachloroethane	<30	<20	25.0*	16.7*	0.0*	157*				46*
Tetrachloroethene	<30	<20	25.0*	16.7*	0.0*	148*				64*
Toluene	<30	<20	25.0*	16.7*	0.0*	150*				47*
1,1,1-Trichloroethane	<30	<20	25.0*	16.7*	0.0*	162*				52*
1,1,2-Trichloroethane	<30	<20	25.0*	16.7*	0.0*	150*				52*
Trichloroethene	<30	<20	25.0*	16.7*	0.0*	157*				71*
Trichlorofluoromethane	<30	<20	25.0*	16.7*	0.0*	181*				17*
Vinyl Chloride	<30	<20	25.0*	16.7*	0.0*	251*				D
Xylenes	<30	<20	25.0*	16.7*	0.0*	150*				50*

SURROGATES:	UCL	LCL
1,2-Dichloroethane	80.0	120.
Toluene-d8	80.0	120.
4-Bromofluorobenzene	80.0	120.

D = Detection Limit

* = Default Limit

Default limits for most of the spikes were established using Table 6 from USEPA method 8240 as listed in SW-846, September 1986.
If no limit was listed there, laboratory default limits were applied.

All limits for this method are defaults due to the fact that a new GC/MS was purchased and was operational late in the Fall of 1992.

ENVIROSCAN CORP.
SEMIVOLATILES BY GC/MS QUALITY CONTROL LIMITS
WATER MATRIX

ANALYSIS	INITIAL CALIBRATION % RSD	CONTINUING CALIBRATION % RD FROM AVG	DUPLICATE PERCENT DIFFERENCE UCL	UWL	AVG	SPIKES - PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL
BASES										
Acenaphthene	<30	<25	25.0*	16.7*	0.0*	145*				47*
Acenaphththylene	<30	<25	25.0*	16.7*	0.0*	145*				33*
Aniline	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Anthracene	<30	<25	25.0*	16.7*	0.0*	133*				27*
Benzidine	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Benzo(a)anthracene	<30	<25	25.0*	16.7*	0.0*	143*				33*
Benzo(b)fluoranthene	<30	<25	25.0*	16.7*	0.0*	159*				24*
Benzo(k)fluoranthene	<30	<25	25.0*	16.7*	0.0*	162*				11*
Benzo(a)pyrene	<30	<25	25.0*	16.7*	0.0*	163*				17*
Benzo(ghi)perylene	<30	<25	25.0*	16.7*	0.0*	219*				D*
Benzyl alcohol	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Benzyl butyl phthalate	<30	<25	25.0*	16.7*	0.0*	152*				D*
Bis(2-chloroethyl)ether	<30	<25	25.0*	16.7*	0.0*	158*				12*
Bis(2-chloroethoxy)methane	<30	<25	25.0*	16.7*	0.0*	184*				33*
Bis(2-chloroisopropyl)ether	<30	<25	25.0*	16.7*	0.0*	166*				36*
Bis(2-ethylhexyl)phthalate	<30	<25	25.0*	16.7*	0.0*	158*				8*
4-Bromophenyl phenyl ether	<30	<25	25.0*	16.7*	0.0*	127*				53*
4-Chloroaniline	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
2-Chloronaphthalene	<30	<25	39.6	30.0	11.0	137.0	124.2	98.5	72.8	60.0
4-Chlorophenyl phenyl ether	<30	<25	25.0*	16.7*	0.0*	158*				25*
Chrysene	<30	<25	25.0*	16.7*	0.0*	168*				17*
Dibenzo(a,h)anthracene	<30	<25	25.0*	16.7*	0.0*	227*				D*
Dibenzofuran	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Di-n-butyl phthalate	<30	<25	25.0*	16.7*	0.0*	118*				1*
1,2-Dichlorobenzene	<30	<25	63.2	47.1	14.9	107.3	93.9	67.0	40.2	26.7
1,3-Dichlorobenzene	<30	<25	64.9	48.2	14.9	100.7	87.3	60.7	34.0	20.7
1,4-Dichlorobenzene	<30	<25	67.4	50.2	15.7	102.2	88.7	61.8	34.9	21.4
3,3-Dichlorobenzidine	<30	<25	25.0*	16.7*	0.0*	262*				D*
Diethyl phthalate	<30	<25	25.0*	16.7*	0.0*	114*				D*
Dimethyl phthalate	<30	<25	25.0*	16.7*	0.0*	112*				D*
2,4-Dinitrotoluene	<30	<25	31.0	23.6	9.0	132.8	123.8	105.8	87.8	78.8
2,6-Dinitrotoluene	<30	<25	29.9	22.8	8.7	115.9	107.9	92.1	76.2	68.2
Di-n-octylphthalate	<30	<25	25.0*	16.7*	0.0*	146*				4*
1,2-Diphenylhydrazine	<30	<25	29.5	22.6	8.6	126.3	116.6	97.4	78.1	68.5
Fluoranthene	<30	<25	25.0*	16.7*	0.0*	137*				26*
Fluorene	<30	<25	25.0*	16.7*	0.0*	121*				59*
Hexachlorobenzene	<30	<25	37.3	28.2	10.1	147.5	132.4	102.2	71.9	56.8
Hexachlorobutadiene	<30	<25	66.5	50.2	17.8	119.1	100.8	64.2	27.5	9.2
Hexachlorocyclopentadiene	<30	<25	63.1	47.7	16.9	166.8	141.5	91.0	40.4	15.1
Hexachloroethane	<30	<25	68.8	51.6	17.4	98.7	84.0	54.6	25.2	10.5
Indeno(1,2,3-cd)pyrene	<30	<25	25.0*	16.7*	0.0*	171*				D*
Isophorone	<30	<25	24.7	18.8	7.1	108.6	100.2	83.5	66.8	58.5
2-Methylnaphthalene	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.*
N-Nitrosomethylamine	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.*
N-Nitrosodiphenylamine	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.*

ANALYSIS	INITIAL CALIBRATION % RSD	CONTINUING CALIBRATION % RD FROM AVG	DUPLICATE PERCENT DIFFERENCE UCL	UWL	AVG	SPIKES - PERCENT RECOVERY UCL	UWL	AVG	LWL	LCL
Naphthalene	<30	<25	25.0*	16.7*	0.0*	133*				21*
2-Nitroaniline	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
3-Nitroaniline	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
4-Nitroaniline	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
Nitrobenzene	<30	<25	46.2	34.5	11.2	117.8	108.0	88.4	68.8	59.0
N-Nitrosodi-n-propylamine	<30	<25	25.0*	16.7*	0.0*	230*				D*
Phenanthrene	<30	<25	25.0*	16.7*	0.0*	120*				54*
Pyrene	<30	<25	25.0*	16.7*	0.0*	115*				52*
1,2,4-Trichlorobenzene	<30	<25	56.8	42.6	14.3	120.8	105.6	75.2	44.9	29.7
ACIDS										
Benzoic acid	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
4-Chloro-3-methylphenol	<30	<25	29.8	22.1	6.7	144.2	131.4	105.8	80.2	67.4
2-Chlorophenol	<30	<25	51.0	37.6	10.6	119.0	106.9	82.7	58.5	46.5
2,4-Chlorophenol	<30	<25	41.4	30.5	8.5	140.2	127.0	100.6	74.1	60.9
2,4-Dimethylphenol	<30	<25	47.3	35.9	12.9	152.0	136.9	106.8	76.7	61.6
2,4-Dinitrophenol	<30	<25	61.7	47.0	17.6	175.7	152.7	106.8	60.8	37.8
2-Methyl-4,6-dinitrophenol	<30	<25	29.7	23.0	9.7	174.9	157.6	123.1	88.7	71.4
2-methylphenol	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
3- and 4-methylphenol	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
2-Nitrophenol	<30	<25	47.7	35.3	10.6	139.8	123.7	91.4	59.1	43.0
4-Nitrophenol	<30	<25	42.0	31.9	11.7	121.2	107.7	80.7	53.7	40.2
Pentachlorophenol	<30	<25	30.4	23.4	9.4	161.3	143.5	107.8	72.1	54.2
Phenol	<30	<25	53.2	38.9	10.5	81.7	74.2	59.1	44.0	36.4
2,4,5-Trichlorophenol	<30	<25	25.0*	16.7*	0.0*	150.*		100.*		50.0*
2,4,6-Trichlorophenol	<30	<25	30.7	23.4	8.6	167.4	151.6	119.9	88.2	72.4

SURROGATES (percent recovery):	UCL	UWL	AVG	LWL	LCL
Nitrobenzene-d5	114.	101.	74.5	48.	35.
2-Fluorobiphenyl	116.	104.	79.5	55.	43.
4-Terphenyl-d14	141.	123.	87.	51.	33.
2-Fluorophenol	100.	87.	60.5	34.	21.
Phenol-d6	94.	80.	52.	24.	10.
2,4,6-Trichlorophenol	123.	104.	66.5	29.	10.

December 22, 1992

* Default limits

D = Detection Limit

Default limits were established for spikes using Table 6 from USEPA method 8270 as listed in SW-846, September 1986. If no limit was listed there, laboratory default limits were applied.

ENVIRONMENTAL
CONTROL
TECHNOLOGY
CORPORATION

3005 RESEARCH PARK DRIVE
ANN ARBOR, MICHIGAN 48103
313/761-1389

September 13, 1993

Ms. Ruth Lewis
Conestoga-Rovers & Associates Limited
1801 Old Highway 8
Suite 114
St. Paul, Minnesota 55112

RE: Wausau Superfund Site
Pest/PCB & Metals Analyses

Dear Ms. Lewis:

Please find attached the ENCOTEC accuracy and precision limits for Pesticides/PCBs analysis by Method 8080. In the case of all TAL metals, the Lab Control Sample (LCS) limits are 80% to 120% recovery, Matrix Spike limits are 75% to 125% recovery, and Matrix Duplicate relative percent difference (RPD) limits are 20%.

Note that the control limits given are periodically updated per ENCOTEC's **Standard Operating Procedure for the Determination of Control Limits** and are subject to change. Therefore, these limits may be updated to reflect the most current control limits. In the event that control limits are updated during the period of the project, the analytical report forms will always reflect the current control limits.

If you have any questions, please give me a call.

Respectfully,

ENVIRONMENTAL CONTROL TECHNOLOGY CORPORATION

Timothy J. Schenk
Program Manager

TJS/rej

Attachment

#33019

PRECISION AND ACCURACY LIMITS
WAUSAU SUPERFUND SITE

PARAMETER

TCL Pesticides/PCBs	Soil & Water LCS Limits Accuracy	Soil & Water MS/MSD Limits Accuracy	RPD
Aldrin	42%-122%	42%-122%	15%
alpha-BHC	37%-134%	37%-134%	15%
beta-BHC	17%-147%	17%-147%	14%
delta-BHC	19%-140%	19%-140%	22%
Lindane	32%-127%	32%-127%	23%
alpha-Chlordane	27%-163%	27%-163%	13%
gamma-Chlordane	20%-193%	20%-193%	13%
4,4'-DDD	31%-141%	31%-141%	17%
4,4'-DDE	30%-145%	30%-145%	16%
4,4'-DDT	25%-160%	25%-160%	19%
Dieldrin	36%-146%	36%-146%	13%
Endosulfan I	45%-153%	45%-153%	20%
Endosulfan II	D-202%	D-202%	18%
Endosulfan Sulfate	26%-144%	26%-144%	16%
Endrin	30%-147%	30%-147%	13%
Endrin Aldehyde	13%-145%	13%-145%	21%
Heptachlor	28%-170%	28%-170%	12%
Heptachlor Epoxide	34%-111%	34%-111%	22%
Methoxychlor	47%-160%	47%-160%	14%

8080 Surrogate	Surrogate Accuracy
Triphenylphosphate	50%-150%

D - Detected

ENCOTEC

T014 Calibration Criteria

Compound	RSD Window
Benzene	30%
Benzyl chloride	30%
Bromomethane	30%
Carbon tetrachloride	30%
Chloroethane	30%
Chloroform	30%
Chloromethane	30%
3-Chloropropene	30%
1,2-Dibromoethane	30%
1,2-Dichlorobenzene	30%
1,3-Dichlorobenzene	30%
1,4-Dichlorobenzene	30%
Dichlorodifluoromethane	30%
1,1-Dichloroethane	30%
1,2-Dichloroethane	30%
1,1-Dichloroethene	30%
cis-1,2-Dichloroethene	30%
1,2-Dichloropropane	30%
1,2-Dichlorotetrafluoroethane	30%
cis-1,3-Dichloropropene	30%
trans-1,3-Dichloropropene	30%
Ethylbenzene	30%
4-Ethyltoluene	30%
Hexachlorobutadiene	30%
Methylene chloride	30%
Styrene	30%
1,1,2,2-Tetrachloroethane	30%
Tetrachloroethene	30%
Toluene	30%
1,2,4-Trichlorobenzene	30%
1,1,1-Trichloroethane	30%
1,1,2-Trichloroethane	30%
Trichloroethene	30%
Trichlorofluoromethane	30%
1,1,2-Trichloro-1,2,2-trifluoroethane	30%
1,2,4-Trimethylbenzene	30%
1,3,5-Trimethylbenzene	30%
Vinyl chloride	30%
total-Xylenes	30%

RSD - Relative Standard Deviation

T014 Surrogate Recovery Limits

Compound	Recovery Window
Toluene-d8	90% - 110%
Bromofluorobenzene	90% - 110%
1,2-Dichloroethane-d4	90% - 110%

ADDENDUM 1
REMEDIAL DESIGN/REMEDIAL ACTION QUALITY ASSURANCE PROJECT PLAN

Wausau Water Supply NPL Site
Wausau, Wisconsin

ADDENDUM 1
REMEDIAL DESIGN/REMEDIAL ACTION QUALITY ASSURANCE PROJECT PLAN

Wausau Water Supply NPL Site
Wausau, Wisconsin

NOVEMBER 1995
REF. NO. 3978 (7)
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CONESTOGA-ROVERS & ASSOCIATES

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PART 1

REVISED TEXT

3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Conestoga-Rovers & Associates (CRA), as contractor to the Wausau PRP Group, has overall responsibility for all phases of the activities at the Site. CRA will perform or supervise all field activities and will report directly to Wausau PRP Group's project manager.

Environmental Control Technology Corporation (Encotec), will perform off-Site chemical analyses of groundwater samples for VOC, BN, metals and pH. In addition, Encotec will analyze off-Site soil gas and exhaust gas samples for VOC. Enviroscan, Inc. (Enviroscan) will analyze soil gas samples on-Site for VOC. The laboratory addresses are as follows:

Enviroscan, Inc.
303 West Military Road
Rothschild, WI 54474

Encotec, Inc.
3985 Research Park Drive
Ann Arbor, MI 48108

All firms will provide project management as appropriate to their responsibilities. CRA will provide administrative oversight and QA/QC for all deliverables. All final project deliverables will be issued by CRA.

Figure 3.1 presents the organizational chart for the project. A summary of each of the key persons responsibilities is presented below:

Jennifer Wendel - Remedial Project Manager - USEPA

- general overview of the project to ensure that the objectives are met;
- participation on key negotiations with CRA and WDNR;
- approval of QAPjP.

- advise on data corrective action procedures;
- assist in the preparation and review of reports;
- QA/QC representation of project activities; and
- approval of QAPjP.

Peter Storlie - QA Officer - Field Activities - CRA

- lead QA/QC for field activities;
- data assessment of field analyses;
- technical representation of field activities; and
- preparation of standard operating procedures (SOPs) for field activities.

Will Elcoate - Laboratory Project Manager - Enviroscan

- ensures all resources of the laboratory are available on an as-required basis;
- overview of final analytical reports; and
- approval of the QAPjP.

Amy Wheaton - Laboratory Project Manager - Encotec

- ensures all resources of the laboratory are available on an as-required basis;
- overview of final analytical reports; and
- approval of the QAPjP.

Primary responsibility for project quality rests with the CRA QA/QC Officer - Analytical Activities and QA Officer - Field Activities. Ultimate responsibility for project quality rests with the CRA Project Manager. Independent quality assurance will be provided by the Laboratory Project Manager and QA Officer prior to release of all data to CRA.

foil and an air tight plastic cap will be placed over the each end of the brass tube.

3) Containers for sample collection (e.g., rinse blanks) will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

4) Soil samples will be labeled noting the sampling location, depth, time and sampler's initials. A separate hard-cover field book will be maintained to document all soil samples and sampling events (including: date and time collected, sample handling and storage, preservation and labeling, field measurements, characteristics of each sample taken, and weather conditions).

5) Samples will be placed on ice or cooler packs in laboratory supplied coolers after collection and labeling.

5.3 GROUNDWATER SAMPLING PROTOCOL

The order of sample collection for each sample fraction will be as follows:

1) VOC fraction
2) Metals fraction
3) BN fraction

5.3.1 Monitoring Well Sampling

All monitoring wells will be sampled according to the following protocols:

1) New disposable latex gloves will be used when sampling each well. Additional glove changes will be made for each sampling.

2) The sampler will measure and record the depth to water in each well to the nearest 0.01 foot using an electric tape or plopper.

3) Prior to sampling, each well will be purged, using a slow flow rate teflon bladder stainless steel pump fitted with teflon purging and air supply lines attached to a nylon rope. A minimum of three times the standing water volume in the well will be removed, or until conductivity, temperature and pH stabilize in the purge water. In the event that a well is purged dry prior to achieving three well volumes, groundwater will be permitted to recover to a level sufficient for sample collection. The time that the well was purged dry will be noted and well recovery will be monitored. Upon recovery, a bladder pump will then be used for sample collection. A bailer will be used to collect the sample if it is physically impossible to use a bladder pump. Prior to use in each well, the bailer or bladder pump will be precleaned as follows:

   1) Washed thoroughly with Alconox or equivalent;
   2) Rinsed with potable water;
   3) Rinsed with isopropanol (pesticide grade);
   4) Allowed to air dry;
   5) Wrap with new aluminum foil; and
   6) A final distilled water rinse prior to purging.

All waste groundwater, not used for samples, will be collected and discharged to the sanitary sewer. Waste groundwater from the west side monitoring well sampling will be discharged to the Interim Action treatment manhole if it is in closer proximity than the sanitary sewer.

