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FILE PLAN
9.3

OU-1/OU-2
SAMPLING AND ANALYSIS PLAN
FOR THE
KN ENERGY GAS COMPRESSOR STATION
CASPER, WYOMING

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1.0 INTRODUCTION

This OU-1/OU-2 Sampling and Analysis Plan (SAP) is designed to "insure that sample collection and analytical activities are conducted in accordance with technically acceptable protocols" (EPA, 1991). The large amount of information and site history developed and reported in prior studies of the KN Energy Gas Compressor Station (KN Facility) and the Mystery Bridge Road/U.S. Highway 20 Superfund Site (Site) and in the past and current remedial activities, have been summarized here, but not reported in detail. The relevant information is provided in the documents listed in Section 5.0 of this SAP. Additional details concerning specific activities are provided in the OU-2 Phase I Workplan (ABC, 1993a), the Remedial Action Groundwater Monitoring Plan (GMP) (ABC, 1993b), the Operation and Maintenance Plan (ABC, 1993c), the Revised Air Sparging Report (Air Sparging Report) (ABC, 1993d), and to a lesser extent in the Site Safety Plan (SSP) (ABC, 1992b). This SAP should be read in conjunction with those documents.

1.1 SITE BACKGROUND

KN has operated the KN Facility since 1965. In 1985, groundwater under and immediately north of the KN Facility was found to contain trace amounts of dissolved hydrocarbons that were suspected to have originated, in part, from the KN Facility (Ecology and Environment, 1987). The constituents of concern at the KN Facility are benzene, ethylbenzene, toluene, and xylene (BETX) for which the maximum contaminant levels (MCLs) are listed in Table 1.

Table 1 Maximum Contaminant Levels for BETX

Constituent	MCL (mg/l)
Benzene	0.005
Ethylbenzene	0.7
Toluene	1
Xylenes	10

Source: EPA Drinking Water Regulations and Health Advisories, December 1992

Since November 1989, KN has undertaken a removal action at the KN Facility, which is part of the Site. EPA divided the Site into two operable units: Operable Unit One (OU-1), which addresses groundwater remediation, and Operable Unit Two (OU-2), which addresses remediation of source areas.

KN's removal action consisted of groundwater pump and treat (PAT) and soil vapor extraction (SVE) systems that remove hydrocarbons via three phases: free floating product, groundwater, and soil vapor. The SVE system extracts vapor phase hydrocarbons from the unsaturated interval between the water table and the ground surface. The PAT system pumps groundwater to the surface where volatile hydrocarbons are removed by air stripping. Floating product, when present, is removed from the groundwater extraction wells when the PAT system is in operation. As part of OU-1, the removal action was selected as the remedy for the KN Facility.

This SAP consists of a Field Sampling Plan (FSP), which "provides guidance for all fieldwork by defining in detail the sampling and data-gathering methods to be used on a project," and a Quality Assurance Project Plan (QAPP), that "describes the policy, organization, functional activities, and quality assurance and quality control protocols necessary to achieve Data Quality Objectives (DQOs) dictated by the intended use of the data." (EPA, 1991). The elements of the SAP are outlined in Table 2.

Table 2 Elements of the Sampling and Analysis Plan (EPA, 1991)

SAP	
FSP	QAPP
Defines in detail the sampling and data gathering methods that will be used during the site characterization.	Describes the project objectives & organization, functional activities, and quality assurance and quality control(QA/QC) protocols.
Will Include: 1. Sampling objectives 2. Sample locations & frequency 3. Sampling equipment & procedures 4. Sample handling and analysis	Will Include: 1. Sampling procedures 2. Sample Custody 3. Analytical Procedures 4. Data Reduction 5. Validation 6. Reporting

1.2 REMEDIAL ACTION OBJECTIVES

1.2.1 OU-1 Objectives

The selected remedy for OU-1 as it pertains to KN is designed to eliminate the threat to public health posed by the constituents of concern in groundwater emanating from the KN Facility. The work performed by KN pursuant to the Consent Decree (CD) shall achieve the following objectives:

1. Remediate groundwater so that concentrations shall not exceed Maximum Contaminant Levels (MCLs) and proposed MCLs, as set forth in the ROD for BETX; and

2. The area of attainment shall include the entire BETX plume, including those areas of the plume within and outside the KN Facility.

1.1.2 OU-2 Objectives

The overall objective for OU-2 at the KN Facility is to "[e]nsure long-term effectiveness and permanence of OU-1 remediation by eliminating the sources of groundwater contamination at the site, such as contaminated subsurface soils or free product (excluding

sources associated with the groundwater plume extending from the LARCO property into the Brookhurst Subdivision), so that the concentration in groundwater of contaminants originating from these sources never exceed Maximum Contaminant Levels (MCLs) or proposed MCLs" (EPA, 1991).

2.0 FIELD SAMPLING PLAN

2.1 SAMPLING OBJECTIVES

2.1.1 OU-1 Sampling Objectives

The objectives of OU-1 sampling are:

1. To monitor the operational status of the remedial system by sampling extracted soil gas, extracted groundwater, treated groundwater, and air discharge in accordance with the Groundwater Monitoring Plan (GMP) (ABC, 1993b); and

2. To gather data to evaluate the near-term and long-term performance of the PAT and SVE systems by sampling the groundwater at designated locations in accordance with the GMP.

2.1.2 OU-2 Sampling Objectives

The objectives of OU-2 sampling are:

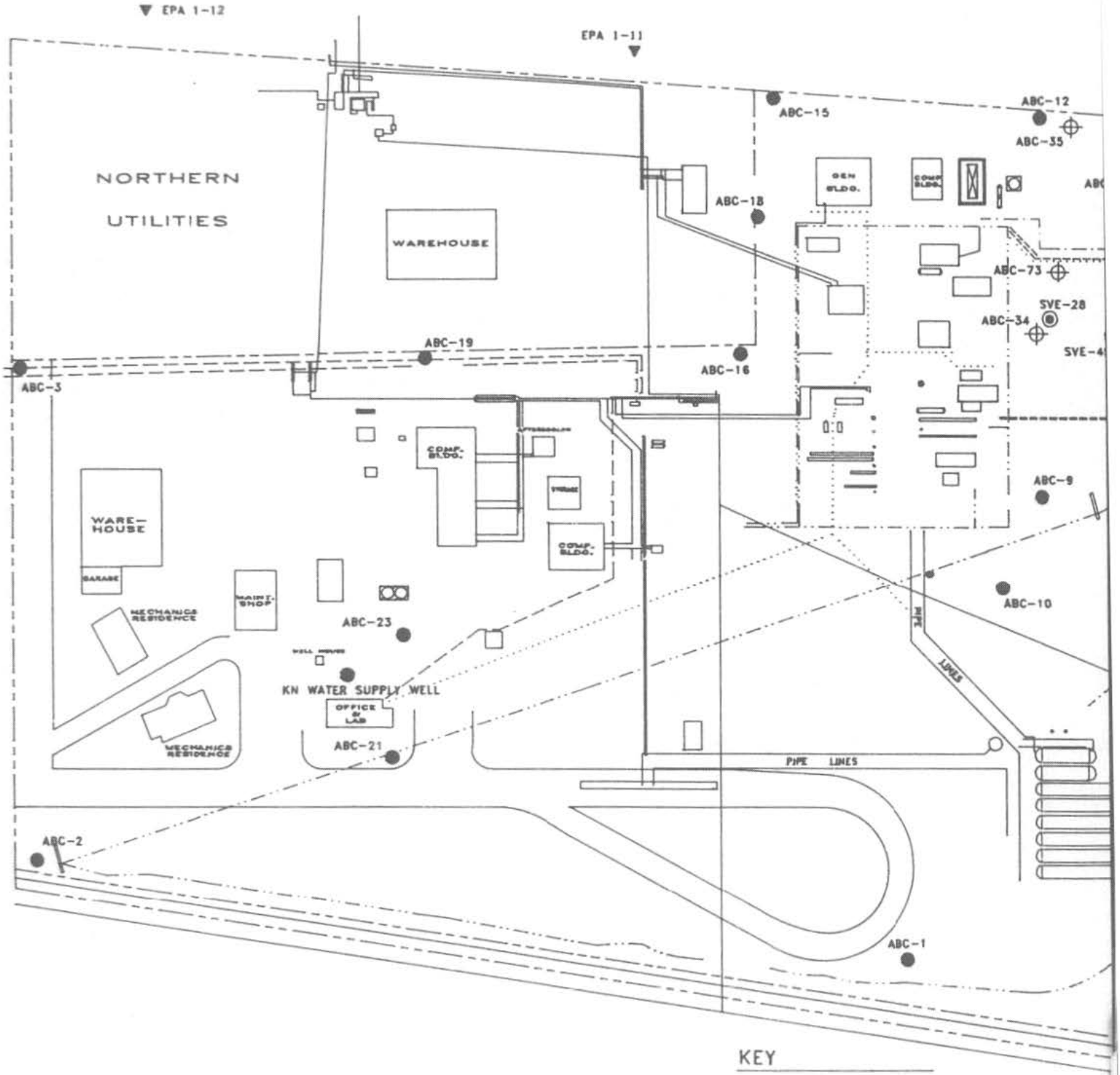
1. To confirm the current soil condition by drilling boreholes for soil sampling; and