4) Field measurements of pH, conductivity and temperature will be recorded prior to sample collection. Calibration of field instruments will be conducted as specified in Section 7.0.

5) After the required standing well water has been purged, water samples will be collected using a teflon bladder stainless steel pump, fitted with teflon purging and air supply lines, attached to a nylon rope. The groundwater samples will be collected from the purge line of the bladder pump used to purge the well. New nylon rope, where applicable, will be used for each monitoring well.

   Filtered monitoring well samples will be submitted to the laboratory for metals analyses. Field filtered samples will be collected using a 0.45 micron filter.

6) Containers for sample collection will be prepared using standard laboratory validated washing procedures that meet or exceed the requirements of the specific methods and "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", USEPA, April 1990 (Attachment A). QA/QC samples will be collected or prepared as specified in Table 2.2.

7) All disposable gloves and nylon ropes will be placed in DOT approved 55-gallon drums and stored at a designated area. All drummed waste will be disposed of in accordance with State and Federal regulations. All rinsings will be handled as discussed in item (3), above.

9.2.4 Surrogates

Surrogates are used in all GC and GC/MS analyses. Every blank, standard, and environmental sample including MS/MSD samples will be spiked with surrogate compounds prior to sample analysis for VOC and base/neutral extractable organic compounds (BN).

Surrogates will be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries will be compared to the control limits set by procedures specified in the method for analytes falling within the quantitation limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates out of the quantitation limit; assessment of analytical quality in these cases will be based in the quality control embodied in the check, matrix spike and matrix spike duplicate samples.

9.2.5 Blind Check Samples

As supplied by the agencies, an analytical batch may contain a blind check sample. In general, the blind check sample will be obtained from EPA Region V and supplied to CRA. The analytes employed in this check sample will be a representative subset of the analytes of interest.

Standard deviations and relative standard deviations will be calculated for the percent recovery of analytes from the check samples. These are defined in Section 13.2.

discrepancies and their effect upon the acceptability of the data. All information garnered for QA/QC checks will be discussed in the final report.

Validation of the analytical data from off-Site analyses will be performed by the CRA QA/QC Officer - Analytical Activities based on the QC criteria outlined in "National Functional Guidelines for Organic Data Review", February 1994 and "National Functional Guidelines for Inorganic Data Review", February 1994. Items 1 through 12 and field QA/QC results will be assessed in accordance with the applicable criteria outlined in the guidance documents. The results of these data validations will be reported to the CRA project managers, noting any discrepancy and their effect upon acceptability of the data.

The field GC data will be reduced and assessed by Enviroscan's field analyst. Preliminary results will be reported to CRA upon request. The analyst will perform a second review of the data before issuing a final report to CRA. The report will include numerical sample results and the associated quality control data. Field GC data (on-Site analyses) will be reviewed by CRA's Field QA/QC Officer. The data will be checked for legibility, completeness and any inconsistent data. Any discrepancies and their effect on the acceptability of the data will be noted in a memo to the CRA Project Manager. A formal data validation of field GC data will not be performed.

Raw data from other field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. In addition, field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

Field and laboratory data will accompany the progress reports that are submitted to the regulatory agencies on a scheduled basis.

11.0 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 RD/RA Work Plan (and Appendices) and QAPjP. The audits of field and laboratory activities include two separate, independent parts; internal and external audits.

11.1 FIELD AUDITS

A internal audit of field activities (sampling and measurements) may be conducted by the CRA QA/QC Officer - Field Activities prior to any investigatory sampling. The audit may include examination of field sampling records, field instrument operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, etc. These audits would be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the project. The audits would involve review of field measurement records, instrumentation calibration records and sample documentation.

External audits of field activities may be conducted by WDNR or USEPA Region V, as required.

11.2 LABORATORY AUDITS

The internal performance and system audits of the project laboratories may be conducted by the CRA QA/QC Officer - Analytical Activities. A systems audit may be conducted prior to any investigatory sample analyses. Additional audits may be conducted as deemed necessary by

either the owner, CRA project manager or the CRA QA/QC Officer - Analytical Activities and will include examination of laboratory documentation of sample receiving, sample log-in, sample storage, chain-of-custody procedure, sample preparation and analysis, instrument operating records, etc. Blind QC samples may be prepared and submitted along with project samples to the laboratory for analysis throughout the project. The QA officer will evaluate the analytical results of these blind performance samples to ensure the laboratories maintain a good performance.

External audits of laboratory activities may be conducted by WDNR or U.S. EPA Region V, as required.

PART 2

REVISED TABLES

TABLE 2.2 (Revised 11-95)

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WAUSAU SUPERFUND SITE*

Sample Matrix	Frequency	Field Parameters	Lab Parameters**	Estimated Number of Investigative Samples	Field (Rinsate) Blanks	Field Duplicates	MS/MSD or MS/DUP***
Groundwater							
Core Locations	Quarterly****	Water Level, pH, Temp., Conductivity	Site VOC	12	2	2	1
Indicator wells	Annually	Water Level, pH, Temp., Conductivity	Select TCL/TAL Parameters	7	1	1	1
Groundwater							
Comprehensive Locations	Annually	Water level, (semi-annual), pH, Temp., Conductivity	Site VOC, Site Metals, Site BN	44	5	5	3
Groundwater Treatment							
System Influent	Monthly	pH, Temp., Conductivity	Site VOC	3	--	1:10	--
System Effluent	Monthly	pH, Temp., Conductivity	pH, Site VOC, Site Metals	2	--	1:10	--
	Annual	pH, Temp., Conductivity	Select TCL/TAL Parameters	2	--	1:10	--

TABLE 2.2 (Revised 11-95)

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
WAUSAU SUPERFUND SITE*

Sample Matrix	Frequency	Field Parameters	Lab Parameters**	Estimated Number of Investigative Samples	Field (Rinsate) Blanks	Field Duplicates	MS/MSD or MS/DUP***
Soil	At end of SVE operation period.	--	Site VOC	150	15 (1:10)	15 (1:10)	8 (1:20)
Soil Gas	Quarterly, Monthly PID reading.	PID	Site VOC**** on-Site Lab	65	--	1:10	--
Exhaust Gas	Annually	--	TCL VOC off-Site TO-14	2	--	--	--

Notes:

* Two filled 40-mL preserved glass vials will be shipped with each cooler of VOC water and/or soil samples to serve as a trip blank. One pre-evacuated Summa canister will be shipped with each set of soil gas and/or exhaust gas samples to serve as a trip blank.

** See Table 4.1 for analytical methods and reporting limits.

*** Matrix spike/matrix spike duplicate (MS/MSD) analyses are required for organic parameters and matrix spike/laboratory duplicate (MS/DUP) analyses are required for inorganic parameters. Samples designated for MS/MSD analyses will be collected, with extra sample volumes for aqueous samples, at a frequency of one per group of twenty (20) or fewer investigative samples.

*** Monitoring well IWD will not be monitored during months of December, January or March, or if it is inaccessible due to weather conditions.

**** The following Site-VOC parameters will not be included in the on-Site soil gas analytical protocol: acetone, chloroform and vinyl chloride.

TABLE 2.3 (Revised 11-95)

DATA QUALITY OBJECTIVES
WAUSAU SUPERFUND SITE

Matrix	*Data Type*	*Investigation Objectives*	*Data Quality Level*	*Data Uses**
Groundwater - Core Locations	Water Level	Evaluate hydraulic capture from groundwater extraction wells	I	MI
	pH, Temp., Conductivity	Characterize general water quality	I	MI
	Site VOC	Evaluate progress of remedial actions	III	MI
	Select TCL/TAL Parameters	Determine the presence of contaminants other than VOCs	III	MI, SC
Groundwater - Comprehensive Locations	Water level	Evaluate hydraulic capture from groundwater extraction wells	I	MI
	pH, Temp., Conductivity	Characterize general water quality	I	MI
	Site VOC, Site Metals, Site BN	Evaluate progress of remedial actions	III	MI
Groundwater - Treatment System Influent	Site VOC	Evaluate removal efficiency and total VOC removal	III	MI

TABLE 2.3 (Revised 11-95)

DATA QUALITY OBJECTIVES
WAUSAU SUPERFUND SITE

Matrix	*Data Type*	*Investigation Objectives*	*Data Quality Level*	*Data Uses**
Groundwater - Treatment System Effluent	pH	Characterize general water quality	I	MI
	pH, Site VOC, Site Metals	Evaluate removal efficiency, total VOC removal and discharge quality	III	MI
	Select TCL/TAL Parameters	Evaluate discharge quality	III	MI
Soil	pH	General soil characterization	I	MI
	Site VOC	Evaluate progress of remedial actions	III	MI
Soil Gas	PID or Colorimetric Indicator Tube	Determine when carbon requires change out	I	MI
	Site VOC --on-Site	Evaluate progress of remedial action	II	MI
	Site VOC --off-Site	Confirm progress of remedial action	III	MI, SC
Exhaust Gas	TCL VOC --off-Site	Evaluate VOC air emissions	III	MI

Notes:

* Intended data uses:

SC - Site Characterization

MI - Monitoring During Implementation of Remedial Action

TABLE 4.1 (Revised 11-95)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER

TCL Volatile Organic Compounds	*Quantitation Limits Low Water (µg/L)*	*Quantitation Limits Low Soil (µg/Kg)*	*Med. Soil (µg/Kg)*
Chloromethane	1	1	5
Bromomethane	1	1	5
Vinyl Chloride*	1	1	5
Chloroethane	1	1	5
Methylene Chloride*	1	1	5
Acetone*	10	10	50
Carbon Disulfide	1	1	5
1,1-Dichloroethene*	1	1	5
1,1-Dichloroethane	1	1	5
cis-1,2-Dichloroethene*	1	1	5
trans-1,2-Dichloroethene	1	1	5
Chloroform*	1	1	5
1,2-Dichloroethane	1	1	5
2-Butanone	10	5	50
1,1,1-Trichloroethane	1	1	5
Carbon Tetrachloride*	1	1	5
Bromodichloromethane	1	1	5
1,2-Dichloropropane	1	1	5
cis-1,3-Dichloropropene	1	1	5
Trichloroethene*	1	1	5
Dibromochloromethane	1	1	5
1,1,2-Trichloroethane*	1	1	5
Benzene*	1	1	5
trans-1,3-Dichloropropene	1	1	5
Bromoform	1	1	5
4-Methyl-2-pentanone	10	10	50
2-Hexanone	10	10	50
Tetrachloroethene*	1	1	5
Toluene*	1	1	5
1,1,2,2-Tetrachloroethane	1	1	5
Chlorobenzene	1	1	5
Ethyl Benzene*	1	1	5
Styrene	1	1	5
Xylenes*	1	1	5

TABLE 4.1 (Revised 11-95) (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	*Quantitation Limits*
TCL Volatile Organic Compounds	*Air (ppbv)*
Benzene	1.0
Bromodichloromethane	1.0
Bromomethane	1.0
Carbon tetrachloride	1.0
Chlorobenzene	1.0
Chloroethane	1.0
Chloromethane	1.0
cis-1,2-Dichloroethene	1.0
cis-1,3-Dichloropropene	1.0
Ethylbenzene	1.0
Xylenes (total)	1.0
Methylene chloride	1.0
Styrene	1.0
Tetrachloroethene	1.0
Toluene	1.0
trans-1,3-Dichloropropene	1.0
Trichloroethene	1.0
Chloroform	1.0
Vinyl chloride	1.0
Dibromochloromethane	1.0
1,1,-Dichloroethane	1.0
1,2-Dichloroethene (total)	1.0
1,1-Dichloroethene	1.0
1,2-Dichloroethane	1.0
1,2-Dichloropropane	1.0
1,1,1-Trichloroethane	1.0
1,1,2-Trichloroethane	1.0
1,1,2,2-Tetrachloroethane	1.0
Acetone	10
2-Butanone	10
2-Hexanone	10
4-Methyl-2-pentanone	10

TABLE 4.1 (Revised 11-95) (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	
TCL Base/Neutral-Extractable Organic Compounds	*Quantitation Limits Water (µg/L)*
Bis(2-Chloroethyl)ether	10
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
Bis(2-Chloroisopropyl)ether	10
N-Nitroso-Di-N-Propylamine	10
Hexachloroethane	10
Nitrobenzene	10
Isophorone	10
Bis(2-Chloroethoxy)methane	10
1,2,4-Trichlorobenzene	10
Naphthalene*	10
4-Chloroaniline	20
Hexachlorobutadiene	10
2-Methylnaphthalene*	10
Hexachlorocyclopentadiene	10
2-Chloronaphthalene	10
2-Nitroaniline	50
Dimethylphthalate	10
Acenapthylene	10
3-Nitroaniline	50
Acenaphthene	10
Dibenzofuran	10
2,4-Dinitrotoluene	10
2,6-Dinitrotoluene	10
Diethylphthalate	10
Carbazole	10

TABLE 4.1 (Revised 11-95) (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	
4-Chlorophenyl phenyl ether	10
Fluorene	10
4-Nitroaniline	10
N-Nitrosodiphenylamine	10
4-Bromophenyl phenyl ether	10
Hexachlorobenzene	10
Phenanthrene	10
Anthracene	10
Di-n-butylphthalate	10
Fluoranthene	10
Pyrene	10
Butyl benzyl phthalate	10
3,3-Dichlorobenzidine	20
Benzo(a)anthracene	10
bis(2-ethylhexyl)phthalate*	10
Chrysene	10
Di-n-octyl phthalate	10
Benzo(b)fluoranthene	10
Benzo(k)fluoranthene	10
Benzo(a)pyrene	10
Indeno(1,2,3-cd)pyrene	10
Dibenz(a,h)anthracene	10
Benzo(ghi)perylene	10

TABLE 4.1 (Revised 11-95) (CONT'D)

TARGETED QUANTITATION LIMITS
WAUSAU SUPERFUND SITE

PARAMETER	*Quantitation Limits* *Water (µg/L)*
TAL Inorganic Parameters	
Aluminum	16
Antimony	75
Arsenic	1.4
Barium*	1
Beryllium	0.2
Cadmium	2
Calcium	19
Chromium*	6
Cobalt	5
Copper	5
Iron*	3
Lead	2
Magnesium	41
Manganese*	2
Mercury	0.2
Nickel	10
Potassium	1200
Selenium	5
Silver	6
Sodium	42
Thallium	5
Vanadium	6
Zinc*	4
pH	**

Notes:

* - Site Target Compounds/Parameters
** - Not Applicable

TABLE 5.1 (Revised 11-95)

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WAUSAU SUPERFUND SITE

Analysis	*Containers*	*Preservation*	*Holding Time**	*Sample Volume***	*Shipping*	*Packaging*
A. Groundwater						
Site/ TCL VOC	Three 40 mL volatile organic analysis (VOA) vials	HCl to pH <2, Iced, 4°C	14 days to analysis	Fill completely, no air bubbles	Overnight Courier or Hand Deliver	Foam Liner or equivalent
Site/TCL BN	Two 1-L amber glass	Iced, 4°C	7 days to extraction; 40 days to analysis	Fill to neck of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
Site/TAL Metals	One 1-liter plastic bottle	HNO3 to pH < 2, Iced, 4°C	6 months to analysis (28 days-Mercury)	Fill to shoulder of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
pH	One 250-ml plastic bottle	Iced, 4°C	24 hours to analysis	Fill to shoulder of bottle	Overnight Courier or Hand Deliver	Bubble Pack or equivalent
B. Soil						
Site VOC	Two 4-ounce wide-mouth glass jars or brass tube	Iced, 4°C	14 days	Fill completely, no headspace	Overnight Courier or Hand Deliver	Bubble Pack or equivalent

TABLE 5.1 (Revised 11-95)

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
WAUSAU SUPERFUND SITE

Analysis	*Containers*	*Preservation*	*Holding Time**	*Sample Volume***	*Shipping*	*Packaging*
C. Soil Gas & Exhaust Gas						
Site VOC/TCL VOC	One 6-liter Summa Passivated Canister	NA	30 days	***	Overnight Courier or Hand Deliver	Bubble Pack or equivalent

Notes:
* Holding time periods are based from time of sample collection to completion of analysis.
** Extra volume (three times the standard volume) will be required for aqueous samples submitted for MS/MSD analysis.
*** For soil gas and exhaust gas samples submitted for VOC analyses, samples are collected by opening the canister valve for a specified period of time or by using a calibrated critical orifice as a sampling device.

TABLE 8.1 (Revised 11-95)
SUMMARY OF ANALYTICAL METHOD SOPS
WAUSAU SUPERFUND SITE

Matrix	*Method (SOP Number)*[1]	*Analysis*
Groundwater	SOP for SW 8260 (8260VOL.r1)	Site/TCL VOC
	SOP for SW 8270 (8270BNA.r1)	Site/TCL BN
	SOP for SW 6010/7000 Series	Site/TAL Metals
	SOP for SW 6010 &6020 (ARLICP.sop & MTLICP.sop)	Aluminum
		Antimony
		Barium
		Beryllium
		Cadmium
		Calcium
		Chromium
		Cobalt
		Copper
		Iron
		Lead
		Magnesium
		Manganese
		Nickel
		Potassium
		Silver
		Sodium
		Thallium
		Vanadium
		Zinc
	SOP for SW 7061 (MTLHYD.mth)	Arsenic
	SOP for SW 7741 (MTLHYD.mth)	Selenium
	SOP for SW 7471 (MTLHG.mth)	Mercury

---

1 Methods were derived from:

SW - "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, November 1986 and current revisions.

TO - "The Determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analyses", EPA Compendium Method TO-14, modified for point source determinations.

EPA - "Methods for Chemical Analysis of Water and Wastes", USEPA-600/4-79-020, revised March 1983.

TABLE 8.1 (Revised 11-95)
SUMMARY OF ANALYTICAL METHOD SOPS
WAUSAU SUPERFUND SITE

Matrix	*Method (SOP Number)*[1]	*Analysis*
Groundwater (Cont'd)	SOP for EPA 150.1 (WSPHWTRS.r11)	pH
	CRA Field SOP #1	pH
	CRA Field SOP #2	Conductivity
	CRA Field SOP #3	Temperature
	CRA Field SOP #7	HNu
	CRA Field SOP #8	Indicator Tube
Soil	SOP for SW 8260 (8260VOL.r1)	Site/TCL VOC
Soil Gas;	SOP for SW 8021 (ES 521)	Site VOC (on-Site)
Exhaust Gas	SOP for TO-14 (TO-14LL.sop)	TCL VOC (off-Site)

Note:
Field SOPs 4 through 6 were removed from this table since they are no longer included in the Scope of Work.

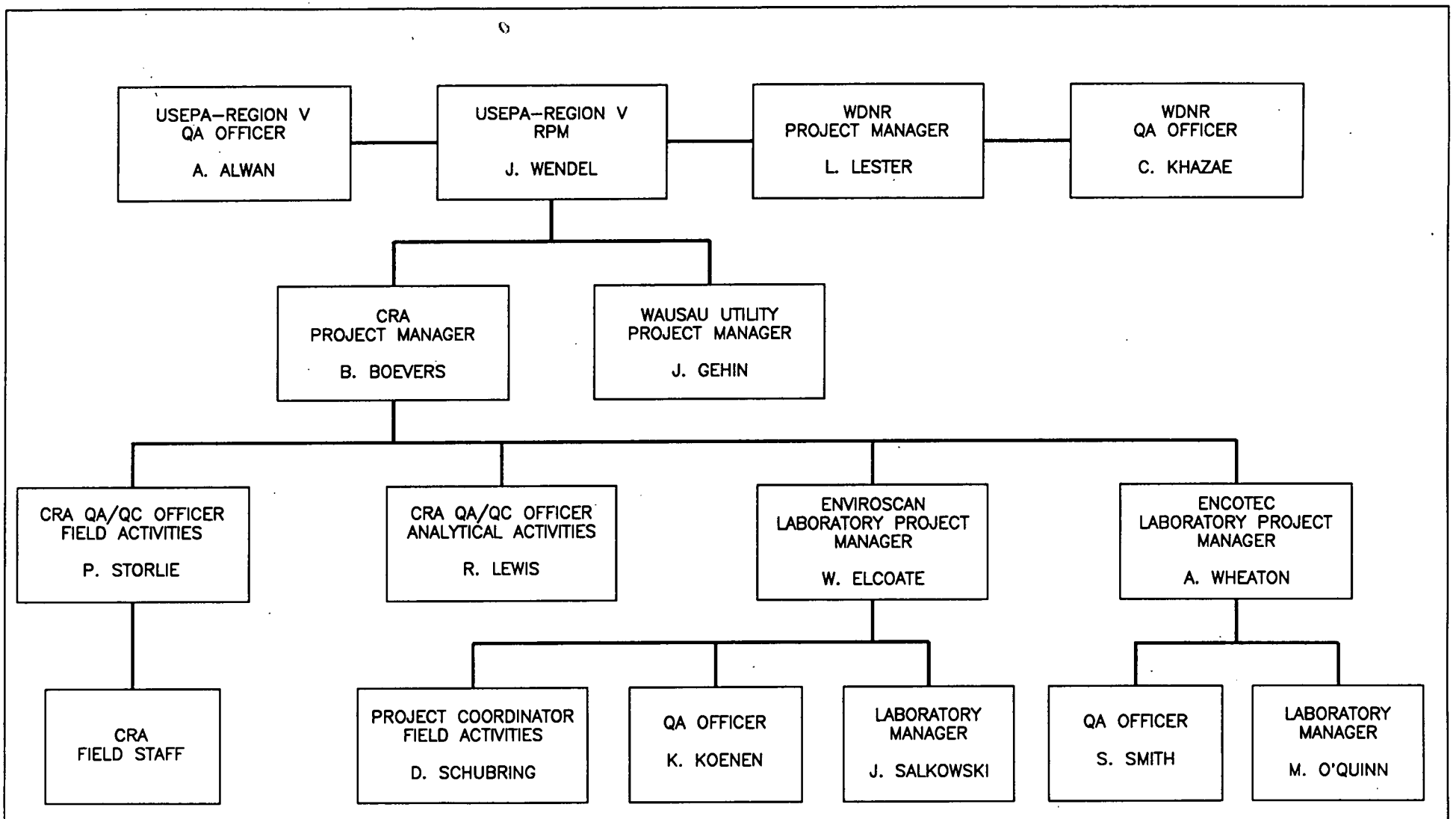

figure 3.1
PROJECT ORGANIZATION
Wausau Water Supply Site

CRA

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
WSPHWTRS.r11	Determination of pH
8260VOL.r1	Method for the determination of volatile organic compounds in liquid and solid matrices using purge and trap with analysis by gas chromatography/mass spectrometry
8270BNA.r1	Method for the determination of semivolatile organic compounds using gas chromatography/mass spectrometry
ES 521	On-Site VOC Analysis of Soil Gas Samples
ES 524	Soil Gas Sampling Procedure
SMPLCOC.sop	Sample Receiving (ENCOTEC)
TO14LL.SOP	Method for the determination of Volatile Organic Compounds in Ambient Air Using Summa Passivated Canisters and Analysis by Gas Chromatography/Ion Trap Mass
EXT&PREP.sop	General Requirements for Organic Extraction and Sample Preparation
CONLLEXT.SOP	Standard Operating Procedure for Continous Liquid-Liquid Extraction
SEPFUNEX.sop	Separatory Funnel Liquid-Liquid Extraction
EXCLN608.sop	Florisil Cleanup - Organochlorine Pesticides/PCB Analysis
8080PEST.sop	Method for the Determination or Organochlorine Pesticides and PCBs by Gas Chromatography/Electron Capture Detection

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
PCBID.sop	Standard Operating Procedure for Identification and Quantitation of
1AQDIG.mth	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by Flame-
1AQMS.mth	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by ICPMS
HYDPREP.mth	Preparation of Metals Digestates for Analysis by Hydride Atomic Absorption (HAS, HSE)
CVAQPREP.mth	Preparation of Aqueous Samples for Analysis for Mercury by Cold Vapor (HGP)
ARLICP.mth	Analysis of Total and Dissolved Metals by the ARL 3560 Simultaneous ICP
MTLICPMS.sop	Analysis of Total and Dissolved Metals by the Perkin-Elmer ELAN 5000 ICP/MS
MTLHYD.mth	Use of Hydride Generation in Analysis for Arsenic and/or Selenium (AS, SE)
MTLHG.mth	Analysis for Mercury by Cold Vapor (HG)
Field SOP No. 1	Procedures for Measuring pH
Field SOP No. 2	Procedures for Measuring Conductivity
Field SOP No. 3	Procedures for Measuring Temperature
Field SOP No. 4	Procedures for Measuring Dissolved Oxygen
Field SOP No. 5	Procedures for Measuring Turbidity

METHOD SOPs
WAUSAU WATER SUPPLY NPL SITE

SOP Number	*Subject/Title*
Field SOP No. 6	Procedures for Measuring Oxidation Reduction Potential (ORP)
Field SOP No. 7	Procedures for HNu Photoionization
Field SOP No. 8	Procedures for Colorimetric Indicator Tubes

PART 3

ENCOTEC RESPONSE TO COMMENTS

3978

ENCOTEC, INC.
AN ENVIRONMENTAL TECHNOLOGY COMPANY

3985 RESEARCH PARK DRIVE
ANN ARBOR, MICHIGAN 48108
PHONE 313 • 761 • 1389
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November 10, 1995

CRA received 11-10-95

Ms. Ruth Lewis
Conestoga-Rovers & Associates, Inc.
1801 Old Highway 8, Suite 114
St. Paul, Minnesota 55112

RE: Revised Standard Operating Procedures,
Requested MDLs, & Comment Responses
Analytical Laboratory Services
Wausau Superfund Site
Wausau, Wisconsin
Reference No. 3978

Dear Ruth:

Please find enclosed the requested documentation as listed above, which has been previously faxed to your attention. Also addressed herein are the responses to the concerns posed by the EPA with regards to ENCOTEC SOPs. These are as follows:

1) SOP for Continuous Liquid-Liquid Extraction SOP, CONLLEXT.sop

The question that has been posed is whether the specific BNA Organic Compounds noted with an * in QAPP Table 4.1 (revised 10/95) can be properly quantified without basic extraction. Those compounds from that table are:

Naphthalene
2-Methylnaphthalene
bis(2-ethylhexyl)phthalate

A Method Detection Limit Study performed in 1/95 using Liquid/Liquid Extraction, is attached. The study includes the three compounds noted above. In all three cases, the amount spiked is 5 ug/L (below the QAPP-specified quantitation limit), average recoveries are greater than 80 percent, and resultant MDLs are less than 2 ug/L. Examination of the remaining compounds in the study demonstrates that the CLP SOW procedure does not compromise the extraction efficiency of the B/N compounds.

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2) Method for the Determination of VOCs in Liquid and Solid Matrices using Purge and Trap with Analysis by GC/MS, 8260VOL.r1

a. The comment that the SOP is not adequate is improper. An MDL study which includes all of the volatile compounds, except cis-1,2-Dichloroethene, listed in Table 4.1 (revised 10/95) is attached. Note that the exclusion of the cis isomer in the tabulated summary was an oversight on the laboratory's behalf. Both the cis and trans isomers are contained as a 50/50 mixture in the certified stock standard. Consequently, the MDL for the cis isomer should be similar to that for the trans isomer which is listed. This will be rectified in future MDL studies. The amount spiked is 1 ug/L or at the quantitation limit (for most compounds) in Table 4.1. The purge volume was 5 ml. Average percent recoveries, excluding methylene chloride and acetone (two common laboratory solvents) are generally good to excellent. Consequently, it is ENCOTEC's opinion that the SOP is adequate insofar as purge volume and analyte sensitivity are concerned.

b. For the purpose of responding to these comments, ENCOTEC is using Table 4.1 (Revised 10-95) instead of that presented in the original QAPP dated February, 1994. The revised table does not include 1,1,2-Trifluoro-1,2,2-trichloroethane as a target analyte; consequently, comment concerning this compound no longer appears to be needed. ENCOTEC will revise its SOP, Table 1, to include cis-1,2-Dichloroethene.

c. ENCOTEC will revise its SOP to address calibration down to 1 ug/L.

d. Per comments provided in (2.a) above, purge volume does not need to be changed to 25 ml. ENCOTEC will however provide an option for the use of a 10 ml purge volume.

e. ENCOTEC will revise its SOP to include a methanol method blank.

f. ENCOTEC does not provide the actual MDL study as part of the SOP but makes reference to it. MDL studies are conducted on an annual basis. SOPs are not necessarily revised at the same frequency or at the same time as the MDL study. See MDL study provided in response to (2.a) above. ENCOTEC does not conduct a separate MDL study on soils for volatiles analysis since the use of blank inert soil has no utility for this analysis.

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3) Method for the Determination of SVOCs using GC/MS, 8270BNA.r1

a. ENCOTEC will revise Table 1 of the SOP to include carbazole.

b. ENCOTEC does not include retention time tables in its SOPs.

c. ENCOTEC will revise its SOP to include a 10 ug/L standard rather than 20 ug/L.

d. See comment to (2.f) above. An MDL study for SVOCs listed in Table 4.1 (revised 10/95) is attached (note bis-(2-chloroisopropyl)ether in Table 4.1 is listed as 2,2'-oxybis(1-chloropropane) in the MDL study. Carbazole is included in the study.

Following review of this information, please feel free to contact me with any further questions or concerns. Thank you for your patience while we addressed these issues. I look forward to working with you on this extended scope of work.

Sincerely,

ENCOTEC, Inc.

Amy D. Wheaton

Amy D. Wheaton
Client Services Manager

ADW/qos

#33019

WAUSAU.cra

PART 4

LAB SOPS AND METHOD DETECTION STUDIES - VOCs, SVOC PART A & B, AND pH

LAB SOP
VOC
METHOD 8260

METHOD FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN LIQUID AND SOLID MATRICES USING PURGE AND TRAP WITH ANALYSIS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for the analysis of volatile organic compounds (VOCs) in a variety of solid and liquid matrices and is based on Method 8260, SW-846, 3rd Edition.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquids, acid liquids, waste solvents, oily wastes, tars, fibrous waste, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 This method can be used to quantify most volatile compounds that have boiling points below 200° Celsius and that are insoluble or slightly insoluble in water.

1.4 Table 1 lists many of the compounds that may be determined by this method and provides the Practical Quantitation Limit (PQL) for aqueous and/or soil matrices.

TABLE 1
VOLATILE COMPOUNDS

COMPOUND[1)]	CAS NUMBER	PQL[2)] (ug/L or ug/Kg)
Acetone	67-64-1	10
Acetonitrile	75-05-8	100
Acrolein	107-02-8	100
Acrylonitrile	107-13-1	50
Benzene	71-43-2	5
Bromodichloromethane	75-27-4	5
Bromoform	75-25-2	5
Bromomethane	74-83-9	10
n-Butanol	71-36-3	500
2-Butanone	78-93-3	10
Carbon disulfide	75-15-0	5
Carbon tetrachloride	56-23-5	5
Chlorobenzene	108-90-7	5
2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	5
Chloroethane	75-00-3	10
2-Chloroethyl vinyl ether	110-75-8	10
Chloroform	67-66-3	5
Chloromethane	74-87-3	10
3-Chloropropene (Allyl chloride)	107-05-1	100
Cyclohexanone	108-94-1	10
Dibromochloromethane	124-48-1	5
1,2-Dibromo-3-chloropropane	96-12-8	5
1,2-Dibromoethane	106-93-4	5
Dibromomethane	74-95-3	5
1,2-Dichlorobenzene	95-50-1	5
1,3-Dichlorobenzene	541-73-1	5
1,4-Dichlorobenzene	106-46-7	5
trans-1,4-Dichloro-2-butene	110-57-6	5
Dichlorodifluoromethane	75-71-8	10
1,1-Dichloroethane	75-34-3	5
1,2-Dichloroethane	107-06-2	5
1,1-Dichloroethene	75-35-4	5
cis-1,2-Dichloroethene	156-59-2	5

1) Appendix IX Regulatory List for Volatile Compounds
2) PQL = Practical Quantitation Limit (A lower PQL can be achieved through manipulation of purge volumns and/or calibration standards' concentrations.)

TABLE 1 (con't.)

COMPOUND[1]	CAS #	PQL[2] (ug/L or ug/Kg)
trans-1,2-Dichlorothene	156-60-5	5
1,2-Dichloropropane	78-87-5	5
cis-1,3-Dichloropropene	10061-01-5	5
trans-1,3-Dichloropropene	10061-02-6	5
1,4-Dioxane	123-91-1	300
Ethyl acetate	141-78-6	100
Ethylbenzene	100-41-4	5
Ethyl ether	60-29-7	50
Ethyl methacrylate	97-63-2	50
Ethylene oxide	75-21-8	20
2-Hexanone	591-78-6	10
Iodomethane	74-88-4	5
Isobutanol	78-83-1	100
Methacrylonitrile	126-98-7	5
Methylene chloride	75-09-2	5
Methyl methacrylate	80-62-6	5
4-Methyl-2-pentanone	108-10-1	10
Propionitrile	107-12-0	100
Pyridine	110-86-1	500
Styrene	100-42-5	5
1,1,1,2-Tetrachloroethane	630-20-6	5
1,1,2,2-Tetrachloroethane	79-34-5	5
Tetrachloroethene	127-18-4	5
Toluene	108-88-3	5
Trichlorofluoromethane	75-69-4	5
1,1,1-Trichloroethane	71-55-6	5
1,1,2-Trichloroethane	79-00-5	5
Trichloroethene	79-01-6	5
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	5
1,2,3-Trichloropropane	96-18-4	5
Vinyl acetate	108-05-4	5
Vinyl chloride	75-01-4	10
<u>total</u>-Xylenes	1330-20-7	5

1) Appendix IX Regulatory List for Volatile Compounds
2) PQL = Practical Quantitation Limit (A lower PQL can be achieved through manipulation of purge volumns and/or calibration standards' concentrations.)

2.0 SUMMARY OF METHOD

2.1 An inert gas is bubbled through an aliquot of sample to transfer the volatile components to a vapor phase. The vapor is passed through a sorbent to capture the volatile components. When purging is completed, the sorbent is

rapidly heated and the inert gas is backflushed through it to shift the volatile components back to the vapor phase.

2.2 The purging procedure varies according to the matrix being purged.

2.2.1 Aqueous matrix: An inert gas is bubbled through a 5mL or 10mL sample at ambient temperature or under heated conditions. After purging is complete, the sorbent is rapidly heated and backflushed with the inert gas to desorb the components onto the wide bore capillary or focused on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature-programmed to separate the components which are then detected with a mass spectrometer.

2.2.2 Low concentration soil/solid matrix: An inert gas is bubbled through a mixture of reagent water and 5 or 10 g of sample contained in a specifically designed purging chamber. The volatile components are transferred from the aqueous phase to the vapor phase. The vapor is then trapped on a sorbent. After purging is complete the sorbent is rapidly heated and backflushed with the inert gas to desorb the components onto the wide bore capillary or focused on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis. The column is temperature programmed to separate the components which are then detected with a mass spectrometer.

2.2.3 Medium concentration soil/solid matrix: A measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to 5 mL with reagent water. An inert gas is bubbled through this solution under heated conditions.

2.3 The gas and components are then either introduced directly into a wide bore capillary column for component separation or passed through a precolumn for introduction into a narrow bore capillary column for component separation.

2.4 The capillary column (wide or narrow bore) is temperature programmed to separate the volatile components, which are then detected by a mass spectrometer.

No significant modifications relative to the referenced methods are noted for the preceding section.

3.0 SAFETY PRECAUTIONS

3.1 All general laboratory safety precauations apply. Safety glasses, gloves, and a lab coat should be worn when handling solvent, samples, and standards. Safety glasses must always be worn in the laboratory. The Material Safety Data Sheets (MSDS) should be consulted for toxicity information.

4.0 INTERFERENCES

4.1 Interferences may be caused by contaminants in purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contaminants under the conditions of analysis by running method blanks.

4.2 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This can also lead to cross-contamination whenever high-concentration and low-concentration samples are analyzed sequentially.

4.2.1 Rinsing the purging device and sampling syringe with reagent water between sample analyses will reduce carryover.

4.2.2 When a sample of unusually high concentration is analyzed, it will be followed by the analysis of reagent water to check for cross-contamination.