2. To monitor the operation of the full-scale air sparging program by sampling groundwater and soil gas.

2.2 SAMPLE LOCATIONS AND FREQUENCY

2.2.1 OU-1 Sampling

Groundwater monitoring wells and groundwater extraction wells will be sampled from amongst the wells shown in Figure 1 as set forth in the GMP (ABC, 1993b). In addition to sampling the groundwater wells, the treated groundwater, soil gas and stripping column air will be sampled from points located in the treatment building. The soil gas and stripping column air are sampled following the same procedures. The locations and frequency of sampling are provided in the GMP (ABC, 1993b) and the Operation and Maintenance Plan (OMP) (ABC, 1993c).



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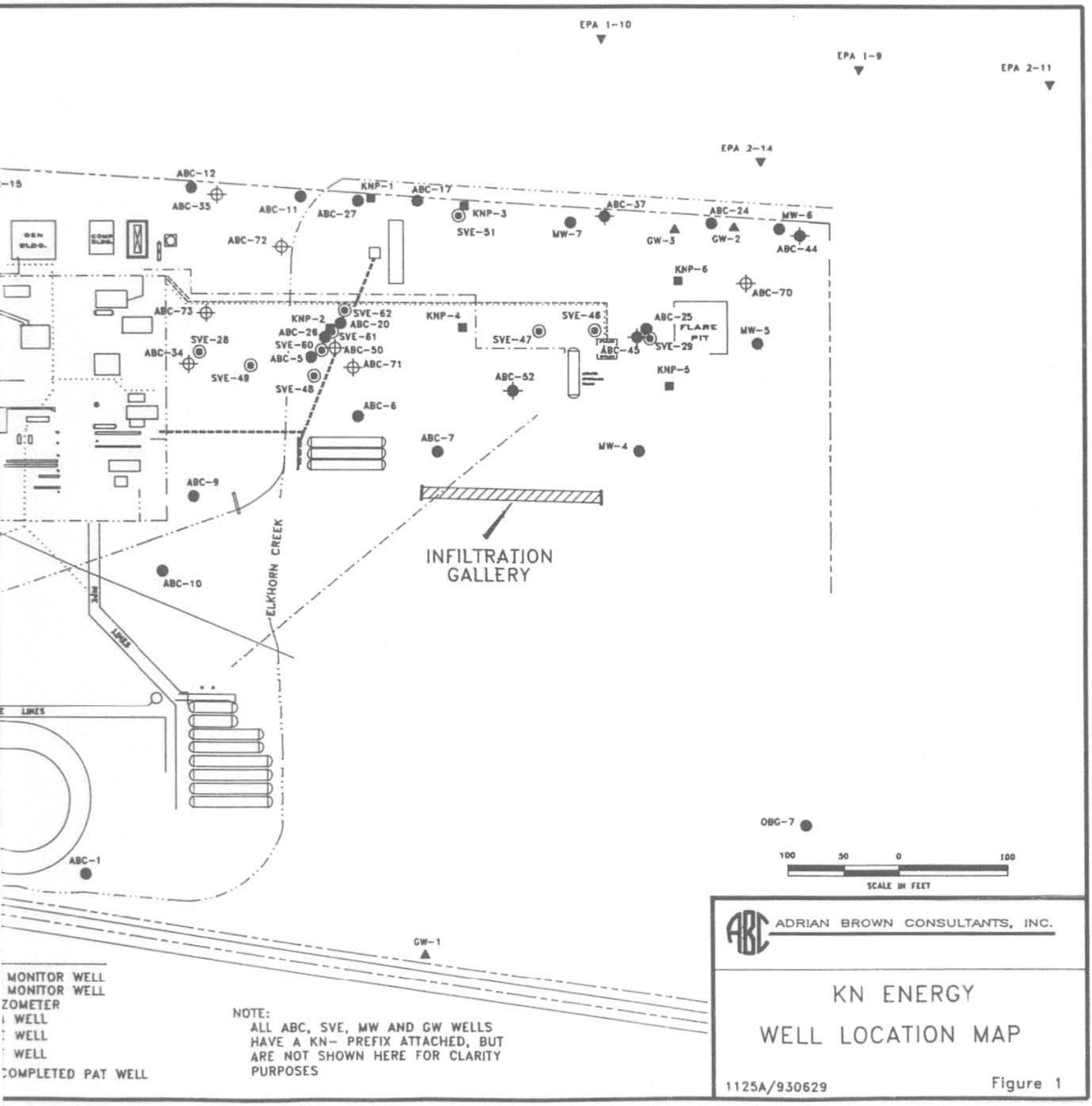