4.2.3 The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration sample has been analyzed.

4.3 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during storage and handling. A trip blank, prepared from reagent water and carried through the sampling and handling protocol, can serve as a check on such contaminants.

5.0 APPARATUS AND MATERIALS

DO NOT C...

Standard Preparation

5.1 Microsyringes: 10uL, 25uL, 100uL, 250uL, 500uL, and 1,000uL.

5.2 Syringes: 10mL and 5mL, gas-tight with shut-off valve.

5.3 Balances: Analytical balance, capable of accurately weighing ± 0.0001 g; top-loading balance capable of weighing ± 0.1 g.

5.4 Glassware: Class A volumetric flasks, 10mL, 50mL, and 100mL, with ground glass stoppers.

Sample Analysis

5.5 Purge-and-trap device: The purge-and-trap system is composed of the following pieces of equipment: the sample purge chamber, the trap, and the desorbing unit.

5.5.1 The sample purge chamber must be able to accept at least 5 mL of sample and provide a water column at least 3 cm deep with a purge gas delivery system no more than 5 mm from the base of the water column and capable of generating bubbles of diameter no greater than 3 mm at origin.

5.5.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.11 inches.

5.5.3 The desorbing unit should be capable of rapidly heating the trap to at least 180°C.

5.5.3.1 The packing material in the desorbing unit is altered to suit the particular application; the trap used is a VOACARB 3000 (Supelco) or equivalent.

5.5.3.2 The trap is conditioned by backflushing with an inert gas for at least one hour at 180°C to 250°C.

5.5.3.3 Condition the trap before daily use by backflushing for at least 10 minutes at 180°C to 250°C.

5.6 Gas Chromatograph: An analytical system which is capable of temperature programming and which is equipped with a flow controller capable of maintaining a constant flow rate during desorption and component separation operations.

5.6.1 All GC carrier gas lines are constructed of stainless steel or copper tubing.

5.6.2 GC column: 75 m X 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), 3 um film thickness, or equivalent.

5.7 GC/MS Interface: Capable of providing acceptable calibration points at 50 ng or less per injection for each compound of interest.

5.8 Mass Spectrometer: Capable of scanning through at least 35-300 amu each second, using 70 volts electron energy in the electron ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 50 ng of *p*-bromofluorobenzene (BFB).

5.9 Data System: An interfaced data system which will acquire, store, reduce, and output mass spectral data.

5.9.1 The computer software will allow searching any GC/MS data file for ions of specific mass and plotting ion abundance versus time or scan number.

No significant modifications relative to the referenced methods are noted for the preceding section.

6.0 REAGENTS

6.1 Reagent water: Prepare as follows:

6.1.1 Pass deionized water through a charcoal filter to remove organic impurities.

6.1.2 Boil the filtered water for approximately one hour to remove any additional impurities.

6.1.3 Purge the boiled water by bubbling ultra-high purity nitrogen at 5-10 psi through it for approximately one hour.

6.1.3.1 A fritted sparger at the end of the purge line greatly increases the purge efficiency by allowing for the evolution of fine bubbles, thus increasing the effective bubble surface area.

6.1.4 Seal the purged water; add it to the apparatus setup before it reaches room temperature.

6.2 Methanol: pesticide quality or equivalent, commercially available.

6.3 Internal standard: Bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Internal standards can be purchased as certified solutions or prepared from pure standard materials. If purchased, skip to step 6.3.2.

6.3.1 Dissolve 250 mg of each compound in methanol in a 50mL Class A volumetric flask and bring to volume with more methanol. The resulting concentration of each compound in this solution is 5000 mg/L.

6.3.2 Dilute the solution further in methanol (again using Class A volumetric flasks) to give a working internal standard solution with a concentration of 50 mg/L.

6.3.3 Add 5 uL of this solution to 5.0 mL of sample, QC sample, or calibration standard for a concentration of 50 ug/L internal standard in the analyzed samples and standards.

6.3.4 Prepare the working internal standard solution fresh weekly.

6.4 Stock standard solution: Stock standard solutions can be purchased as certified solutions or are prepared from pure standard materials as follows:

6.4.1 Place about 9.8 mL of methanol in a 10mL ground glass-stoppered Class A volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes, or until the alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.4.2 If the compound to be added is liquid at room temperature, use a 100uL syringe to add two or more drops of assayed reference material, making sure that all drops fall directly into the methanol. Reweigh the flask immediately.

6.4.3 If the compound is a gas at room temperature, fill a 5mL valved gas-tight syringe with the reference standard to the 5 mL mark. Lower the needle of the syringe to 5 mm above the methanol meniscus and slowly introduce the reference standard above the surface of the methanol. (The gas will rapidly dissolve into the methanol.) Reweigh the flask immediately.

6.4.4 Dilute the mixture to volume using methanol, stopper the flask, then mix by inverting it three times.

6.4.5 Calculate the concentration of liquid standards in ug/uL from the net gain in weight. Calculate the concentration of gaseous standards in ug/uL using the Ideal Gas Law, taking in account the temperature and pressure conditions in the laboratory.

6.4.6 After the stock standard solution has been confirmed by analysis to be within 90%-110% of the theoretical value for that EPA reference standard, transfer the stock standard solution to a teflon-sealed screw cap bottle, with minimal headspace, and store at -10°C to -20°C.

6.4.7 Prepare gas standards fresh every two months or more frequently if recoveries for QC samples warrant it; prepare all other standards every six months or more frequently if recoveries for QC samples warrant it.

6.5 Secondary standard solution: Dilute the stock standard solution in methanol in Class A volumetric flasks to give a concentration of (nominal) 100 mg/L for all compounds of interest. Prepare this solution weekly.

6.6 Calibration standards: Prepare calibration standards on a daily basis in reagent water in Class A volumetric flasks from the secondary standard solution at five concentration levels, nominally 10, 50, 100, 150, and 200 ug/L. The standards should calibrate for all the analytes of interest.

6.6.1 When analysis for compounds listed in Appendix IX, Land Disposal Restrictions, or other applications is required, prepare additional calibration standards, as appropriate, at five concentration levels.

6.6.2 Prepare the additional standards so that the standard of highest concentraton will define the linear range of the instrument and the standard of lowest concentraton will be at or near the PQL.

6.6.3 When regulatory requirements mandate it, prepare five standards containing the analytes of interest at the following concentration levels: 1, 2, 5, 15, and 25 ug/L. These will be used in calibration for low level analyses.

6.7 Surrogate standard solution: The surrogate compounds are

- toluene-d_8,
- *p*-bromofluorobenzene,

and

- 1,2-dichloroethane-d_4.

6.7.1 Purchase a certified solution or prepare a stock surrogate solution using the procedure described for the internal standard solution (Section 6.4) on a weekly basis.

6.7.2 Dilute the stock surrogate standard solution to a concentration of 50 mg/L. Add 5 uL of this working surrogate solution to 5.0 mL of sample, QC sample, or calibration standard to give a concentration of 50 ug/L of surrogate in the analyzed sample.

6.7.3 When regulatory requirements mandate low level analysis, add 1 uL of the working surrogate solution to 10 mL of sample, QC sample, or calibration standard, so that surrogate concentration in the analyzed material will be 5 ug/L.

6.8 Instrument performance check solution: Prepare a solution of *p*-bromofluorobenzene (BFB) (using reagent water as diluent for the injected solution) such that 50 ng of BFB is injected and purged onto the column.

6.9 Matrix spike standard: The matrix spike standard solution contains

- benzene,
- chlorobenzene,
- 1,1-dichloroethene,
- toluene,

and

- trichloroethene.

6.9.1 Prepare the solution in methanol to give a concentration of 50 mg/L. Add 5 uL of this solution to 5.0 mL sample to give a concentration of 50 ug/L for each compound.

6.9.2 When regulatory requirements mandate low level analyses, add 1 uL of the spiking solution to 10 mL of sample to give a concentration of 5 ug/L for each compound.

6.9.3 Prepare the matrix spike standard solution fresh weekly.

No significant modifications relative to the referenced methods are noted for the preceding section.

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Samples are stored at ≤4°C in an environment free of the volatile compounds of interest. Several common laboratory solvents such as methylene chloride and acetone are difficult to completely eliminate and appropriate precautions should be taken to minimize their potential impact. Samples are to be completely analyzed within 14 days of the date of sample collection.

No significant modifications relative to the referenced methods are noted for the preceding section.

8.0 PROCEDURE

Instrument conditions

8.1 Purge and trap device:

8.1.1 Purge conditions:

Purge gas:	nitrogen.
Purge time:	11 minutes.
Purge flow rate:	25-40 mL/min.
Purge temperature:	ambient to 40°C.

8.1.2 Desorb conditions:

Desorb time:	4 minutes.
Desorb flow rate:	15 mL/min.
Desorb temperature:	180°C to 250°C.

8.1.3 Trap reconditioning conditions:

Reconditioning time:	at least 7 minutes.
Reconditioning temperature:	180°C to 250°C.

8.2 Gas chromatograph: Temperature programs may vary from instrument to instrument. The following is a typical set of ramp instructions.

Initial column temperature:	45°C for 3 minutes.
Temperature program:	45-195°C at 8°C/min.
Final temperature:	195°C for 12 minutes.
Transfer line temperature:	180oC to 240°C.
Carrier gas:	Helium at 5 to 15 mL/min.
Make-up gas:	Helium at 15 to 30 ml/min.
Chromatographic column:	capillary column (see section 4.6.2 for specifics)

8.3 Mass spectrometer:

Electron energy:	70 volts.
Mass range:	35-300 amu.
Scan time:	to give at least 5 scans per peak, not to exceed 1 sec/scan.

Calibration

8.4 Inject and analyze 50 ng of the instrument performance check solution, *p*-bromofluorobenzene (BFB), once at the beginning of each analytical period during which standards and samples are analyzed.

8.5 Check that the ion abundance criteria given in Table 2, below, are met before analyzing standards, blanks or samples.

TABLE 2
BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criterion
50	15.0% - 40.0% of mass 95
75	30.0% - 60.0% of mass 95
95	**Base peak**, 100% relative abundance
96	5.0% - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	Greater than 50.0% of mass 95
175	5.0% - 9.0% of mass 174
176	Greater than 95.0% but less than 101.0% of mass 174
177	5.0% - 9.0% of mass 176

8.6 After the instrument performance check solution criteria have been met, determine whether analysis will be low level and calibrate the GC/MS system with five concentrations of each compound of interest.

8.7 Make certain all standards contain internal standards and surrogates (see sections 5.3 and 5.7, above). The quantitation ions for the internal standards are as follows:

INTERNAL STANDARD	QUANTITATION ION
Bromochloromethane	128
1,4-Difluorobenzene	114
Chlorobenzene-d_5	117

NOTE: If bromochloromethane is an analyte of interest, substitute

INTERNAL STANDARD	QUANTITATION ION
Methylene chloride-d_2	51

8.8 Table 3, below, presents the compounds of interest assigned to the internal standards. Use these references in quantifying sample response.

TABLE 3
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION

Bromochloromethane[1]	1,4-Difluorobenzene	Chlorobenzene-d_5
Acetone	Benzene	Chlorobenzene
Acetonitrile	Bromodichloromethane	1,2-Dibromoethane
Acrolein	Bromoform	2-Chloro-1,3-butadiene
Acrylonitrile	2-Butanone	1,2-Dibromo-3-chloropropane
Bromomethane	Carbon tetrachloride	*trans*-1,4-Dichloro-2-butene
Carbon disulfide	2-Chloroethyl vinyl ether	Ethylbenzene
Chloroethane	Dibromochloromethane	2-Hexanone
Chloroform	1,2-Dichloropropane	4-Methyl-2-pentanone
Chloromethane	*cis*-1,3-Dichloropropene	Styrene
1,2-Dichloroethane	*trans*-1,3-Dichloropropene	1,1,1,2-Tetrachloroethane
3-Chloropropene (Allyl chloride)	1,4-Dioxane	1,1,2,2-Tetrachloroethane
Dibromomethane	Ethyl methacrylate	Tetrachloroethene
Dichlorodifluoromethane	Methyl methacrylate	Toluene
1,1-Dichloroethane	Pyridine	1,1,2-Trichloroethane
1,1-Dichloroethene	1,1,1-Trichloroethane	1,2,3-Trichloropropane
cis-1,2-Dichloroethene	Trichloroethene	**total**-Xylenes
trans-1,2-Dichloroethene	Vinyl acetate	Cyclohexanone
Iodomethane	*n*-Butanol	
Isobutyl alcohol	Ethyl acetate	
Methacrylonitrile		
Methylene chloride		
Propionitrile		
Trichlorofluoromethane		
Vinyl chloride		
Ethyl ether		
Ethylene oxide		
Isobutanol		
1,1,2-Trichloro-1,2,2-trifluoroethane		

[1] When methylene chloride-d_2 has been substituted for bromochloromethane, these compounds are assigned to the substitute.

8.9 Tabulate the area response for each calibration standard (as indicated in Table 4, below) against the standard's theoretical concentration for each compound. Calculate the response factors (RFs) for each compound as follows:

$$RF = \frac{A_x \times C_{is}}{A_{is} \times C_x}$$

where

A_x = Area of the characteristic ion for the compound to be measured (from Table 4).

A_{is} = Area of the characteristic ion for the specific internal standard (from Table 4).

C_{is} = Concentration of the internal standard, in ug/L.

C_x = Concentration of the compound to be measured, in ug/L.

TABLE 4

CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS AND SURROGATES

Parameter	Primary Ion	Parameter	Primary Ion
Acetone	43	*cis*-1,3-Dichloro-propene	75
Acetonitrile	41	*trans*-1,3-Dichloro propene	75
Acrolein	56	1,4-Dioxane	88
Acrylonitrile	52	Ethyl acetate	43
Benzene	78	Ethylbenzene (CCC)	106
Bromodichloromethane	83	Ethyl ether	59
Bromoform (SPCC)	173	Ethyl methacrylate	69
Bromomethane	94	Ethylene oxide	44
n-Butanol	74	2-Hexanone	43
2-Butanone	72	Iodomethane	142
Carbon disulfide	76	Isobutyl alcohol	43
Carbon tetrachloride	117	Methacrylonitrile	67
Chlorobenzene (SPCC)	112	Methylene chloride	84
2-Chloro-1,3-butadiene	88	Methyl methacrylate	69
Chloroethane	64	4-Methyl-2-pentanone	43
2-Chloroethyl vinyl ether	63	Propionitrile	54
Chloroform (CCC)	83	Pyridine	79
Chloromethane (SPCC)	50	Styrene	104
3-Chloropropene (Allyl Chloride)	76	1,1,1,2-Tetra-chloroethane	131
Cyclohexanone	98	1,1,2,2-Tetra-chloroethane (SPCC)	83
Dibromochloromethane	129	Tetrachloro-ethene	164
1,2-Dibromo-3-chloropropane	157	Toluene (CCC)	92
1,2-Dibromoethane	107	Trichlorofluoro-methane	101
Dibromomethane	93	1,1,1-Trichloro-ethane	97
trans-1,4-Dichloro-2-butene	88	1,1,2-Trichloro-ethane	97
Dichlorodifluoro-methane	85	Trichloroethene	130
1,1-Dichloroethane (SPCC)	63	1,1,2-Trichloro-1,2,2-trifluoroethane	151
1,2-Dicloroethane	62	1,2,3-Trichloro-propane	110
1,1-Dichloro-ethene (CCC)	96	Vinyl acetate	43
cis-1,2-Dichloro-ethene	96	Vinyl chloride (CCC)	62
trans-1,2-Dichloro-ethene	96	total-Xylenes	106
1,2-Dichloro-propane (CCC)	63		

8.10 The average response factor ($\overline{RF}$) is calculated for all TCL compounds from the five different levels at which the standards were run. The percent relative standard deviation (%RSD = 100% * [sd/$\overline{RF}$]) is calculated for each compound.

8.11 Evaluate the %RSD for each of the following calibration check compounds (CCCs); do not proceed with analysis unless the %RSD is $\leq$ 30%.

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

8.12 If the %RSD for the CCC analysis is satisfactory, analyze a system performance check solution (SPCC) composed of the following compounds.

- Bromoform
- Chlorobenzene
- Chloromethane
- 1,1-Dichloroethane
- 1,1,2,2-Tetrachloroethane

The minimum acceptable RF for bromoform is 0.250; the minimum acceptable RF for the other compounds is 0.300.

8.13 If time remains in the 12 hour period after meeting acceptance criteria for the initial calibration, begin sample analysis. If there is no time remaining, analyze an instrument performance check solution (see 8.4 and 8.5, above). If the BFB meets the ion abundance criteria, analyze a continuing calibration standard (CCV).

8.13.1 Samples may not be analyzed after the expiration of the 12 hour period following a BFB injection.

8.14 Calculate the response factors for the continuing calibration and the percent differences of the response factors from the mean response factors in the initial calibration.

8.14.1 Percent difference is defined as follows:

$$\%D = \frac{RF - \overline{RF}}{(RF + \overline{RF})/2}$$

where

RF = the response factor for the continuing calibration compound under review.

$\overline{RF}$ = the mean response factor for that compound in the initial calibration.

8.14.2 The percent difference for each CCC (see 8.11, above) must be $\leq$ 25.0%. The minimum acceptable response factor (RF) for bromoform (see 8.12, above) is 0.250; the minimum RF for the other SPCCs is 0.300.

8.14.3 In addition, if the retention time for any internal standard in the calibration check analysis differs by more than 30 sec from that observed at either the initial calibration or the most recent continuing calibration, inspect and repair the system and reanalyze those samples analyzed since the last accurate CCV.

8.14.4 Similarly, if the EICP area for an internal standard varies more than 50% - 150% of the initial observed value, inspect and repair the system and reanalyze all samples that had been analyzed while the EICP was out of control.

8.14.5 Determine relative retention times for the standards as follows:

$$RRT = \frac{RT_c}{RT_i}$$

where

RT_c = Retention time for compound.

RT_i = Retention time for assigned internal standard.

Sample Analysis

8.15 Begin sample analysis only after the GC/MS system has met the instrument performance check and the initial or continuing calibration criteria.

8.16 Aqueous Matrix

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

8.16.2 Check to make certain the purge flow is adjusted to between 25-40 mL/min. (This should have been performed before any standards were analyzed. Once the purge flow is set do not readjust it for the rest of the analytical sequence.