MONITOR WELL
MONITOR WELL
ZOMETER
WELL
WELL
WELL
COMPLETED PAT WELL

NOTE:
ALL ABC, SVE, MW AND GW WELLS HAVE A KN- PREFIX ATTACHED, BUT ARE NOT SHOWN HERE FOR CLARITY PURPOSES

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KN ENERGY
WELL LOCATION MAP

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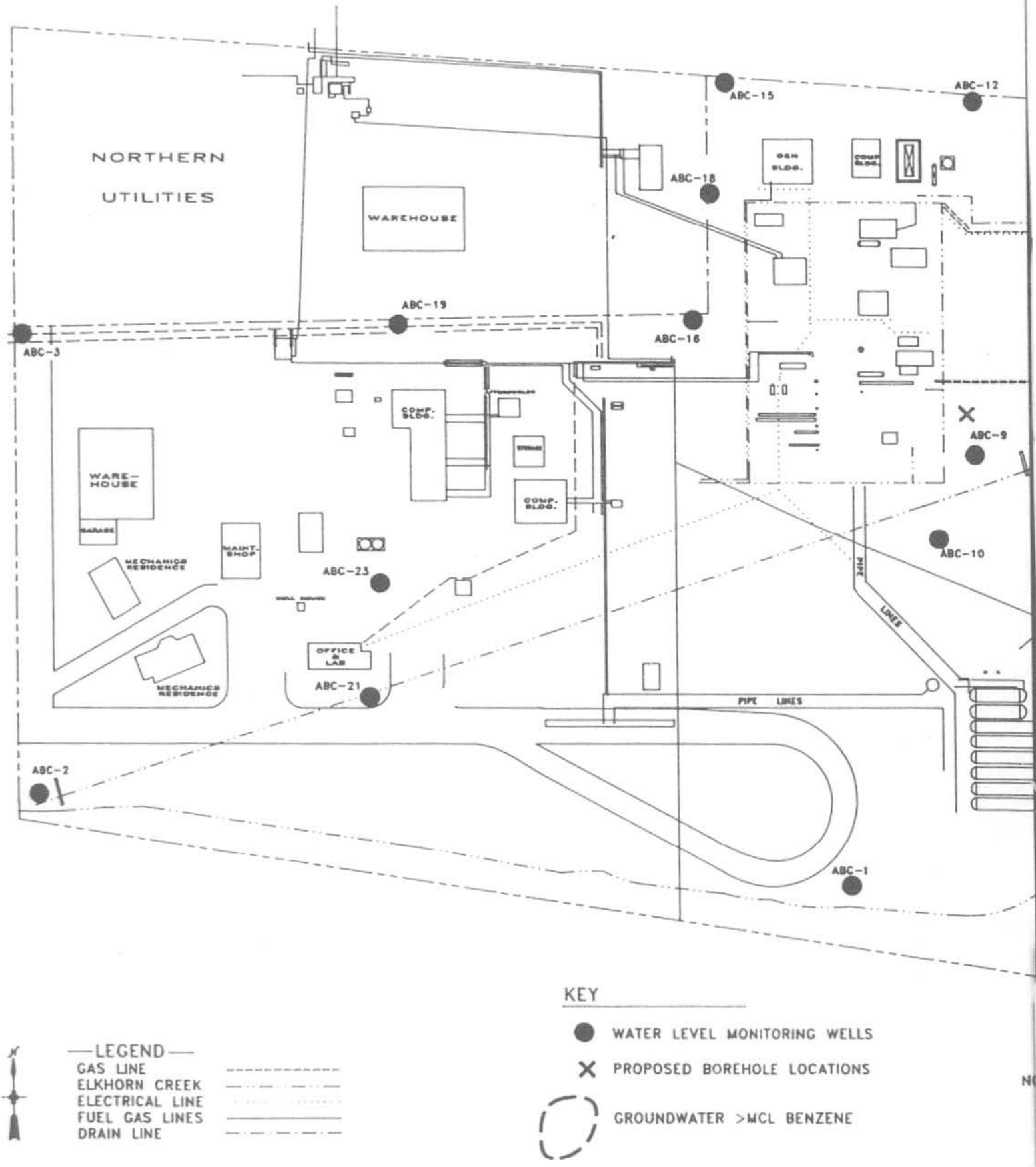
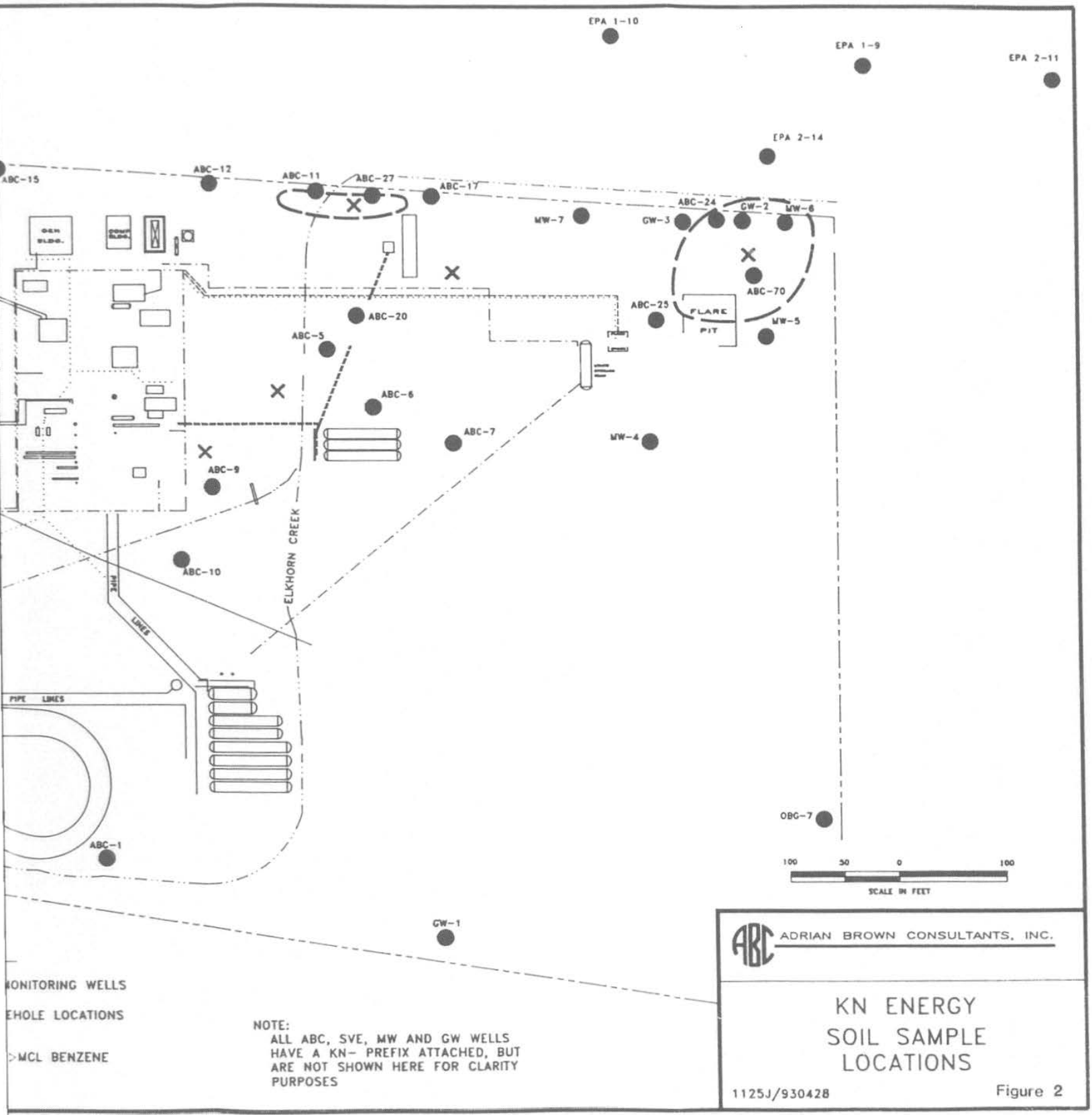
Figure 1

2.2.2 OU-2 Sampling

Soil samples to confirm the current and post-air sparging soil conditions at the KN Facility will be collected from the locations shown in Figure 2 as set forth in the OU-2 Phase I Workplan (ABC, 1993a). Sampling for operational monitoring purposes during the air sparging program will include collecting samples from amongst the groundwater monitoring wells shown in Figure 1 and from amongst the SVE wells shown in Figure 3. Specific locations and frequencies are set forth in the Revised Air Sparging Report (ABC, 1993d).


NORTHERN
UTILITIES
WAREHOUSE
ABC-15
ABC-12
ABC-18
ABC-19
ABC-16
ABC-3
ABC-9
ABC-10
ABC-23
ABC-21
ABC-2
ABC-1
WARE-HOUSE
GARAGE
MAINT. SHOP
MECHANICS RESIDENCE
COMP. BLDG.
OFFICE & LAB
PIPE LINES
24IN LINES
—LEGEND—
GAS LINE
ELKHORN CREEK
ELECTRICAL LINE
FUEL GAS LINES
DRAIN LINE
KEY
WATER LEVEL MONITORING WELLS
PROPOSED BOREHOLE LOCATIONS
GROUNDWATER >MCL BENZENE



ONITORING WELLS

EHOLE LOCATIONS

>MCL BENZENE

NOTE:
ALL ABC, SVE, MW AND GW WELLS HAVE A KN- PREFIX ATTACHED, BUT ARE NOT SHOWN HERE FOR CLARITY PURPOSES

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KN ENERGY
SOIL SAMPLE LOCATIONS

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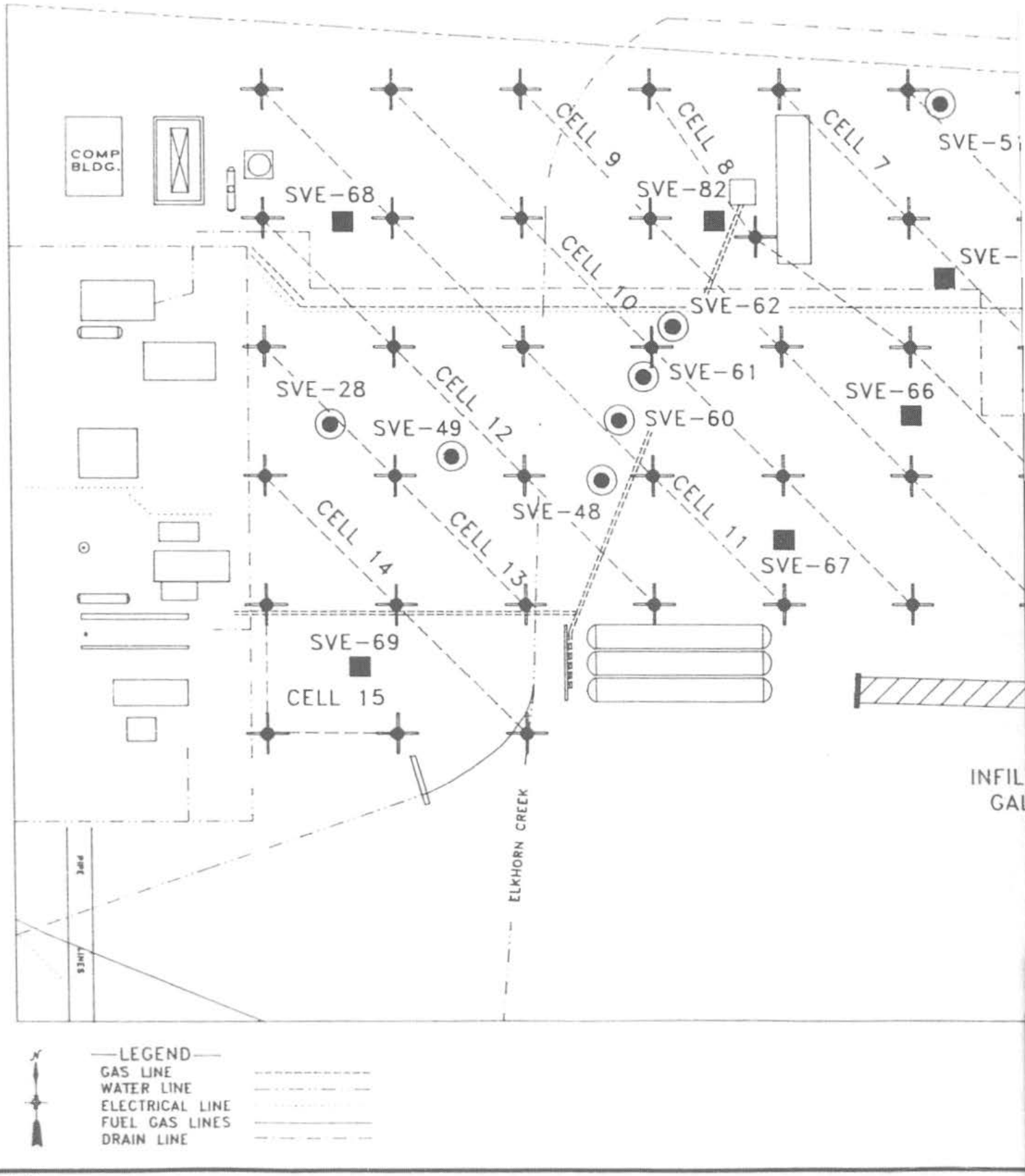
Figure 2



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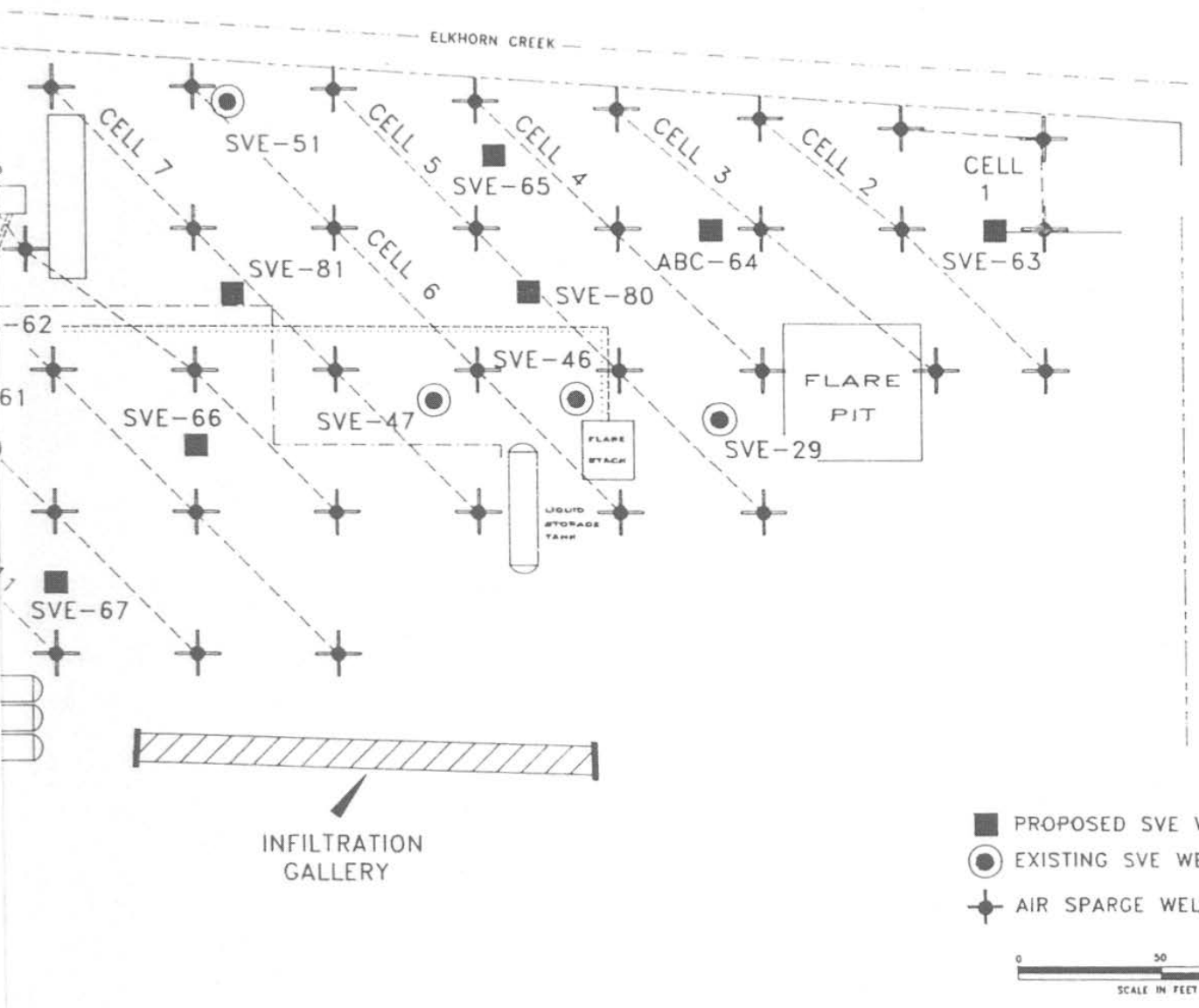

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KN ENERGY EXISTING AND PROPOSED SVE WELLS

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Figure 3

3.0 ANALYSIS PLAN

Split samples will be collected in conjunction with regular samples for data quality verification purposes. Every tenth sample will be split and submitted to a second laboratory and analyzed utilizing the same methodology to verify reliability. The data quality will be assessed as described in Section 4.8, and the precision is expected to fall within the parameters of Table 3 or corrective action as described in Section 4.9 will be taken.

3.1 ANALYSIS OF BETX IN SOIL

Each soil sample to be analyzed will be collected in a brass sleeve and sealed with a teflon liner to preserve volatiles (See SOP SLS023). For each analysis, a minimum of 10 grams of soil is required, and must be analyzed within 14 days of collection. Soil samples will be analyzed for BETX by EPA Method 8260 modified to include selected ion monitoring (SIM) (Appendix A).

3.2 ANALYSIS OF BETX IN GAS

Each gas sample will be collected in a Tenex tube as set forth in SOP AIRO22. Each sample collected is 50 ml in volume and must be analyzed within 7 days of collection. Gas samples will be analyzed for BETX by EPA Method 8260 (Appendix A).

3.3 ANALYSIS OF BETX IN GROUNDWATER

Each groundwater sample will be collected in a 40 ml VOA vial with zero headspace as set forth in SOP GWS016, SOP SAM039, or SOP TWS040. Each sample collected is 40 ml in volume and must be analyzed within 14 days of collection. Groundwater samples will be analyzed for BETX by EPA Method 8260 (Appendix A).