8.16.3 Carefully pour sample into the 5mL syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample to 5 mL volume.

8.16.3.1 When performing low level analyses, use 10 mL of sample in a 10mL syringe.

8.16.4 Fortify each sample with the correct amounts of both the surrogate solution and the internal standard solution as you are loading the trap with the sample.

8.16.4.1 The addition of 5 uL of surrogate solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

8.16.4.2 When performing low level analyses, add 1 uL of surrogate to 10 mL of sample, for a concentration of 5 ug/L of surrogate standard.

8.16.4.3 The surrogate and internal standard solutions can be mixed and added as a single solution.

8.16.5 Proceed with the analysis of the sample as outlined in sections 8.19 through 8.22.

8.16.6 If the initial analysis of a sample or analysis of a diluted sample has analyte concentrations exceeding the initial calibration range, reanalyze the sample at a greater dilution.

8.16.7 For matrix spike and matrix spike duplicate analysis, add the proper amount of the matrix spike solution to the aqueous sample.

8.16.7.1 Adding 5 uL of spike solution to 5 mL of aqueous sample is equivalent to a concentration of 50 ug/L of each matrix spike compound.

8.16.7.2 Adding 1 uL of spike solution to 10 mL of aqueous sample is equivalent to a concentration of 5 ug/L of the matrix spike compounds.

8.17 Low concentration soil

8.17.1 Remove the plunger from the 5 mL syringe and fill the syringe until overflowing with reagent water. Adjust the syringe volume to 5 mL and add 5 uL of the surrogate solution and 5 uL of the internal standard solution.

8.17.2 Weigh out 5.0 g of soil sample in the purging vessel. Add the treated reagent water to the sample.

8.17.2.1 The surrogate and internal standard concentrations in the sample will be 50 ug/Kg.

8.17.3 For low level analyses weigh out 10 g of sample in the purging vessel and add a combination of 10mL of reagent water and 1uL each of surrogate and internal standard solutions.

8.17.3.1 The surrogate and internal standard concentrations in the sample will be 5 ug/Kg.

8.17.4 Load the sample on the purge-and-trap device as rapidly as possible to avoid any losses of volatile compounds and heat to 40°C. All initial and continuing calibrations will also be heated to 40°C.

8.17.5 Proceed with the analysis of the sample as outlined in sections 8.19 through 8.22.

8.17.6 When saturation occurs, repeat analysis with a smaller weight of sample; if saturation occurs when the sample weight is 0.5 g, follow analysis procedure for medium concentration soils (see 8.18, below).

8.17.7 For matrix spikes add the proper amount of the matrix spiking solution to the reagent water.

8.17.7.1 Adding 5 uL of spike solution to 5 mL of reagent water gives a concentration for a 5 g sample of 50 ug/Kg of each matrix spike compound.

8.17.7.2 Adding 1 uL of spike solution to 10 mL of reagent water gives a concentration for a 5 g sample of 1 ug/Kg of each spike compound.

8.18 Medium concentration soils

8.18.1 Weigh out 4.0 g of the sample in a tared 20mL vial using a top-loading balance. Add 9.0 mL of methanol and 1.0 mL of the surrogate solution to the vial. Cap and shake for 2 minutes.

8.18.2 Add 100 uL of this extract to 4.9 mL of reagent water, along with 5 uL of the internal standard solution. (The addition of a 100 uL aliquot of the extract is the equivalent to 6,200 ug/Kg of each surrogate standard.)

8.18.3 Load the extract/reagent water mixture into the trap as if it were an aqueous sample (section 8.16, above). Proceed with analysis as outlined in sections 8.19 through 8.22.

8.18.4 For matrix spikes add 8.0 mL of methanol, 1.0 mL of surrogate solution and 1.0 mL of matrix spike solution to the sample in the 20mL vial. This results in a 6,200 ug/Kg concentration of each matrix spike compound when added to a 4.0 g sample. Add a 100 uL aliquot of this extract to 4.9 mL of reagent water and 5 uL of the internal standard solution.

8.19 Inject the fortified aqueous sample or reagent water into the purge chamber and purge the sample for 11 minutes.

8.19.1 At the conclusion of the purge time, the purge-and-trap unit is set in the desorb mode. (This step in most cases is automated).

8.20 At the beginning of the desorb period the GC/MS is automatically triggered to scan the eluting carrier gas over the range from 35 to 300 amu.

8.21 After desorbing the sample for 4 minutes at 180°C, the trap is reconditioned by stepping the purge-and-trap unit to the bake mode.

8.21.1 The trap should remain in this mode for at least 7 minutes at a temperature of 180°C to 250°. (The advancement from desorb to bake in most cases is automated.)

8.21.2 After the bake time is complete, turn off the trap heater and allow it to cool to ambient temperature. When cool, the trap is ready for the next sample.

8.22 Tentative identification of a compound of interest in a sample is based upon retention time and relative abundance of eluting ions as compared to the spectral libraries stored on the GC/MS computer.

8.23 The compounds listed in this method must be identified by the analyst through the comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Verify the identification by satisfying the following two criteria.

8.23.1 <u>The elution of the sample component at the GC relative retention time of the standard component</u>: In order to establish the relative retention time (RRT), the sample component RRT (calculated as in 8.14.5, above) must compare within ± 0.06 RRT units of the RRT of the midlevel standard component. For reference, the standard must be analyzed on the same shift as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, assign the RRT by using extracted ion current profiles (EICP) for ions unique to the component of interest.

8.23.2 <u>Correspondence of the sample component and standard component mass spectra</u>: The relative intensities of the characteristic ions of the sample component must agree within 20% with the relative intensities of those of the standard component. The analyst making the comparison must consider and account for those ions accounting for more than 10% of the sample spectra but not present in the standard spectra for the same component.

8.23.3 If a compound cannot be verified by these criteria, but, in the technical judgement of the mass spectral interpretation specialist, the identification is correct, report and quantify the compound.

No significant modifications relative to the referenced methods are noted for the preceding section.

9.0 MAINTENANCE PROCEDURES

9.1 Purge-and-trap unit: Condition the trap before initial use for at least one hour at a temperature of 180°C to 250°C. Condition the trap every day prior to sample analysis for at least 10 minutes at a temperature of 180°C to 250°C.

9.1.1 Clean the purging vessels of the purge-and-trap unit prior to sample analysis and after each sample analysis. This will help avoid cross-contamination from sample to sample.

9.1.2 The purge-and-trap unit may also have to be cleaned or all temperatures of the unit elevated to help reduce active sites which may inhibit the response of some compounds.

9.2 Gas chromatograph: Many compounds will show a decrease in response when the chromatographic system starts to deteriorate. The area that will usually deteriorate first is the first few inches of the capillary column. The most common maintenance performed on the column is the removal of these first few inches of the column or the replacement of the entire column. This will, in most cases, help those compounds that are sensitive to poor chromatographic conditions.

9.3 Mass spectrometer: Clean the mass spectrometer source when the instrument performance check solution (BFB) does not meet acceptable ion abundance criteria.

10.0 CALCULATIONS

10.1 The quantitation of an identified compound is based on the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion (Table 4). Use the internal standard technique for quantitation; the internal standard assignments are found in Table 3. The concentration of each identified analyte is calculated as follows.

Water:

$$ug/L = \frac{A_x \times I_s}{A_{is} \times RF \times V_o}$$

where

A_x = area of the characteristic ion for the compound measured.

I_s = amount of internal standard present in ng.

A_{is} = area of the characteristic ion for the internal standard.

RF = response factor for the analyte being measured.

V_o = Volume of water purged, in mL, taking into account any dilutions made.

Low concentration soil:

$$ug/Kg = \frac{A_x \times I_s}{A_{is} \times RF \times W_s}$$

where

A_x, I_s, A_{is} and RF are the same as for water.

W_s = Weight of sample added to purge vessel, in g.

Medium concentration soil:

$$ug/Kg = \frac{A_x \times I_s \times V_t \times 1000\ uL/mL}{A_{is} \times RF \times V_a \times W_s}$$

where

A_x, I_s, A_{is} and RF are given for water

V_t = Total volume of the methanol extract, in mL.

V_a = Volume of the aliquot of the methanol extract added to reagent water for purging, in uL.

W_s = weight of soil extracted, in g.

11.0 QUALITY CONTROL

11.1 Check that the GC/MS system is tuned to the criteria specified for BFB in Section 8.5 prior to analyzing any samples. All instrument conditions must be identical to those used during sample analysis.

11.2 Follow instrument calibration with an initial calibration verification (ICV). Do not attempt sample analysis unless the recoveries for the ICV compounds satisfy the criteria specified in Sections 8.11, 8.12, and 8.14.

11.3 Every 12 hours during an analytical run, reanalyze the calibration verification compounds. Do not continue with sample analysis unless calibration verification compound recoveries satisfy the criteria specified in Sections 8.11, 8.12, and 8.14.

11.4 Method Blank (MB): Analyze a reagent blank in order to demonstrate that the analytical system does not contribute to the presence of target compounds (i.e., those listed in Table 1, above) at or above the Practical Quantitation Limit (PQL). When medium concentration soil analyses are included in the analytical set, also analyze a blank composed of 4.9 mL reagent water and 100 uL methanol.

11.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD): Prepare and analyze a matrix spike and a matrix spike duplicate on the same sample for each group of samples analyzed or for every 20 samples, whichever is more frequent. Calculate and report percent recoveries and relative percent differences (RPDs). If QC criteria are not achieved, take corrective action, as described in **Standard Operating Procedure for Corrective Action - Blanks, Laboratory Control Samples, Surrogates, Matrix Spikes and Duplicates.**

11.6 Laboratory Control Sample (LCS): Once for every 20 samples or once for the analytical run (whichever occurs more frequently), analyze an aliquot of reagent water which has been treated as if it were a Matrix Spike. Calculate and report the percent recoveries for the compounds added. If these are not within QC criteria, take corrective action as described in **Standard Operating Procedure for Corrective Action - Blanks, Laboratory Control Samples, Surrogates, Matrix Spikes, and Duplicates.**

11.6.1 Occasionally a client requests that the LCS should be analyzed in two replicates, each spiked at the same level. In that case, label the second replicate Laboratory Control Sample Duplicate (LCD), and calculate and report the relative percent difference between the two replicates as well as the percent recoveries for each.

12.0 METHOD PERFORMANCE

The laboratory's method detection limits and precision and accuracy evaluation for this method are on file. The method detection limits were established by spiking known concentrations of the analytes into laboratory reagent water and analyzing the resulting solution according to the procedures specified for sample analysis. See, also, **Standard Operating Procedure for the Determination of the Method Detection Limit and/or Instrument Detection Limit.**

13.0 REFERENCES

13.1 Test Methods for Evaluation of Solid Waste, SW-846, Method 8260, Rev. 0, July, 1992.

14.0 PROVENANCE

This method was written by

Chemistry Laboratory Manager 11 / 06 / 95

Technical Documentation Officer 11 / 06 / 95

It has been reviewed and accepted by

Technical Documentation Officer 11 / 06 / 95

GC/MS Group Leader 11 / 06 / 95

Chemistry Laboratory Manager 11 / 06 / 95

Technical Director 11 / 6 / 95

Implementation Date: 11 / 13 / 95

ENCOTEC, Inc.

METHOD DETECTION LIMIT

Parameter : Volatile Organic Compounds

Method(s) :

Sample Prep/Extraction : 5030A Purge & Trap
Analysis : 8240 / 8260

Date(s) of Analysis : 01/09/95

Analyst(s) : S.Carter

Instrument Type : GC/MS

Instrument Model : Hewlett Packard 5971A

Instrument I.D. : 007

Instrument Configuration :

P & T : Purge Time 11 minutes
Purge temp.: 40 C
Desorb temp.: 260 C
Desorb time: 4 minutes
5mL sample volume

GC : 35 C for 3 min. -> 135 C @ 5 C/min ->195 C @ 10 C/min.

MS : Scan Range: 35 - 300 amu
Scan Time: 1sec/scan

Referenced Protocol :
__X__ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit"
_____ Chapter One, Method Detection LImit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846"
Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis."

Matrix :
__X__ Laboratory Reagent Water
_____ Aqueous Environmental Sample (specifiy origin):
_____ Soil/Solid Environmental Sample (specify origin):
_____ Other (specify):

METHOD DETECTION LIMIT

Parameter : Volatile Organic Compounds

Method(s) :
Sample Prep/Extraction: 5030A Purge & Trap
Analysis: 8240 / 8260

Compound	Amount Spiked (ug/L)	Replicate Recoveries (ug/L) 1	2	3	4	5	6	7	Average Recovery	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjuated MDL 1)
CHLOROMETHANE	1.00	1.04	1.02	1.03	1.13	1.07	0.98	0.88	1.02	0.078	0.24	102	0.24
VINYL CHLORIDE	1.00	0.93	0.89	0.85	0.92	0.80	0.85	0.77	0.86	0.060	0.19	86	0.22
BROMOMETHANE	1.00	1.43	1.25	1.62	1.48	1.67	1.47	1.43	1.48	0.138	0.43	148	0.43
CHLOROETHANE	1.00	1.10	1.05	1.01	1.09	1.08	1.05	0.98	1.05	0.044	0.14	105	0.14
1,1-DICHLOROETHENE	1.00	1.02	0.90	0.98	0.91	0.88	0.80	0.78	0.90	0.087	0.27	90	0.31
ACETONE	1.00	6.93	6.64	7.10	7.54	8.32	7.12	7.81	7.35	0.575	1.81	735	1.81
CARBON DISULFIDE	1.00	0.89	0.82	0.84	0.88	0.82	0.85	0.80	0.84	0.033	0.10	84	0.12
METHYLENE CHLORIDE	1.00	2.46	2.40	2.39	2.43	2.50	2.50	2.61	2.47	0.076	0.24	247	0.24
TRANS-1,2-DICHLOROE	1.00	1.01	0.99	0.98	1.09	0.99	0.98	0.92	0.99	0.051	0.16	99	0.16
1,1-DICHLOROETHANE	1.00	1.04	0.99	1.03	1.02	0.99	0.97	0.94	1.00	0.035	0.11	100	0.11
VINYL ACETATE	1.00	0.83	0.90	0.88	0.97	0.90	1.00	0.93	0.92	0.057	0.18	92	0.20
2-BUTANONE	1.00	3.94	3.84	3.91	4.32	4.67	4.30	4.10	4.15	0.295	0.93	415	0.93
CHLOROFORM	1.00	0.99	0.97	0.97	1.04	1.00	1.02	0.96	0.99	0.029	0.09	99	0.09
1,1,1-TRICHLOROETHAN	1.00	1.03	0.99	0.97	1.02	0.93	0.93	0.89	0.97	0.052	0.16	97	0.17
CARBON TETRACHLORI	1.00	0.97	0.95	0.94	0.93	0.94	0.97	0.79	0.93	0.062	0.20	93	0.21
BENZENE	1.00	1.11	1.06	1.05	1.14	1.07	1.10	1.12	1.09	0.034	0.11	109	0.11
1,2-DICHLOROETHANE	1.00	1.13	1.07	1.07	1.31	0.66	1.24	1.18	1.09	0.211	0.66	109	0.66
TRICHLOROETHENE	1.00	1.01	0.97	0.94	1.00	0.99	1.04	0.91	0.98	0.044	0.14	98	0.14
1,2-DICHLOROPROPANE	1.00	1.05	1.03	1.02	1.19	1.09	1.13	1.08	1.08	0.060	0.19	108	0.19
BROMODICHLOROMET	1.00	0.85	0.87	0.86	1.00	0.92	0.96	0.89	0.91	0.056	0.18	91	0.19
CIS-1,3-DICHLOROPROP	1.00	0.96	0.91	0.89	0.94	0.95	1.02	0.97	0.95	0.042	0.13	95	0.14
4-METHYL-2-PENTANO	1.00	1.18	1.14	1.13	1.43	1.24	1.37	1.39	1.27	0.126	0.40	127	0.40
TOLUENE	1.00	1.10	1.10	1.08	1.15	1.12	1.16	1.09	1.11	0.030	0.10	111	0.10
TRANS-1,3-DICHLOROP	1.00	0.89	0.94	0.96	1.04	1.05	1.06	0.99	0.99	0.064	0.20	99	0.20

ENCOTEC, Inc.

METHOD DETECTION LIMIT

Parameter : Volatile Organic Compounds

Method(s) :
Sample Prep/Extraction: 5030A Purge & Trap
Analysis: 8240/8260

Compound	Amount Spiked (ug/L)	Replicate Recoveries (ug/L) 1	2	3	4	5	6	7	Average Recovery	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjuated MDL 1)
1,1,2-TRICHLOROETHEN	1.00	0.97	1.05	1.06	1.31	1.20	1.23	1.09	1.13	0.120	0.38	113	0.38
TETRACHLOROETHENE	1.00	1.05	1.08	1.00	1.01	1.03	1.00	0.92	1.01	0.050	0.16	101	0.16
2-HEXANONE	1.00	0.73	1.40	1.37	1.38	1.45	1.50	1.54	1.34	0.276	0.87	134	0.87
DIBROMOCHLOROMET	1.00	0.84	0.90	0.87	1.10	0.97	1.02	0.89	0.94	0.093	0.29	94	0.31
CHLOROBENZENE	1.00	1.00	0.99	1.01	1.10	1.04	1.08	1.02	1.03	0.042	0.13	103	0.13
ETHYLBENZENE	1.00	0.98	1.05	0.99	1.10	1.04	1.08	0.98	1.03	0.049	0.15	103	0.15
M&P-XYLENE	2.00	2.01	1.97	2.04	2.11	2.06	2.04	2.04	2.04	0.043	0.14	102	0.14
O-XYLENE	1.00	0.99	1.01	0.98	1.07	1.07	1.10	0.96	1.03	0.054	0.17	103	0.17
STYRENE	1.00	0.95	0.93	0.94	1.04	1.00	1.01	0.94	0.97	0.043	0.14	97	0.14
BROMOFORM	1.00	0.76	0.79	0.81	1.14	0.95	0.97	0.84	0.89	0.134	0.42	89	0.47
1,1,2,2-TETRACHLOROE	1.00	1.00	1.05	1.06	1.41	1.33	1.37	1.17	1.20	0.170	0.53	120	0.53
1,3-DICHLOROBENZENE	1.00	0.99	1.03	1.01	1.01	1.04	1.03	1.01	1.02	0.017	0.05	102	0.05
1,4-DICHLOROBENZENE	1.00	1.03	1.03	0.98	1.03	0.96	0.99	1.01	1.00	0.028	0.09	100	0.09
1,2-DICHLOROBENZENE	1.00	0.99	1.02	0.97	1.06	0.98	1.03	1.02	1.01	0.032	0.10	101	0.10
ETHYLENE OXIDE	10.00	10.69	11.45	11.93	11.62	12.33	12.28	11.03	11.62	0.616	1.94	116	1.94
T-METHYLBUTYL ETH	1.00	1.01	1.06	1.10	1.13	1.09	1.14	1.11	1.09	0.045	0.14	109	0.14
1,2-DIBROMOMETHANE	1.00	1.01	0.99	1.01	1.01	1.00	1.06	1.02	1.01	0.022	0.07	101	0.07
METHYLACETATE	1.00	1.23	1.18	1.39	1.30	1.49	1.48	1.34	1.34	0.118	0.37	134	0.37
ISOPROPYLACETATE	1.00	0.98	1.12	1.08	1.11	1.14	1.20	1.19	1.12	0.074	0.23	112	0.23
N-BUTYLACETATE	1.00	1.14	1.25	0.93	1.13	1.33	1.26	1.26	1.19	0.133	0.42	119	0.42
2-HEPTANONE	1.00	1.44	1.56	1.60	1.47	1.55	1.23	1.73	1.51	0.156	0.49	151	0.49
DIISOBUTYLACETATE	1.00	1.16	1.02	1.15	1.15	1.17	1.13	1.17	1.14	0.053	0.17	114	0.17

1) Note: No provision exists in the above protocal for evaluation of the determined MDL with respect to analyte recovery. An 'Adjusted MDL,' taking into account the Average Percent Recovery, is also given.