4.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

4.1 INTRODUCTION

This QAPP has been prepared to assure that all data collected during the investigation is sufficient and reliable to meet the objectives of the project. Specific variables that may affect data reliability are:

1. Sampling Procedures
2. Sample Custody
3. Analytical Procedures
4. Data Reduction
5. Data Validation
6. Data Reporting

The goals of the QAPP are to address these specific variables and present policies, requirements, and objectives to assure precision, accuracy, completeness, and representativeness of all laboratory and field determinations (EPA, 1991). Sections of the laboratory QA/QC addressing these specific variables can be found in Appendix C.

4.2 PROJECT ORGANIZATION AND RESPONSIBILITY

The following personnel will be responsible for acquisition of field data, measurements, personnel safety, and routine evaluation of quality assurance procedures.

Adrian Brown - Project Coordinator, Senior Engineer, Senior Hydrogeologist, Project Quality Assurance Manager

Joseph Pollara - OU-1 and OU-2 Project Manager, and Project Health and Safety Officer

Armand Morris - Environmental Geologist, and Site Equipment Manager

Lorraine Miller - Corporate Health and Safety Officer

A corporate organizational chart for overall project management is shown in Figure 4.

4.3 QUALITY ASSURANCE OBJECTIVE

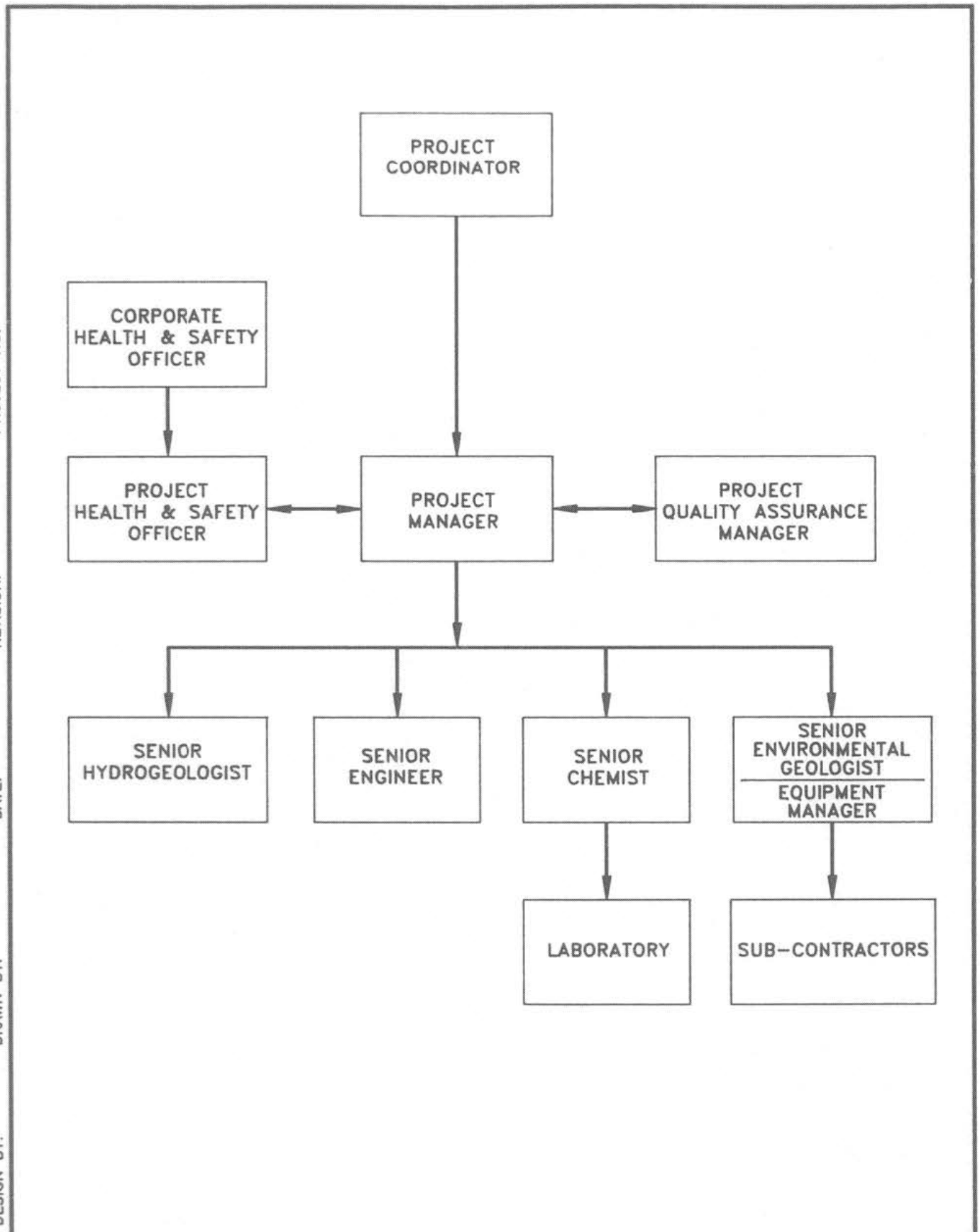
The QAPP is written to maintain consistent quality of technical data. This objective will be achieved by using formal standardized procedures for collecting, documenting, analyzing, and reporting laboratory and field data. Activities to accomplish this objective are discussed below in Sections 4.4 through 4.10.

The data quality objective for this project is to perform sampling and analysis in such a way as to identify the BETX concentrations in samples of soil, soil gas, stripping tower air, and groundwater with precision to within detection limits. This will allow evaluation of the status of the samples when compared with the relevant ARARS. Detection and precision levels are found in Table 3.

Table 3 BETX Detection and Precision Levels

MATRIX	LAB
BETX in Soil: Detection Precision	 10 ppb ± (10 ppb + 20%)
BETX in Gas: Detection Precision	 1 ppb ± (1 ppb + 20%)
BETX in Water: Detection Precision	 1 ppb ± (1 ppb + 20%)

These precisions and detections will be adequate for the purposes of this project.



PROJECT NO.

REVISION:

DATE:

DRAWN BY:

DESIGN BY:

ADRIAN BROWN CONSULTANTS, INC.

PROJECT ORGANIZATION CHART

Figure 4

4.4 METHODS OF MEETING QUALITY ASSURANCE OBJECTIVES

Any procedural error made in the field will probably result in lower BETX levels in the sample than actually exist in the field. To meet the Quality Assurance Objectives (QAOs), the following steps will be taken.

4.4.1 Field Sampling Procedures

The following samples will be collected during the OU-1 and OU-2 activities:

- subsurface soils
- soil gas
- groundwater (monitoring well and pumping well)
- stripping tower air
- treated groundwater

Procedures for data acquisition, when appropriate, will be consistent with Adrian Brown Consultant's Standard Operating Procedures (SOP). Data quality objectives will be met by following these SOPs. These SOPs ensure QAOs because they effectively eliminate the loss of BETX through volatilization and the possiblity of sample contamination.

1. Soil Sampling: The drilling technique will involve split spoon sampling with the use of a hollowstem auger to bedrock and will be performed according to SOP SLS023. The soil samples will be collected in brass sleeves, covered with teflon sheets, and capped with plastic lids under EPA guidelines provided in SOP SLS023.

2. Gas Sampling: This sampling technique is equal for sampling both soil gas and stripping tower air. The sampling method will employ the use of absorbant media Tenex tubes capped at the end with rubber stoppers. Sampling techniques are set forth in SOP AIR022.

3. Monitoring Well Groundwater Sampling: Groundwater samples will be collected from a Tri-loc pump into a teflon sealed vial with zero headspace. Sampling techniques are set forth in SOP GWS016.

4. Extraction Well Groundwater Sampling: Groundwater samples will be collected from the wellheads of operating groundwater extraction wells as set forth in SOP SAM039.

5. Treated Groundwater Sampling: Treated groundwater will be sampled from the treated water injection side of the sump at the base of the air stripping tower. Sampling procedures are set forth in SOP TWS040.

6. Decontamination: A decontamination area will be set up on site to accommodate cleaning of all equipment and personnel. Decontamination fluids will be collected and disposed of appropriately. Decontamination procedures are outlined in SOP DEC019. The decontamination procedure will be as follows[1]:

   1. Remove gross impacted materials with high pressure hot water rinse and wire brush, if necessary.
   2. Wash equipment with detergent soap and tap water.
   3. Rinse with tap water.
   4. Rinse with methanol.
   5. Rinse with deionized water.

4.4.2 Sample Containers and Preservation

1. Sample Containers and Volume: Appropriate containers for specific analytical procedures are listed in Table 3. Preservation, required volumes, and recommended holding times are also indicated on this table. All containers for field samples are washed in conjunction with the procedures set by EPA for quality controlled Level II certified sample containters.

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[1] EPA commented that the decontamination procedure in the original KN QAPP (submitted in December 1987) did not include a triple hexane rinse and air dry procedure prior to a triple deionized water rinse. The use of a triple hexane rinse of drilling and sampling equipment had previously been considered and was rejected. This decision was based in part on Phase I results which demonstrated, through field blanks, that constituents of concern were adequately removed from field equipment. An important factor in deciding not to use hexane in the field is based on its potent neurotoxicity effects, particularly in combination with other n-alkanes which may be present. In addition, hexane effectively removes the natural protective oils from skin, should there be accidental contact, and increases the potential for dermatitis.

Table 4 Sample Containers, Preservation and Volume

Parameter	Container	Preservation	Absolute Minimum Sample Volume	Holding Time
Sample Type:				
Soil: Volatile Organics	Brass sleeves	4°C	10 grams	14 days
Gas: Volatile Organics	Tenex tubes	4°C	50 ml	7 days
Water: Volatile Organics	40 ml VOA vial	4°C, no headspace	40 ml	14 days

2. Sample Labeling: At the time each sample is collected, the sample containers will be labeled in the following manner:
Labels: 8 Digit Number
1,2 Sample Type
SL=Soil
WA=Water
AR=Air
3,4 Location
EW=Extraction Well
TW=Treated Water
MW=Monitoring Well
HL=Drill Hole
ST=Stripping Tower
5,6 Identifier
##=Hole Number
##=Well Number
7,8 Sequence
##=Sample Number
OR ##= Depth (soil samples)

E.g. FPHL2601 = floating product, hole 26, sample #1

4.4.3 Calibration

None

4.4.4 Sample Handling and Custody

1. Chain-of-Custody: All samples shipped for analysis will be documented with a chain-of-custody (COC) form. A blank COC form can be found in Appendix D. During field sampling activities, traceability of the sample must be maintained from the time the samples are collected until final laboratory results are reported. Initial information concerning collection of the samples will be recorded in the field log book as described above. Information on the custody, transfer, handling, and shipping of samples will be recorded on a COC form.

   The sampler will be responsible for initiating and filling out the COC form. The COC form will be signed by the sampler when the sampler relinquishes the samples to anyone else. The person responsible for delivery of the samples to the laboratory will sign the COC form, retain the last copy of the three-part COC form, document the method of shipment, and send the original and the second copy of the COC form with the samples. Upon receipt at the laboratory, the person receiving the samples will sign the COC form and return the second copy to the Project Manager. Copies of the COC forms documenting custody changes and all custody documentation will be received and kept in the central files. The original COC forms will remain with the samples until final disposition of the samples by the laboratory.

   Sample handling procedures will ensure QAOs by eliminating tampering, mistaken sample identities, and recording holding times.

2. Sample Packaging and Shipping: Samples will be shipped by overnight courier to the laboratory for next day arrival. Sample will be packaged according to SOP SAM020 for water, SOP SAM041 for soil, and SOP SAM042 for air. Copies of all shipment records will be retained as required in the Consent Decree. Shipment of samples will comply with United States Department of Transportation regulations.

4.4.5 Field Sampling and Handling Log Books

At the end of each day's activity, the field log book will contain a detailed record of the daily program with signed and dated entries for each day that sampling and field activities occurred. At a minimum, the following information, when appropriate, will be entered in the field log book:

- Dates
- Times
- A list of ABC, client, government, and subcontractor personnel on site
- Weather conditions
- Any unusual circumstances
- Subcontractor progress and/or problems, results of subcontractor inspections
- Notes regarding any changes to the SAP, QAPP, or Site Safety Plan
- A list of samples collected (by sample number), sampling points, and analyses to be obtained
- The lot number and a copy of the certification of cleanliness for sample bottles
- Identification of quality assurance samples (blanks, duplicates, overspikes, etc.)
- A list of samples shipped and their destination
- COC tape numbers and form numbers associated with each batch of samples shipped
- Any notes or elaboration required to clarify sample logs, boring logs, and other related records
- Results of field screening of samples
- Time of occurrence and nature of any malfunctions of field measurement instruments

Information in the field log book will be supplemented by information on field forms for each respective activity (i.e., log of borehole, COC, etc.).

4.4.6 Lab Procedures

Quality assurance objectives for laboratory and field data will be expressed in terms of precision, accuracy, and completeness. Laboratory analyses will meet the objectives for the SW-846 Test Methods for Solid Waste, 3rd Edition. As defined under SW-846 by EPA Method 8260, laboratory reports will include internal QA/QC expressed in terms of precision and accuracy. All relevant laboratory documentation will be maintained in the laboratory's file as required by the Consent Decree.

Table 5 Laboratory Program Analytical Procedures

Parameter	Matrix	Method	Reference
Volatile Organics	Soil	8260* SIM	40 CFR 261
Volatile Organics	Soil Gas	8260	40 CFR 261
Volatile Organics	Water	8260	40 CFR 261

40 CFR 261: Federal Register, App. 3, EPA, 40 CFR Part 261, Section 4.3.2, July 1, 1991.

*EPA Method 8260 will be modified to incorporate Selective Ion Monitoring (SIM) if necessary to achieve the lower limits of detection.

4.4.7 Internal Quality Control Checks

Quality Assurance/Quality Control (QA/QC) procedures are designed to provide consistency in the technical data quality as well as to help identify any potential sources of sample contamination which may be introduced by sample collection, sample handling, or laboratory analytical techniques. Confidence in the analytical results is directly related to having and following a QA/QC Plan, and also having the documentation demonstrate:

1) Use of clean sampling equipment,
2) Use of clean sample containers,
3) Proper sample collection procedures,
4) Quality of the preservatives used, and
5) COC protocol followed.

Internal quality control provides specific measures for both laboratory and field measurements to ensure data reliability. QC for laboratory analyses is outlined by the requirements of EPA Method 8260 (Appendix A). Ten percent of the samples collected in the field will consist of QA/QC samples. In the event that less than 10 samples are collected in any given sampling event, one suite of appropriate QA/QC samples will be collected.

The QA/QC suite may be comprised of the following:

- Duplicate samples (minimum 1 per 10 samples)
- Field blanks (minimum 1 per 10 samples)
- Trip blanks (minimum 1 per cooler)

- Split samples (minimum of 10% for Method 8260 and SIM for the laboratory analysis technique)
- Rinsate samples (minimum 1 per borehole drilled)

QA/QC field procedures will include collection of the following samples:

1. One duplicate sample in every ten samples will be collected and submitted to the laboratory. The duplicate is collected alongside any one of the randomly selected primary samples in exactly the same manner with exactly the same matrix. The duplicate sample is assigned a different identification number, has its own documentation, and is stored in the ice chest and shipped in the same manner as the primary sample. The duplicate sampling serves as a check for the natural sample variance and the consistency of field and laboratory techniques.

2. One field blank will be submitted to the laboratory each sampling round. The field blank is prepared at any one of the randomly selected sample sites with distilled water. The field blank bottles are taken empty to the field and filled with distilled water following as closely as possible the same sampling protocol for the collection of a water sample. The field blank serves as a check on field contamination at the sampling site.

3. One equipment or rinsate sample is to be collected upon completion of the bore hole and drill rig decontamination. The rinsate is a collection of the final rinse water and ensures that the equipment does not cause cross-contamination between sample sites.

4. One trip blank will accompany samples from each sampling event. Trip blanks test the integrity of the sample storage, handling and transport procedures and serve to detect any potential contamination which could be introduced by the laboratory. A trip blank accompanies the samples as though it was already collected. Each cooler containing samples will include a trip blank.