826A0195.mdl

LAB SOP
SVOC PART A
METHOD 8270

METHOD FOR THE DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of certain semivolatile compounds found in all types of solid waste matrices, soils, and ground water. It is based upon Method 8270, SW-846, 3rd edition.

1.2 Table 1 lists compounds that may be determined by this method and provides the Practical Quantitation Limit (PQL) for aqueous and soil matrices.

2.0 SUMMARY OF METHOD

2.1 This method provides for gas chromatographic separation and analysis by mass spectrometry of certain semivolatile compounds. Prior to use of this method, appropriate sampling and extraction techniques, described elsewhere, must be used. Results from the analysis are used to calculate the concentrations of target compounds present in the original solid or aqueous sample.

2.2 The sensitivity of this method depends upon the volume or weight of the sample extracted, the level of interferences encountered (if any) during the extraction process, as well as instrumental limitations.

TABLE 1
SEMIVOLATILE ORGANICS

Compound[1)]	CAS #	Practical Quantitation Limits Water ug/L	Soil ug/Kg
Acenaphthene	83-32-9	10	330
Acenaphthylene	208-96-8	10	330
Acetophenone	98-86-2	10	330
2-Acetylaminofluorene	53-96-3	10	330
4-Aminobiphenyl	92-67-1	10	330
Aniline	62-53-3	10	330
Anthracene	120-12-7	10	330
Aramite	140-57-8	10	330
Benzidine	92-87-5	80	2660
Benzo(*a*)anthracene	56-55-3	10	330
Benzo(*b*)fluoranthene	205-99-2	10	330
Benzo(*k*)fluoranthene	207-08-9	10	330
Benzo(*ghi*)perylene	191-24-2	10	330
Benzo(*a*)pyrene	50-32-8	10	330
Benzoic acid	65-85-0	50	1670
Benzyl alcohol	100-51-6	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Butyl benzyl phthalate	85-68-7	10	330
Carbazole	86-74-8	10	330
4-Chloroaniline	106-47-8	10	330
Chlorobenzilate	510-15-6	10	330
bis(2-Chloroethoxy) methane	111-91-1	10	330
bis(2-Chloroethyl) ether	111-44-4	10	330
bis(2-Chloroisopropyl ether	39638-32-9	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Chlorophenol	95-57-8	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Chrysene	218-01-9	10	330
Dibenz(*a*,*h*)anthracene	53-70-3	10	330
Dibenzofuran	132-64-9	10	330
Di-*n*-butyl phthalate	84-74-2	10	330
1,2-Dichlorobenzene	95-50-1	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
3,3'-Dichlorobenzidine	91-94-1	20	670
2,4-Dichlorophenol	120-83-2	10	330
2,6-Dichlorophenol	87-65-0	10	330
Diethyl phthalate	84-66-2	10	330
Dimethyl phthalate	131-11-3	10	330

TABLE 1 (con't.)

Compound[1)]	CAS #	ug/L	ug/Kg
Dimethoate	60-51-5	10	330
p-(Dimethylamino) azobenzene	60-11-7	10	330
7,12-Dimethylbenz(*a*) anthracene	57-97-6	10	330
3,3'-Dimethylbenzidine	119-93-7	40	1330
α, α -Dimethylphenethylamine	122-09-8	100	3300
2,4-Dimethylphenol	105-67-9	10	330
1,3-Dinitrobenzene	99-65-0	10	330
4,6-Dinitro-2-methylphenol	534-52-1	50	1670
2,4-Dinitrophenol	51-28-5	50	1670
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Dinoseb	88-85-7	20	660
Di-*n*-octyl phthalate	117-84-0	10	330
Diphenylamine[2)]	122-39-4	10	330
bis(2-Ethylhexyl) phthalate	117-81-7	10	330
Ethyl methanesulfonate	62-50-0	10	330
Fluoranthene	206-44-0	10	330
Fluorene	86-73-7	10	330
Hexachlorobenzene	118-74-1	10	330
Hexachlorobutadiene	87-68-3	10	330
Hexachlorocyclopentadiene	77-47-4	10	330
Hexachlorodibenzofurans	---	10	330
Hexachlorodibenzo-*p*-dioxins	---	10	330
Hexachloroethane	67-72-1	10	330
Hexachlorophene	70-30-4	80	2670
Hexachloropropene	1888-71-7	80	2670
Indeno(1,2,3-*cd*)pyrene	193-39-5	10	330
Isophorone	78-59-1	10	330
Isosafrole	120-58-1	10	330
Methapyrilene	91-80-5	10	330
3-Methylcholanthrene	56-49-5	80	2670
Methyl methanesulfonate	66-27-3	40	1330
2-Methylnaphthalene	91-57-6	10	330
2-Methylphenol	95-48-7	10	330
3-Methylphenol	108-39-4	10	330
4-Methylphenol	106-44-5	10	330
Naphthalene	91-20-3	10	330
1,4-Naphthoquinone	130-15-4	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2-Nitroaniline	88-74-4	50	1670
3-Nitroaniline	99-09-2	50	1670
4-Nitroaniline	100-01-6	50	1670

TABLE 1 (con't.)

Compound[1]	CAS #	ug/L	ug/Kg
Nitrobenzene	98-95-3	10	330
2-Nitrophenol	88-75-5	10	330
4-Nitrophenol	100-02-7	50	1670
4-Nitroquinoline-1-oxide	56-57-5	10	330
5-Nitro-*o*-toluidine	99-55-8	10	330
N-Nitroso-di-*n*-butylamine	924-16-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
N-Nitrosodimethylamine	62-75-9	10	330
N-Nitrosodiphenylamine[3]	86-30-6	10	330
N-Nitrosomethylethylamine	10595-95-6	10	330
N-Nitrosomorpholine	59-89-2	10	330
N-Nitrosopiperdine	100-75-4	10	330
N-Nitroso-di-*n*-propylamine	621-64-7	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
Pentachlorobenzene	608-93-5	10	330
Pentachlorodibenzofurans	---	10	330
Pentachlorodibenzo-*p*-dioxins	---	10	330
Pentachloroethane	76-01-7	10	330
Pentachloronitrobenzene	82-68-8	10	330
Pentachlorophenol	87-86-5	50	1670
Phenacetin	62-44-2	10	330
Phenanthrene	85-01-8	10	330
Phenol	108-95-2	10	330
p-Phenylene diamine	106-50-3	10	330
2-Picoline	109-06-8	80	2670
Pronamide	23950-58-5	80	2670
Pyrene	129-00-0	10	330
Safrole	94-59-7	10	330
Sulfotepp	3689-24-5	10	330
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Tetrachlorodibenzofurans	---	10	330
Tetrachlorodibenzo-*p*-dioxins	---	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	10	330
o-Toluidine	95-53-4	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2,4,6-Trichlorophenol	88-06-2	10	330
o,o,o-Triethylphosphoro-thioate	126-68-1	10	330
1,3,5-Trinitrobenzene	99-35-4	10	330

[1] Appendix IX Regulatory List for Semivolatile Compounds.
[2] Compound cannot be separated from N-Nitrosodiphenylamine.
[3] Compound cannot be separated from Diphenylamine.

3.0 SAFETY PRECAUTIONS

3.1 All general laboratory safety precauations apply. Safety glasses, gloves, and a lab coat should be worn when handling solvent, samples, and standards. Safety glasses must always be worn in the laboratory. The Material Safety Data Sheets (MSDS) should be consulted for toxicity information.

4.0 INTERFERENCES

4.1 Method blanks, samples and spikes must be evaluated for interference. Method interference may be caused by contamination in solvent, reagents, glassware, and other sample processing hardware.

4.2 Contamination by carryover can occur whenever high concentration and low concentration samples are sequentially analyzed. The reduction of carry-over may be minimized by rinsing the sample syringe with solvent between analytical runs. The use of an autosampler will also help to minimize this potential problem. Analysis of a solvent blank should be performed to check for cross contamination when carryover has been demonstrated.

5.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system (GC/MS/DS)

5.1 Gas chromatograph (GC): A GC capable of temperature programming and equipped with splitless injection and all required accessories, including syringes, analytical column and carrier gases. The capillary column should be directly coupled to the mass spectrometer source.

5.2 Column: 30m x 0.25mm ID (or 0.32mm ID) 1um film thickness fused silica capillary column (J&W Scientific DB-5).

5.3 Mass spectrometer: Capable of scanning 35-500 amu every second or less, using 70 volts electron energy in the electron ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 50 ng of decafluorotriphenylphosphine (DFTPP).

5.4 GC/MS interface: Any GC to MS interface that gives an acceptable GC calibration at 20 ng per injection for each compound of interest may be used.

5.5 Data system: An interfaced data system which will acquire, store, reduce and output mass spectral data. The computer software will allow searching any GC/MS data file for ions of specific mass and plotting ion abundance versus time or scan number.

5.6 Syringes, 10uL.

5.7 Bottles, glass, 1.5mL, with Teflon-lined screw caps.

6.0 REAGENTS

6.1 Solvents: Methylene chloride, hexane, acetone, carbon disulfide, and other appropriate solvents, pesticide grade or equivalent, commercially available.

6.2 Internal standard: 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}. The internal standard solution can be prepared by dissolving 200 mg of each compound in 50 mL of different percentages of methylene chloride, acetone, benzene, and carbon disulfide. The resulting concentration of each compound in this solution is 4000 ng/uL. A 5uL portion will be added to each 1 mL of sample extract. This will result in 40 ng of each internal standard in the 2uL volume of extract injected into the GC/MS unit.

6.3 Stock standard solution: Standard solution can be prepared from pure standard materials or purchased as certified solutions.

6.3.1 Prepare stock solutions by weighing 0.200 g of neat standard. Dissolve in pesticide grade methylene chloride or other suitable solvent and dilute to volume in a 100mL volumetric flask. This will result in a final concentration of 2000 ug/uL. After the solution has been confirmed to be within 90%-110% of EPA reference standard value, transfer the stock standard solution into 2mL amber vials and seal.

6.4 Calibration standards: Prepare calibration standards containing the hazardous substance list semivolatile compounds at five concentration levels (nominally) 10, 50, 80, 120 and 160 total ng per 2 uL. Prepare additional calibration standards at five concentration levels for Appendix IX and Land Disposal Restriction regulation compounds, or other applications as needed, such that the high standard will define the linear range

of the instrument and the low standard will be at or near the PQL.

6.5 Instrument performance check solution: Prepare a solution of decafluorotriphenylphosphine (DFTPP) such that a 2 ul injection will contain 50 ng of DFTPP.

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Sample extracts are stored at ≤ 4° Celsius until preparation and analysis. Extracts are to be completely analyzed within 40 days of the date of extraction.

8.0 PROCEDURE

8.1 See the following SOPs for sample extractions.

- **General Requirements for Organic Extraction and Sample Preparation**
- **Separatory Funnel Liquid-Liquid Extraction**

or

- **Sonication Extraction** (for Soils)

or

- **Waste Dilution, Method 3580, SW-846**

Instrument conditions

8.2 Gas chromatograph: The following are the operating conditions for the gas chromatograph.

Initial column temperature:	40°C for 4 minutes
Temperature program:	40-300°C at 8°C/min
Final temperature:	300°C for 3.5 minutes
Injector temperature:	270°C
Transfer line temperature:	270°C
Source temperature:	190°C
Injector:	Grob style, splitless
Sample volume:	2 uL
Carrier gas:	Helium at 30 cm/sec

8.3 Mass Spectrometer: The following are the operating conditions for the mass spectrometer.

Electron energy:	70 volts
Mass range:	35-500 amu
Scan time:	1 sec/scan

Calibration

8.4 Prior to the analysis of standards, blanks and any samples, the GC/MS system must meet the mass spectral ion abundance criteria for a 50 ng injection for the instrument performance check solution, decafluorotriphenylphosphine (DFTPP). The ion abundance criteria that must be met are given in Table 2.

TABLE 2
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criterion
51	30.0% - 60.0% of mass 198
68	< 2.0% of mass 69
70	< 2.0% of mass 69
127	40.0% - 60.0% of mass 198
197	< 1.0% of mass 198
198	**base peak**, 100% of relative abundance
199	5.0% - 9.0% of mass 198
275	10.0% - 30.0% of mass 198
365	> 1.00% of mass 198
441	present, but < mass 443
442	> 40.0% of mass 198
443	17.0% - 23.0% of mass 442

The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which standards and samples are analyzed. The 12-hour time period for the GC/MS instrument performance check sample begins at the moment of injection of DFTPP. The time period ends after twelve hours have elapsed as measured by the GC/MS system clock.

8.5 After the instrument performance check criteria have been met, calibrate the GC/MS system with five concentrations of each compound of interest. Make certain all standards include surrogates and internal standards.

8.6 The quantification ions for each internal standard are as follows:

INTERNAL STANDARD	QUANTIFICATION ION
1,4-Dichlorobenzene-d_4	152
Naphthalene-d_8	136
Acenaphthene-d_{10}	164
Phenanthrene-d_{10}	188
Chrysene-d_{12}	240
Perylene-d_{12}	264

The corresponding assignments of internal standards to the compounds of interest are given in Table 3. These references are used for quantitation purposes.

TABLE 3
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene
bis(2-Chloroethyl) ether	Isophorone	2,4,6-Trichloro-phenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichloro-phenol
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethyl phthalate
2-Methylphenol	1,2,4-Trichloro-benzene	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloraniline	Acenaphthene
N-Nitroso-di-*n*-propylamine	Hexachloro-butadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Fluorophenol (surr)	2-Methylnaphth-alene	Dibenzofuran
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene
Benzyl alcohol	N-Nitrosopmor-pholine	2,6-Dinitrotoluene
N-Nitrosodi-methylamine	3-Methylphenol	Diethyl phthalate
2-Picoline	*o*-Toluidine	4-Chlorophenyl-phenyl ether
N-Nitrosomethylethylamine	N-Nitro-sopiperdine	Fluorene
Methyl methanesulfonate	alpha, alpha-Dimethylphen-ethylamine	4-Nitroaniline
N-Nitrosodiethylamine	*o,o,o*-Triethyl-phosphorothioate	2-Fluorobiphenyl (surr)
Ethyl methanesulfonate	2,6-Dichloro-phenol	2,4,6-Tribromo-phenol (surr)
Pentachloroethane	Hexachloro-propene	1,2,4,5-Tetra-chlorobenzene
Aniline	*p*-Phenylene diamine	Isosafrole
Acetophenone	N-Nitroso-di-*n*-butylamine	1,4-Naphtho-quinone
N-Nitrosopyrrolidine	Safrole	1,3-Dinitro-benzene
		Pentachloro-benzene
		1-Naphthylamine
(surr) - surrogate compounds		2-Naphthylamine
		2,3,4,6-Tetra-chlorophenol
		5-Nitro-*o*-toluidine

TABLE 3 (con't.)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methylphenol	Pyrene	Di-*n*-octyl-phthalate
N-Nitrosodi-phenylamine	Butyl benzyl-phthalate	Benzo(*b*) fluor-anthene
4-Bromophenyl-phenyl ether	3,3'-Dichloro-benzidine	Benzo(*k*)-fluor-anthene
Hexachloro-benzene	Benzo(*a*)-anthracene	Benzo(*a*) pyrene
Pentachloro-phenol	Bis(2-ethyl-hexyl)phthalate	Indeno(1,2,3-*cd*)-pyrene
Phenanthrene	Chrysene	Dibenz(*a*,*h*)-anthracene
Anthracene	Terphenyl-d_{14} (surr)	Benzo(*ghi*) perylene
Di-*n*-butyl-phthalate	*p*-(Dimethylamino) azobenzene	7,12-Dimethyl benz(*a*) anthracene
Fluoranthene	Aramite	Hexachloro-phene
Diphenylamine	Chlorobenzilate	3-Methyl-chol-anthrene
1,3,5-Trinitro-benzene	3,3'-Dimethyl-benzidine	
Sulfotepp	2-Acetylamino-fluorene	
Diallate		
Phenacetin		
Dimethoate		
4-Aminobiphenyl		
Pentachloro-nitrobenzene		
Pronamide		
Dinoseb		
4-Nitroquinoline-1-oxide		
Methapyrilene		

(surr) - surrogate compounds

8.7 Analyze 2 uL of each calibration standard and tabulate the area of the primary characteristic ion (as indicated in Table 4, below) against the concentration for each compound. Calculate the response factor (RF) for each compound as follows:

$$RF = \frac{A_s}{A_{is}} \times \frac{C_{is}}{C_x}$$

where

A_x = Area of the characteristic ion for the compound to be measured (see Table 4)

A_{is} = Area of the characteristic ion for the specific internal standard (see Table 3)

C_{is} = Concentration of the internal standard(ng/ul)

C_x = Concentration of the compound to be measured(ng/ul)

TABLE 4
CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS AND SURROGATES

Parameter	Primary Ion
Phenol	94
bis(2-Chloroethyl) ether	93
2-Chlorophenol	128
1,3-Dichlorobenzene	146
1,4-Dichlorobenzene	146
1,2-Dichlorobenzene	146
Benzyl alcohol	108
2-Methylphenol	108
2,2'-oxybis(1-Chloropropane)	45
4-Methylphenol	108
N-Nitroso-di-propylamine	70
Hexachloroethane	117
Nitrobenzene	77
Isophorone	82
2-Nitrophenol	139
2,4-Dimethylphenol	107
bis(2-Chloroethoxy)methane	93
2,4-Dichlorophenol	162
1,2,4-Trichlorobenzene	180
Naphthalene	128
4-Chloroaniline	127
Hexachlorobutadiene	225
4-Chloro-3-methylphenol	107
2-Methylnaphthalene	142
Hexachlorocyclopentadiene	237
2,4,6-Trichlorophenol	196
2,4,5-Trichlorophenol	196
2-Chloronaphthalene	162
2-Nitroaniline	65
Dimethyl phthalate	163
Acenaphthylene	152
3-Nitroaniline	138
Acenaphthene	153
2,4-Dinitrophenol	184
4-Nitrophenol	109
Dibenzofuran	168
2,4-Dinitrotoluene	165
2,6-Dinitrotoluene	165
Diethyl phthalate	149
4-Chlorophenyl phenyl ether	204
Fluorene	166
4-Nitroaniline	138

TABLE 4 (con't.)