The QA/QC samples are generally labeled as described in Section 4.4.2. The sample type abbreviations will be as follows:

Trip Blank - TB
Field Blank - FB
Duplicate Sample - DS
Rinseate Sample - RS

The complete sample number for the QA samples should be noted in the field log book.

4.5 DATA REDUCTION, VALIDATION, AND REPORTING

4.5.1 Data Reduction

Procedures for data reduction will be performed by the subcontracting laboratory as specified in Table 5. All data submitted by the laboratory will be reviewed by the Project Quality Assurance Manager to verify that appropriate units are assigned to all concentration values. In addition to the reduction of laboratory data, further data reduction may include graphing the data using existing software such as Quattro-Pro. If necessary, simple descriptive statistics (mean and standard deviation) may be performed.

4.5.2 Data Validation

Analytical and field measurement data will be validated by reviewing results from the quality control samples which were discussed in Section 4.4.7 and the results of laboratory-generated QA data. Objectives for quality control samples collected in the field will be consistent with the laboratory objectives for precision and accuracy as outlined in the EPA SW-846 Methods and Phoenix Analytical Laboratory, Inc. (PAL) QA/QC for analysis of chemical parameters (See Appendices A and C). Field quality control samples which do not meet the objectives for precision and accuracy will be documented in the monthly progress report along with any possible explanation for the discrepancies. Procedures for handling quality control problems are discussed in Section 4.9.

4.5.3 Data Reporting

All analytical data reports will be forwarded to the Project Quality Assurance Manager who will compile the data and check

quality control results. Any obvious data errors beyond the EPA tolerance levels, such as exceedence of holding times, laboratory instrument anomalies, or laboratory technique errors shall be noted and included in any reports submitted to EPA.

4.6 PERFORMANCE AND SYSTEM AUDITS

4.6.1 Performance Audits

1. An onsite audit will be conducted during the soil sampling portion of the OU-2 program.

2. An onsite audit will be conducted during the soil gas sampling portion of the OU-2 program.

3. An onsite audit will be conducted during the groundwater sampling portion of the OU-1 program.

4. An audit of laboratory QC will be accomplished by reviewing the results from the soil, soil gas, and groundwater samples. This audit will include the QC requirements of EPA Method 8260, including a check on holding times, instrument calibrations, and spike recoveries.

4.6.2 System Audits

1. An onsite audit will be performed when the full-scale air sparging system is put online.

2. Quarterly audits will be performed during the air sparge system operation.

These audits will consist of a system check, including air flow rates checking to make sure gauges are working to verify that the sparge system is operating properly. The results of these audits will be noted and reported to EPA in the Phase I Summary Report.

4.6.3 Organization of Auditors

All audits will be performed by the Project Quality Assurance Manager to determine that the required level of QC is maintained during operations. Any QC problems will be reported to the Project Manager who will decide if corrective action is required. If corrective action is necessary, then the appropriate actions will be discussed with the Project Coordinator.

4.7 PREVENTIVE MAINTENANCE

None.

4.8 DATA ASSESSMENT PROCEDURES

Data quality will be evaluated based on sampling techniques and analytical quality controls. Formalized audits of laboratory and field systems will not be conducted other than the Project Quality Assurance Manager verifying the use of the QAPP procedures. The Laboratory Quality Assurance Director will be responsible for QA/QC protocols. Performance of both field and laboratory QA systems will be based on results of laboratory and field quality control samples. Evaluation of data quality will consider three potential sources of error.

- Gross Errors
- Systematic Errors
- Random Errors

Data quality will be assessed using the following formulas:

- Precision (duplicates) % Difference = $\frac{2\ (D_1 - D_2)}{D_1 + D_2} \times 100$

Where: D_1 = First sample value
D_2 = Second sample value (duplicate)

- Accuracy (spikes samples) % Recovery = $\frac{(0 - X)}{T} \times 100$

Where: 0 = Measured value of sample plus spiked solution
X = Measured value of sample prior to spiking
T = Value of spiking solution

- Completeness % completeness = $\frac{V}{T} \times 100$

Where: V = Number of validated analyses
T = Total number of samples submitted for validation

Objectives for the quality of laboratory and field data will attempt to achieve the limits outlined in the EPA and PAL guidelines. Variance from these limits may require corrective action.

4.9 CORRECTIVE ACTION

The data will be reviewed by the Project Quality Assurance Manager who will report any data anomalies to the Project Manager. The appropriate corrective action will then be decided upon and any data that is rejected or eliminated will be brought to the Project Coordinator's attention.

4.9.1 Invalid Data

Data which is found to be invalid after review according to procedures discussed in Section 4.8 may require corrective action measures depending on the ultimate use of the data. The following corrective action procedures will be available:

- samples will be reanalyzed;
- samples will be recollected for analysis; or
- data will be rejected.

4.9.2 Missing or Destroyed Samples

If the subcontracting laboratory notifies the field team of missing, broken, or lost samples the following sequential actions will be available:

- resampling, if possible; or
- elimination of the data.

Corrective action procedures will be determined by the Project Manager in all cases.

4.10 QUALITY ASSURANCE REPORTS

Data collected during the investigation will be examined according to the procedures outlined in the QAPP. The progress reports will contain appropriate quality assurance data and will be completed and submitted to EPA Region VIII as described in Section 4.5, and the results of the investigation will be provided in a Phase I Summary Report.

5.0 REFERENCES

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ABC, 1993c, Operation and Maintenance Plan for the KN Energy Gas Compressor Station, Casper, Wyoming, Adrian Brown Consultants, Inc., Denver, Colorado, in preparation.

ABC, 1993d, Revised Air Sparging Report for the KN Energy Gas Compressor Station, Casper, Wyoming, Adrian Brown Consultants, Inc., Denver, Colorado, June 1993.

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March 30, 1992

Denise Hosler
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PHOENIX ANALYTICAL LABORATORIES INC.

Client Project: OU-2 Phase I Work Plan
REF: EPA Request for Analytical Rationale

Dear Denise:

The detection limits (PQL's) needed for the project would normally be accessible by EPA 8020, 8020A (Nov. 1990), or EPA 8260. However, as pointed out in all these methods, actual PQL's are matrix-dependent. I have attached a page from Method 8020A which indicates that approximate EQL's (estimated quantification limits) to be expected from high-concentration soil and waste would be around 250 ug/Kg for BTEX, even with MDL's of 0.2 ug/L in low-level water. This occurs because non-BTEX aromatics and other substances in these samples cause such contamination of the analytical system that the sample has to be diluted in order for it to be run.

Data previously collected at your site apparently show detection limits of ca. 500 ug/Kg for BTEX and high levels of non-BTEX hydrocarbons in many of the soils tested. This indicates that a severe matrix limitation exists at this site. The distillation curves that you showed me are consistent with this. It is extremely unlikely that application of EPA 8020 in any of its revisions will allow analysis for BTEX at anywhere near the goal stated for your project. As I have told you, we have had this experience with hydrocarbon-contaminated samples.

We have shown in our laboratory that when EPA 8020 gives PQL's on the order of 500 ug/Kg due to hydrocarbon interference, that modifying EPA 8260 to operate in the selected ion mode is a good way of overcoming this matrix limitation. We have routinely obtained PQL's of 5 ug/Kg and lower in this manner on samples of this type.

Clearly, for samples that do not show the matrix problem, then either EPA 8020 or EPA 8260 can be used to obtain acceptable detection limits.

Sincerely,

John G. Huntington, Ph.D.
Laboratory Director
JGH:jh

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Col. 2	Method detection limit[a] µg/L)
Benzene	3.33	2.75	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

a Using purge-and-trap method (Method 5030).

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs)
FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

EPA METHOD 8260
ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

METHOD 8260

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

1.0 SCOPE AND APPLICATION

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

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

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

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

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

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

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

2.0 SUMMARY OF METHOD

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

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

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

3.0 INTERFERENCES

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

result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

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

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

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

4.0 APPARATUS AND MATERIALS

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

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

4.1.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Traps normally last 2-3 months when used daily. Some signs of a deteriorating trap are: uncharacteristic recoveries of surrogates, especially toluene-d_8; a loss of the response of the internal standards during a 12 hour shift; and/or a rise in the baseline in the early portion of the scan.