Parameter	Primary Ion
4,6-Dinitro-2-methylphenol	198
N-Nitrosodiphenylamine	169
4-Bromophenyl phenyl ether	248
Hexachlorobenzene	284
Pentachlorophenol	266
Phenanthrene	178
Anthracene	178
Di-*n*-butyl phthalate	149
Fluoranthene	202
Pyrene	202
Butyl benzyl phthalate	149
3,3'-Dichlorobenzidine	252
Benzo(*a*)anthracene	228
bis(2-ethylhexyl) phthalate	149
Chrysene	228
Di-*n*-octyl phthalate	149
Benzo(*b*)fluoranthene	252
Benzo(*k*)fluoranthene	252
Benzo(*a*)pyrene	252
Indeno(1,2,3-*cd*)pyrene	276
Dibenz(*a*,*h*)anthracene	278
Benzo(*ghi*)perylene	276
N-Nitrosodimethylamine	74
2-Picoline	93
N-Nitrosomethylethylamine	88
Methyl methanesulfonate	79
N-Nitrosodiethylamine	102
Ethyl methanesulfonate	79
Pentachloroethane	117
Aniline	93
Acetophenone	77
N-Nitrosopyrrolidine	100
N-Nitrosomorpholine	56
3-Methylphenol	107
o-Toluidine	106
N-Nitrosopiperdine	114
o,*o*,*o* Triethylphosphorothioate	121
2,6-Dichlorophenol	63
Hexachloropropene	213
P-Phenylene diamine	108
N-Nitroso-di-*n*-butylamine	57
Safrole	162
1,2,4,5-Tetrachlorobenzene	216

TABLE 4 (con't.)

Parameter	Primary Ion
Isosafrole	162
Pentachlorobenzene	252
1-Naphthylamine	143
2-Naphthylamine	143
2,3,4,6-Tetrachlorophenol	230
5-Nitro-*o*-toluidine	77
Diphenylamine	169
1,3,5-Trinitrobenzene	75
Sulfotepp	97
Diallate	86
Phenacetin	108
Dimethoate	87
4-Aminobiphenyl	169
Pentachloronitrobenzene	188
Pronamide	173
Dinoseb	211
4-Nitroquinoline-1-oxide	190
Methapyrilene	58
p-(Dimethylamino) azobenzene	120
Aramite	185
Chlorobenzilate	139
3,3'-Dimethylbenzidine	212
2-Acetylaminofluorene	181
7-12-Dimethylbenz(a) anthracene	256
3-Methylcholanthrene	268
alpha, alpha-Dimethylphenethylamine	58
1,3-Dinitrobenzene	168
Hexachlorodibenzofurans	374
Hexachlorodibenzo-*p*-dioxins	390
1,4-Naphthoquinone	158
Pentachlorodibenzofurans	340
Pentachlorodibenzo-*p*-dioxins	356
Tetrachlorodibenzofurans	306
Tetrachlorodibenzo-*p*-dioxins	322
Hexachlorophene	196

8.8 The mean response factor (RF_{ave}) is calculated for all TCL compounds from the five different levels at which the standards were run. The percent relative standard deviation (%RSD = 100% x [sd/RF]) is calculated for each compound. The %RSD should be less than 30% for each compound. The %RSD for each individual calibration check compound (CCC) (see table 5, below) must be less than 30%.

8.9 A system performance check is also performed to ensure that minimum RFs are met before the calibration curve is used. The system performance check compounds (SPCC) are:

N-nitroso-di-*n*-propylamine
hexachlorocyclopentadiene
2,4-dinitrophenol
4-nitrophenol

The minimum acceptable average RF for these compounds is 0.050.

TABLE 5
CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-*n*-phenylamine	Phenol
Di-*n*-Octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(*a*)pyrene	
Methyl methane sulfonate	
Acetophenone	
N-Nitrosopiperdine	
2-Naphthylamine	
Pronamide	
p-(Dimethylamine)azobenzene	
Chlorobenzilate	
3-Methylcholanthrene	

8.10 If time remains in the 12 hour period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. If there is no time remaining, an instrument performance check solution (see 8.4, above) must be analyzed. If the DFTPP meets the ion abundance criteria, a continuing calibration standard containing 50 ng/2uL should be analyzed (see 8.8 and Table 5, above). Calculate the response factors for the continuing calibration and the percent differences of the response factors from the mean response factors in the initial calibration. The minimum acceptable response factor (RF) for each of the SPCCs (see 8.8, above) must be 0.050. The percent difference for each CCC must be $\leq$25.0%. Samples may not be analyzed after the expiration of the 12 hour period following a DFTPP injection.

Sample Analysis

8.11 Samples may be analyzed only after the GC/MS system has met the instrument performance check, initial calibration and/or continuing calibration requirements specified above. The exact instrument conditions must be employed for the analysis of samples as were used for the calibration standards. Add 5 uL of the 4000 ng/uL internal standard solution to each accurately measured 1.0 mL of sample extract. Inject 2 uL of each sample extract, containing 40 ng of each internal standard, into the GC/MS. If the response for any quantitation ion exceeds the initial calibration range for the GC/MS system, extract dilution must be performed. Additional internal standard must be added to maintain the required 40 ng of each internal standard.

Suggested system maintenance

8.12 The following is a list of routine maintenance items performed on the GC/MS system.

8.12.1 Gas chromatograph: Many compounds will show a decrease in response when the chromatographic system starts to deteriorate. The area that will usually deteriorate first is the injector port. The most common maintenance performed on the injector port is the replacement of the injector sleeve liner and/or the removal of the first few centimeters of the analytical column. This will, in most cases, help those compounds that are susceptible to poor chromatographic conditions.

8.12.2 Mass spectrometer: The mass spectrometer will require routine maintenance generally proportional to the usage of the instrument. The most commonly performed maintenance is the cleaning of the mass spectrometer source. This maintenance is performed when the instrument performance check solution (DFTPP, see 8.4, above) does not meet acceptable ion abundance criteria.

Calculations

8.13 Qualitative analysis: The compounds listed in this method must be identified by the analyst through the comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. The two criteria that must be satisfied to verify the identification are:

8.14 The elution of the sample component at the GC relative retention time of the standard component. For the establishment of the relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be analyzed on the same twelve hour shift as the sample. If co-elution 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 (EICP) for ions unique to the component of interest.

8.14.1 Correspondence of the sample component and standard component mass spectra. The relative intensities of the characteristic ions of the sample component must agree within 20% of the relative intensities of those of the standard component. Ions present at a ratio greater than 10% in the sample spectra but not present in the standard spectra for the same component must be considered and accounted for by the analyst making the comparison. If a compound cannot be verified by all of these criteria, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then the compound shall be reported and quantified.

8.14.2 Quantitative analysis: The quantitation of an identified compound will be based on the integrated abundance from the extracted ion current profile (EICP) of the primary characteristic ion (see Table 4, above). The internal standard technique will be used for quantitation. (The internal standard used for a given analyte is found in Table 3, above.) The concentration of each identified analyte is calculated as follows:

Water

$$ug/L = \frac{A_x * I_s * V_t * DF}{A_{is} * RF * V_i * V_s}$$

where

A_x = area of the characteristic ion for the compound measured.
I_s = amount of internal standard injected, ug.
V_t = volume of concentrated extract, mL
DF = dilution factor, if dilution was performed on the sample extract prior to analysis. If no dilution was made DF = 1.0.
A_{is}= area of the characteristic ion for the internal standard.
RF= response factor for the analyte being measured.
V_i = volume of extract injected, mL.
V_s = volume of water sample extracted, mL.

Sediment/Soil Sludge(on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$ug/Kg = \frac{A_x * I_s * V_t * DF}{A_{is} * RF * V_i * W_s * D}$$

where

A_x, I_s, V_t, DF, A_{is}, RF, V_i are already defined.
W_s = Weight of sample extracted or diluted in grams.
D = percent dry weight of sample/100, or 1 for wet-weight basis.

8.15 Quantitation of unknowns: An estimate of concentration for non-calibrated components in the sample can be made by using the above formulas 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 nearest internal standard free of interference should be used.

9.0 QUALITY CONTROL

9.1 The GC/MS system must be tuned to meet the tuning criteria for DFTPP specified in Section 8.4.1.

9.2 There must be an initial or continuing calibration analyzed every 12 hours, with recoveries as specified in Sections 8.4.2 through 8.4.6

9.3 It must be demonstrated, through the analysis of a method blank, that the analytical system, comprised of extraction and analysis activities, does not contribute to the presence of target compounds (*i.e.*, those listed in Table 1, above) at or above the Practical Quantitation Limit (PQL).

9.4 Surrogate recoveries must be calculated from the analysis of samples and method blanks as described in Section 8.6.2. The percent recovery (%R) of the surrogates are calculated as follows:

$$\%R = \frac{\text{Mass found}}{\text{Mass spiked}} \times 100\%$$

The following criteria are used to determine if the sample surrogate meets acceptable quality control limits.If a single surrogate recovery from any group is not within percent recovery windows, the sample does not require reanalysis or re-extraction.If a single surrogate recovery from the base/neutral group and a single surrogate recovery from the acid group are not within percent recovery windows, the sample does not require reanalysis or re-extraction.

3) If a single surrogate recovery from either the base/neutral or acid group are outside of percent recovery windows the sample does not require reanalysis or re-extraction.

If the sample surrogate recoveries do not meet the above criteria, the following are required:

1) Check to ensure that there are no errors in the calculations, surrogate solution, or standards. If errors are found, recalculate the data accordingly.

2) Check instrument performance. If an instrument problem identified, correct the problem and re-analyze the extract.

3) If no problem is found, re-extract and re-analyze the sample.

9.5 A matrix spike and matrix spike duplicate is prepared and analyzed for each group of samples extracted or every 20 samples, whichever is less. The recoveries of the matrix spike and matrix spike duplicate are calculated using the same equation used for calculating the surrogate recoveries. Calculate the percent recovery of each LCS as follows:

$$\%R = \frac{\text{Mass found}}{\text{Mass spiked}} \times 100\%$$

Calculate the relative percent difference of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

$$RPD = \frac{(MSR - MSDR)}{(1/2)(MSR + MSDR)} * 100\%$$

where:
RPD = Relative Percent Difference
MSR = Matrix Spike Recovery
MSDR = Matrix Spike Duplicate Recovery

9.6 A laboratory control sample (LCS) is prepared and analyzed for each group of samples extracted or every 20 samples, whichever is less. The recoveries of the LCS are calculated using the same equation used for calculating the surrogate recoveries. Calculate the percent recovery of each LCS as follows:

$$\%R = \frac{\text{Mass found}}{\text{Mass spiked}} \times 100\%$$

10.0 METHOD PERFORMANCE

The method detection limits and precision and accuracy evaluation for this method are on file. The method detection limits for these compounds were established by spiking a known concentration (i.e., test concentration) of analyte into one liter of reagent water, extracting the resulting solution, and

conducting the analysis according to the procedures specified in this method.

11.0 REFERENCES

11.1 Test Methods for the Evaluation of Solid Waste, SW-846, Method 8270, Rev. 0, Sept., 1986

12.0 PROVENANCE

This method was written by

_____ Laboratory Manager 11 / 06 / 95

_____ Technical Documentation Officer 11 / 06 / 95

It has been reviewed and accepted by

_____ Technical Documentation Officer 11 / 06 / 95

_____ GC/MS Group Leader 11 / 06 / 95

_____ Laboratory Manager 11 / 06 / 95

_____ Technical Director 11 / 6 / 95

Implementation Date: 11 / 13 / 95

ENCOTEC, Inc.

METHOD DETECTION LIMIT

Parameter :	Semi-Volatile Extractable Organics
Method(s) :	
Sample Prep/Extraction :	3520 Liquid/Liquid (modified)
Analysis :	8270
Date(s) of Analysis :	1/12/95
Analyst(s) :	D. Tjiok
Instrument Type :	GC/MS
Instrument Model :	Finnigan 4500
Instrument I.D. :	001

Instrument Configuration :

Autosampler :	2 ul injection
GC :	40 C for 4 min. -> 300 C @ 8 C/min -> hold 3.5 min.
MS :	Scan Range: 35-550 amu Scan Time: 1 sec/scan

Referenced Protocol :

- __X__ Appendix B, 40 CFR, Part 136, Oct. 1984, "Definition and Procedure for the Determination of the Method Detection Limit"
- _____ Chapter One, Method Detection LImit, Rev. 2, May 1991, "Test Methods for Evaluating Solid Waste, SW-846"
- _____ Exhibit E, Section V, 10., March 1991, "USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis."

Matrix :

- __X__ Laboratory Reagent Water
- _____ Aqueous Environmental Sample (specifiy origin):
- _____ Soil/Solid Environmental Sample (specify or Sodium Sulfate
- Other (specify): soil substitute

827A1295.mdl

METHOD DETECTION LIMIT

Parameter : Semi-Volatile Extractable Organics

Method(s) :
Sample Prep/Extraction : 3520 Liquid/Liquid
Analysis : 8270

Compound	Amount Spiked (ug/L)	Replicate Recoveries (ug/L) 1	2	3	4	5	6	7	Average Recovery	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
Phenol	5.0	2.0	2.3	2.3	2.0	2.9	2.1	1.8	2.2	0.35	1.1	43	2.5
Bis(2-chloroethyl)ether	5.0	4.8	5.1	5.0	4.3	4.7	4.6	3.7	4.6	0.49	1.5	92	1.7
2-Chlorophenol	5.0	4.0	4.5	4.7	4.0	4.6	4.6	3.4	4.2	0.47	1.5	85	1.7
1,3-Dichlorobenzene	5.0	4.5	4.8	4.8	4.2	4.5	4.6	3.8	4.5	0.35	1.1	89	1.2
1,4-dichlorobenzene	5.0	4.5	4.8	4.7	4.0	4.4	4.4	3.7	4.4	0.37	1.2	87	1.3
benzyl alcohol	5.0	4.5	4.6	4.6	4.2	4.3	4.2	3.4	4.3	0.41	1.3	85	1.5
1,2-dichlorobenzene	5.0	4.3	4.9	4.6	4.0	4.5	4.6	3.6	4.3	0.43	1.4	87	1.6
2-methylphenol	5.0	4.1	4.2	4.3	3.7	4.2	4.0	3.3	4.0	0.35	1.1	79	1.4
2,2'-oxybis(1-chloropropan	5.0	4.6	4.9	5.0	4.3	4.7	4.6	3.6	4.5	0.47	1.5	91	1.6
4-methylphenol	5.0	3.5	3.7	3.8	3.2	3.7	3.6	2.8	3.5	0.35	1.1	70	1.6
n-nitroso-di-n-propylamine	20.0	18.5	19.8	19.3	16.8	18.4	19.0	15.4	18.2	1.55	4.9	91	5.4
hexachloroethane	5.0	4.0	4.4	4.3	3.9	4.4	4.5	3.6	4.2	0.33	1.1	83	1.3
nitrobenzene	5.0	4.3	4.6	4.6	4.2	4.4	5.0	3.6	4.4	0.44	1.4	87	1.6
isophorone	5.0	4.3	4.6	4.5	4.2	4.4	4.8	3.5	4.3	0.40	1.3	86	1.4
2-nitrophenol	5.0	3.3	3.8	4.0	3.6	4.2	4.2	3.0	3.7	0.47	1.5	75	2.0
2,4-dimethylphenol	5.0	3.3	3.1	3.4	2.9	3.3	3.1	2.7	3.1	0.24	0.8	62	1.2
bis(2-chloroethoxy) methan	5.0	4.4	4.6	4.7	4.2	4.5	4.7	3.6	4.4	0.39	1.2	88	1.4
2,4-dichlorophenol	5.0	3.3	3.7	4.0	3.7	4.1	4.2	3.0	3.7	0.42	1.3	74	1.8
1,2,4-trichlorobenzene	5.0	4.0	4.6	4.5	3.8	4.2	4.7	3.5	4.2	0.44	1.4	84	1.7
naphthalene	5.0	4.4	4.7	4.6	4.3	4.5	4.7	3.6	4.4	0.39	1.2	88	1.4
4-chloroaniline	5.0	3.9	4.2	4.1	3.7	4.0	4.3	3.3	3.9	0.34	1.1	79	1.3
hexachlorobutadiene	5.0	3.7	4.1	4.3	3.5	3.8	4.3	3.2	3.8	0.42	1.3	77	1.7
4-chloro-3-methylphenol	5.0	4.0	4.3	4.4	4.0	4.2	4.4	3.3	4.1	0.38	1.2	82	1.5
2-methylnaphthalene	5.0	4.2	4.3	4.2	3.9	4.1	4.5	3.4	4.1	0.37	1.2	82	1.4
hexachlorocyclopentadiene	5.0	2.6	2.3	2.4	2.2	2.5	3.0	2.2	2.5	0.28	0.9	49	1.8

ENCOTEC, Inc.

METHOD DETECTION LIMIT

Parameter : Semi-Volatile Extractable Organics

Method(s) :
Sample Prep/Extraction : 3520 Liquid/Liquid
Analysis : 8270

Compound	Amount Spiked (ug/L)	Replicate Recoveries (ug/L) 1	2	3	4	5	6	7	Average Recovery	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
2,4,6-trichlorophenol	5.0	3.1	3.3	4.2	4.0	4.4	4.4	2.8	3.7	0.66	2.1	75	2.8
2,4,5-trichlorophenol	20.0	17.1	19.1	22.5	20.7	23.0	23.9	16.1	20.3	3.02	9.5	102	9.5
2-chloronaphthalene	5.0	4.6	4.8	4.7	4.1	4.5	4.8	4.0	4.5	0.33	1.0	90	1.1
2-nitroaniline	20.0	21.0	22.3	21.9	19.7	21.8	22.6	17.2	20.9	1.90	6.0	105	6.0
dimethylphthalate	5.0	0.6	0.8	0.9	0.9	1.2	1.3	0.9	0.9	0.25	0.8	19	4.2
acenaphthylene	5.0	4.4	4.7	4.7	4.3	4.7	5.0	3.7	4.5	0.40	1.3	90	1.4
3-nitroaniline	20.0	20.8	22.6	22.4	20.0	22.2	22.1	16.8	21.0	2.09	6.6	105	6.6
acenaphthene	5.0	4.6	4.8	4.9	4.4	4.7	4.8	3.8	4.6	0.39	1.2	91	1.4
2,4-dinitrophenol	20.0	7.5	8.4	8.3	9.6	9.1	9.7	4.0	8.1	1.95	6.1	40	15.1
4-nitrophenol	20.0	6.5	6.3	7.4	6.3	7.7	7.7	4.5	6.6	1.16	3.6	33	11.0
dibenzofuran	5.0	4.4	4.8	4.7	4.3	4.7	4.7	3.7	4.5	0.39	1.2	90	1.4
2,4-dinitrotoluene	5.0	3.8	4.4	4.2	4.0	4.3	4.6	3.2	4.0	0.46	1.4	81	1.8
2,6-dinitrotoluene	5.0	3.8	4.0	4.3	3.6	4.0	4.0	3.1	3.8	0.39	1.2	77	1.6
diethyl phthalate	5.0	2.5	2.9	3.1	2.9	3.1	3.5	2.6	2.9	0.34	1.1	59	1.8
4-chlorophenyl phenylether	5.0	4.5	4.9	4.9	4.5	4.5	4.9	3.8	4.6	0.38	1.2	91	1.3
fluorene	5.0	4.4	4.7	4.6	4.3	4.6	4.7	3.6	4.4	0.39	1.2	88	1.4
4-nitroaniline	20.0	22.7	24.9	23.9	22.6	24.5	24.6	17.8	23.0	2.46	7.7	115	7.7
4,6-dinitro-2-methylphenol	20.0	14.0	14.3	18.4	19.7	19.5	21.0	12.2	17.0	3.44	10.8	85	12.7
n-nitrosodiphenylamine	5.0	4.8	4.8	4.8	4.7	4.6	4.8	4.0	4.6	0.30	0.9	93	1.0
4-bromophenyl phenylether	5.0	4.6	4.5	4.5	4.2	4.4	4.7	3.7	4.4	0.33	1.0	87	1.2
hexachlorobenzene	5.0	4.2	4.4	4.5	3.9	4.3	4.3	3.6	4.2	0.32	1.0	84	1.2
pentachlorophenol	20.0	9.0	10.2	11.1	13.2	11.7	13.3	5.1	10.5	2.82	8.9	53	16.8
phenanthrene	5.0	4.5	4.7	4.7	4.8	4.8	4.9	3.7	4.6	0.43	1.3	92	1.5
anthracene	5.0	4.6	5.0	5.0	4.9	4.7	4.9	3.8	4.7	0.43	1.4	94	1.4
carbazole	5.0	4.8	5.1	4.8	4.7	4.9	4.7	3.5	4.6	0.52	1.6	93	1.8

827A1295.mdl

METHOD DETECTION LIMIT

Parameter : Semi-Volatile Extractable Organics

Method(s) :
Sample Prep/Extraction : 3520 Liquid/Liquid
Analysis : 8270

Compound	Amount Spiked (ug/L)	Replicate Recoveries (ug/L) 1	2	3	4	5	6	7	Average Recovery	Standard Deviation	Method Detection Limit	Average Percent Recovery	Adjusted MDL 1)
di-n-butyl phthalate	5.0	3.7	7.3	13.3	7.2	12.1	5.1	7.2	8.0	3.52	11.1	160	11.1
fluoranthene	5.0	5.5	5.8	4.7	5.5	5.6	5.4	4.2	5.2	0.58	1.8	105	1.8
pyrene	5.0	4.2	4.2	4.7	4.4	4.4	4.2	3.4	4.2	0.40	1.3	84	1.5
butyl benzylphthalate	5.0	1.2	1.4	1.6	1.5	1.8	1.8	1.2	1.5	0.26	0.8	30	2.7
3,3'-dichlorobenzidine	5.0	4.1	3.9	4.2	3.6	3.9	3.8	3.1	3.8	0.37	1.2	76	1.5
benzo(a) anthracene	5.0	4.9	5.1	5.2	4.3	4.9	5.0	3.9	4.8	0.49	1.6	95	1.6
bis(2-ethylhexyl) phthalate	5.0	4.4	4.6	4.5	4.3	5.0	4.6	3.4	4.4	0.48	1.5	88	1.7
chrysene	5.0	4.7	5.0	4.5	4.6	4.2	4.6	3.8	4.5	0.39	1.2	90	1.4
di-n-octyl phthalate	5.0	3.9	4.4	4.5	4.1	4.4	4.4	3.4	4.2	0.39	1.2	83	1.5
benzo (b) fluoranthene	5.0	4.1	4.3	4.7	4.4	4.4	4.7	3.7	4.3	0.33	1.0	86	1.2
benzo (k) fluoranthene	5.0	5.0	5.2	4.9	4.4	4.7	4.7	3.6	4.7	0.52	1.6	93	1.7
benzo (a) pyrene	5.0	4.2	4.5	4.5	4.0	4.5	4.6	3.5	4.2	0.39	1.2	85	1.4
indeno(1,2,3-cd) pyrene	5.0	3.8	4.3	4.0	3.8	4.1	4.2	3.2	3.9	0.37	1.2	78	1.5
dibenz(a,h) anthracene	5.0	3.5	3.9	3.7	3.3	3.8	3.8	3.0	3.6	0.34	1.1	71	1.5
benzo(ghi) perylene	5.0	4.3	4.7	4.7	4.1	4.7	4.5	3.6	4.3	0.40	1.3	87	1.5

1) Note: No provision exists in the above protocol for evaluation of the determined MDL with respect to analyte recovery. An 'Adjusted MDL,' taking into account the Average Percent Recovery, is also given.

LAB SOP
SVOC PART B
LIQUID - LIQUID EXTRACTION

STANDARD OPERATING PROCEDURE FOR CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

This method serves to isolate organic compounds from aqueous samples, by employing a solvent which has a density greater than that of the aqueous sample. The final extract is suitable for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

A one liter aliquot of sample is acidified to pH = 2 ($\pm$0.5), extracted with methylene chloride and partially concentrated using a continuous liquid-liquid extractor-concentrator. The methylene chloride extract is then concentrated to a final volume of 1.0 mL using a micro Snyder apparatus.

3.0 SAFETY MEASURES

All general laboratory safety precautions apply. Safety glasses, gloves, and a lab coat should be worn when handling solvent, samples, sample extracts, and standards. All work should be performed in the hood. Safety glasses must always be worn in the laboratory. The Material Safety Data Sheets (MSDS) should be consulted for toxicity information.

4.0 INTERFERENCES

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

5.0 APPARATUS AND MATERIALS

Extraction

5.1 Continuous liquid-liquid extractor, Pyrex One-Step Extractor-Concentrator (Corning Modular, Heavier than Water, 3928-M, or equivalent).

5.2 Jacketed Kuderna-Danish concentrator tube, Pyrex, 2158-1JTO, or equivalent.

5.3 Drying Adapter, Pyrex, 3940-M, or equivalent.

5.4 Cold water recirculation system, Lauda Circulating Cooling Unit, Model # UKT 1500, or equivalent.

5.5 Hot water recirculation system, Lauda Circulating Heating Unit, Model # M3, or equivalent.

Concentration

5.6 Kuderna-Danish concentrator tube, 10 mL, graduated, Kontes K-570050-1025 or Pyrex 2158, or equivalent.

5.7 Tube heater/concentrator, Kontes 720003-0000, or equivalent.

5.8 Snyder column, three-balled micro, Kontes K569001-0319, or equivalent.

Miscellaneous

5.9 Graduated cylinder, 1000mL.

5.10 Wide-range pH paper.

5.11 Teflon PTFE boiling stones.

5.11.1 Rinse boiling stones with methylene chloride three times, and bake them at 100°C for one hour prior to use.

5.12 Vials, 1.5 mL capacity with Teflon©-lined screw cap.

6.0 REAGENTS

6.1 Reagent water: ASTM Type II water, aka Super Q water.

6.2 Sulfuric acid (H_2SO_4) solution (1:1): Combine equal volumes of concentrated sulfuric acid and reagent water.

6.3 Acetone, methylene chloride: Pesticide residue analysis grade, commercially available.

6.4 Sodium sulfate, anhydrous (Na_2SO_4): granular, 12-60 mesh, JT Baker 3375-5 (or equivalent).

6.4.1 Purify by heating at 500°C for four hours in shallow crucibles,

6.4.2 Cool to 110°C for approximately one hour. Store in glass.

7.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

All samples must be kept at ≤ 4° Celsius from the time of collection until extraction. Extraction must be completed within seven days of the date of sampling.

8.0 PROCEDURE

8.1 Rinse the drying adaptor three times with acetone and three times with methylene chloride.

8.2 Place a glass wool plug just below the bulb of the adaptor.

8.3 Pour approximately 35 g of sodium sulfate into the bulb and rinse the bulb with two separate 60mL volumes of methylene chloride.

Continuous liquid-liquid extraction

8.4 Rinse all glassware three times with acetone then three times with methylene chloride.

8.5 Assemble with a jacketed Kuderna-Danish concentrator tube placed between the Snyder column and the Kuderna-Danish flask of the adaptor.

8.6 Close the stopcock in the crossover tube and add 600 mL methylene chloride to the bottom of the extractor body.

8.7 Measure 1.0 L of sample into a 1L graduated cylinder. Check the pH of the sample with wide-range pH paper.

8.7.1 If the pH is >2.0, adjust it to 2.0 (±0.5), using 1:1 sulfuric acid.

8.8 Add 1.0 mL of the Surrogate Spiking Standards described in **General Requirements for Organic Extraction and Sample Preparation** to the sample and mix well. Add the mixture to the extractor body.

8.9 Start the hot water recirculation pump (circulating water through a jacket surrounding the concentrator tube) and allow it to reach 85°C-90°C.

8.10 Open the stopcock of the crossover tube, to allow solvent into the K-D flask and the concentrator tube.

8.11 Let the extraction system proceed uninterrupted for 18 hours.

Concentration

8.12 After 18 hours, close the stopcock of the crossover tube to eliminate the recirculation of solvent into the K-D flask and the concentrator tube.

8.13 Let the hot water recirculation pump run until the extract in the concentrator tube is reduced to a volume of 2-4 mL.

8.14 Turn off the hot water recirculation pump. Cool the extract for 10 minutes.

8.15 Detach the jacketed Kuderna-Danish (K-D) concentrator tube from the extraction apparatus and quantitatively transfer the extract to another Kuderna-Danish concentrator tube.

8.15.1 Rinse the jacketed K-D concentrator tube with 3-5 mL methylene chloride and add the rinsate to the extract in the new K-D tube.

8.16 Add one or two clean boiling chips and attach a three-ball micro-Snyder column to the K-D tube. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column.

8.17 Place the K-D apparatus in the tube heater/concentrator. Adjust the heater so that the temperature ranges from 85°C to 90°C.

8.18 When the apparent volume of the extract reaches ~0.5 mL, remove the K-D apparatus from the tube heater/concentrator and allow to cool for 10 minutes.

8.19 Remove the Snyder column and rinse its lower joint with 0.2 mL of methylene chloride. Combine the rinsate with the extract in a vial with a Teflon-sealed screw-cap.

8.20 Adjust the extract final volume to 1.0 mL, label the vial with the ENCOTEC identification for the sample, and store at 4°C. The extract is ready for analysis for semivolatiles.

9.0 QUALITY CONTROL

9.1 Method Blank: Fortify a 1L aliquot of reagent water with the Surrogate Spiking Standards and carry it through the continuous liquid-liquid extraction and concentration procedures with every batch of samples prepared.

9.2 Laboratory Control Sample: Once for every 20 samples extracted (or once every 30 days, whichever occurs more frequently) fortify a 1L aliquot of reagent water with the Surrogate Spiking Standards and with the Matrix Spiking Solutions described in **General Requirements for Organic Extraction and Sample Preparation**. Carry the fortified aliquot through the extraction and concentration procedures as if it were a sample.

9.3 Matrix Spike/Matrix Spike Duplicate: Once for every 20 samples extracted (or once every 30 days, whichever occurs more frequently) fortify two additional 1L aliquots of one sample with the Surrogate Spiking Standards and the Matrix Spiking Solutions. Carry the two fortified aliquots through the extraction and concentration procedures with the unfortified sample.

10.0 REFERENCES

10.1 Test Methods for Evaluating Solid Waste, USEPA SW-846, July 1992.

10.2 Corning, Pyrex One-Step Extractor-Concentrator Technical Information, Operating Instructions, Document No. 3928-M.

11.0 PROVENANCE

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LAB SOP
pH
METHOD 150.1

pH ELECTRODE METHOD

A. INTRODUCTION

1. Applicability: This method is applicable to aqueous samples without significant amounts of particulates, oils or greases and where the aqueous phase constitutes at least 20% of the total volume of the waste.

2. Purpose of Testing: pH is a parameter which helps to establish corrosivity and/or reactivity of a substance. When the substance is a waste, the information becomes useful in determining proper storage, transport, and disposal. It is also helpful for the safe and proper handling of the waste in the course of performing other analyses.

3. Method Detection Limit: Method range is 1.0 s.u. to 14.0 s.u. Report all pH measurements by electrode to the nearest 0.1 s.u.

4. Reference Methods: RCRA SW-846, 3rd edition, Rev. 0, Method 9040.

5. Summary of Method: An aliquot of sample is tested with a pH meter using a pH combination electrode.

6. Interferences:

   a. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

   b. Soils and oils may inhibit activity at the membrane. The electrode should be kept as free from such materials as possible.

   c. Temperature effects on the electrometric determination of pH arise from the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation.

7. Sample Collection and Preservation: Samples usually are examined for pH on arrival.

8. Holding Time: 24 hours.

9. Safety Precaution: Most waste samples being analyzed for pH are known or suspected hazardous wastes. Extreme caution should be exercised when handling these samples. Lab coats, safety glasses, gloves, and fume hoods are strongly recommended.

The following significant modification(s), relative to the referenced method(s), are noted for the preceding section.

- Holding time is specified as 24 hours. In cases where pH is determined in the field, it should be determined "immediately". However, practicality dictates that a holding time of 24 hours be specified for the laboratory.

B. APPARATUS

1. pH meter with temperature sensor for automatic compensation

2. pH electrode and reference electrode, temperature probe (combination electrode)

3. 100mL beakers

4. Stir plate and Teflon-coated stir bar

No significant modification(s) relative to the referenced method(s) are noted for the preceding section.

C. REAGENTS AND STANDARDS

1. Primary Standard Buffers: traceable to NIST standards, at pH 4,7,10.

2. Secondary Standard Buffers: traceable to NIST standards as are primary buffers but obtained from a different source.

No significant modification(s) relative to the referenced method(s) are noted for the preceding section.

D. METHOD

Calibration

1. Calibrate the pH meter between two buffer solutions, either 4 and 7 or 7 and 10, depending on the suspected pH of the sample.

   a. In order to calibrate, enter the theoretical values of each buffer into the pH meter. Read the low buffer.

   b. Allow the reading to equilibrate and set it equal to the theoretical value.

c. Read the high buffer and repeat the same operation.

d. Once this is done, read both buffers. They should be within 0.05 s.u. of the theoretical values. Repeat calibration until this is so.

Sample Analysis

2. Place a sufficient volume of sample in the beaker to cover the electrode's sensing elements and to give adequate clearance for the magnetic stir bar.

3. Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrode into the sample beaker and gently stir at a constant rate to provide homogeneity and suspension of (any) solids. Allow the reading to equilibrate.

4. Repeat measurement on successive volumes of sample until values differ by <0.1 pH units. Disregard smaller fluctuations in precision.

   a. Two or three volume changes are usually sufficient.

5. Record the pH, noting that the value is entered in the pH determination log.

6. If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to the manufacturer's instructions.

No significant modification(s) relative to the referenced method(s) are noted for the preceding section.

E. CALCULATIONS

1. pH is read directly from the pH meter.

F. QUALITY CONTROL

1. Matrix Duplicate: Since the procedure calls for repeated measures until two consecutive measurements differ by no more than 0.1 pH unit, all aqueous samples are measured in duplicate.

2. Calibration Verification: A standard buffer from a secondary source (see C. 2 above) should be used to check the validity of the calibration. This buffer should be chosen such that it corresponds to the range calibrated

(i.e. pH 4 and 7, pH 7 and 10) and agree within 0.05 pH units of the theoretical pH. Calibration verification should be performed with each batch of samples analyzed.

G. **PROVENANCE**

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