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

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

4.1.5 Trap Packing Materials

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

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

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

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

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

4.3 Gas chromatography/mass spectrometer/data system

4.3.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout

desorption and temperature program operation. For some column configuration, the column oven must be cooled to < 30°C, therefore, a subambient oven controller may be required. The capillary column should be directly coupled to the source.

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

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

4.3.2 Gas chromatographic columns

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

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

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

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

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

4.3.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

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

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

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

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

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

4.10 Vials - 2 mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

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

4.13 Spatula - Stainless steel.

5.0 REAGENTS

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

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

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

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

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

5.4.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$ - Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

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

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

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

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

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

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

5.7.2 Add the assayed reference material, as described below.

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

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard

above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

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

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

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

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

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

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

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

5.12 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 5.7 and 5.8). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Calibration standards must be prepared daily.

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

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

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

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

7.2 Chromatographic conditions

7.2.1 General:

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

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

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

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

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

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

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

Initial temperature:	45°C, hold for 2 minutes
Temperature program:	8°C/min to 200°C
Final temperature:	200°C, hold for 6 minutes.

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

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

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

7.3 Initial calibration for purge-and-trap procedure

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50 ng injection or purging of 4-bromofluorobenzene (2 µL injection of the BFB standard). Analyses must not begin until these criteria are met.

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

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

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

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

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

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

where:

A_x = Area of the characteristic ion for the compound being measured.

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

C_{is} = Concentration of the specific internal standard.
C_s = Concentration of the compound being measured.

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

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

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

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

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

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

where:

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

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

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

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

7.4 Daily GC/MS calibration

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

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

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

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

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

where:

$\overline{RF_i}$ = Average response factor from initial calibration.
RF_c = Response factor from current verification check standard.

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

by the permit, then all required analytes must meet the 25% difference criterion.

7.4.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.5 GC/MS analysis

7.5.1 Water samples

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

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

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

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

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

7.5.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial,

the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

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

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

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

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

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

7.5.1.8 Compositing samples prior to GC/MS analysis

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

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

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

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

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

7.5.1.9 Add 10.0 µL of surrogate spiking solution (Section 5.9) and 10 µL of internal standard spiking solution (Section 5.10) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

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

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

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

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

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

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

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

to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

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

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

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

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

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

7.5.1.17 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the

linear range of the curve. Proceed to Sections 7.6.1 and 7.6.2 for qualitative and quantitative analysis.

7.5.2 Water-miscible liquids

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

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

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

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

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

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

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

7.5.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until

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

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

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

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

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

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

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

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

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

7.5.3.1.8 Proceed with the analysis as outlined in Sections 7.5.1.12-7.5.1.17. Use 5 mL of the same organic-free reagent water as in the blank. If saturated peaks occurred

or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.5.3.1.9 For low-concentration sediment/soils, add 10 µL of the matrix spike solution (Section 5.7) to the 5 mL of organic-free reagent water (Section 7.5.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/Kg of each matrix spike standard.

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

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

7.5.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

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

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

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

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

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

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

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

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

7.6 Data interpretation

7.6.1 Qualitative analysis

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

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

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

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

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

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

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

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

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

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting

peaks. Data system library reduction programs can sometimes create these discrepancies.

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

7.6.2 Quantitative analysis

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

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

Water and Water-Miscible Waste:

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

where:

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

Sediment/Soil, Sludge, and Waste:

High-concentration:

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

Low-concentration:

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

where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).
V_i = Volume of extract added (μL) for purging.
W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

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

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

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Required instrument QC is found in the following sections:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.3.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Section 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria specified in Section 7.4.3 and the CCC criteria in Section 7.4.4, each 12 hours.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.3.2 Prepare a QC reference sample to contain 20 µg/L of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of organic-free reagent water.

8.3.3 Four 5 mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Section 7.5.1.

8.3.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte using the four results.

8.3.5 Tables 7 and 8 provide single laboratory recovery and precision data obtained for the method analytes from water. Similar results from dosed water should be expected by any experienced laboratory. Compare s and $\bar{x}$ (Section 8.3.4) for each analyte to the single laboratory recovery and precision data. Results are comparable if the calculated standard deviation of the recovery does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater, and the mean recovery lies within the interval $\bar{x} \pm 3S$ or $\bar{x} \pm 30\%$, whichever is greater.

NOTE: The large number of analytes in Tables 7 and 8 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.3.6 When one or more of the analytes tested are not comparable to the data in Table 7 or 8, the analyst must proceed according to Section 8.3.6.1 or 8.3.6.2.

8.3.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.3.2.

8.3.6.2 Beginning with Section 8.3.2, repeat the test only for those analytes that are not comparable. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.3.2.

8.4 For aqueous and soil matrices, laboratory established surrogate control limits should be compared with the control limits listed in Table 9.

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

8.4.1.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.4.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.4.1.3 If no problem is found, re-extract and re-analyze the sample.

8.4.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

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

9.0 METHOD PERFORMANCE

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

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

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

10.0 REFERENCES

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

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

TABLE 1.
(Continued)

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

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

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

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

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

TABLE 1.
(Continued)

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

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

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

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

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

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

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

TABLE 2.
(Continued)

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

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

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

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

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

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

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

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

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

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

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

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

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

TABLE 5.
(Continued)

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

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

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

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

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

TABLE 7.
(Continued)

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

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

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

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

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

TABLE 8.
(Continued)

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

* Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

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

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

[a] Single laboratory data for guidance only.

TABLE 10.

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SAMPLES

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

Calculate appropriate dilution factor for concentrations exceeding this table.

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

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

FIGURE 1.
PURGING DEVICE

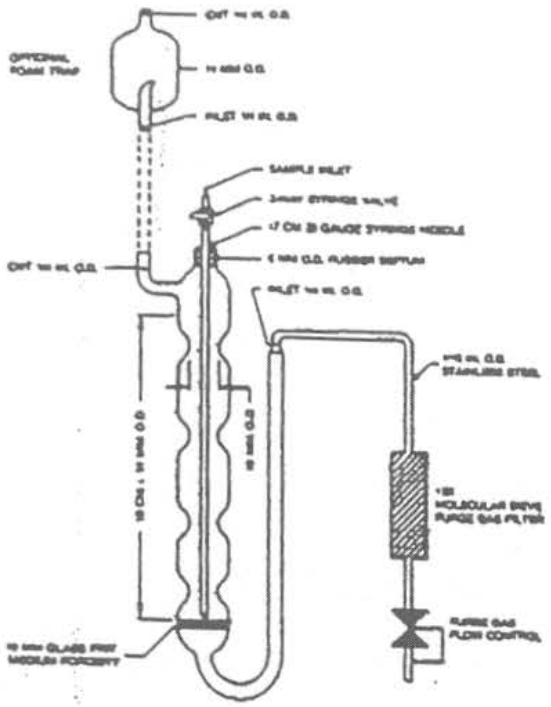


FIGURE 2.
TRAP PACKING AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

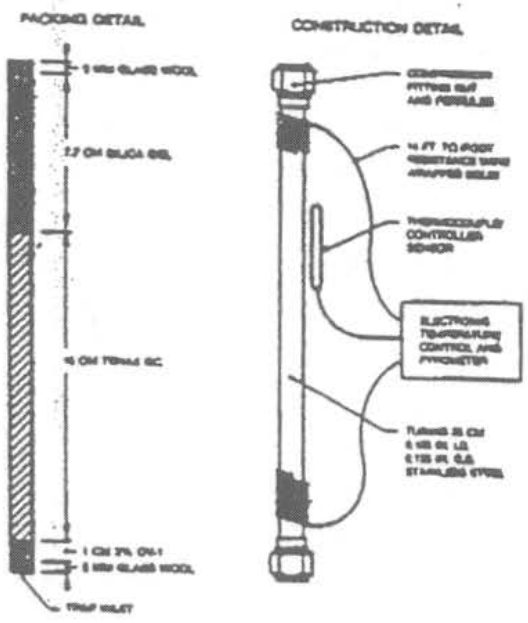


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE

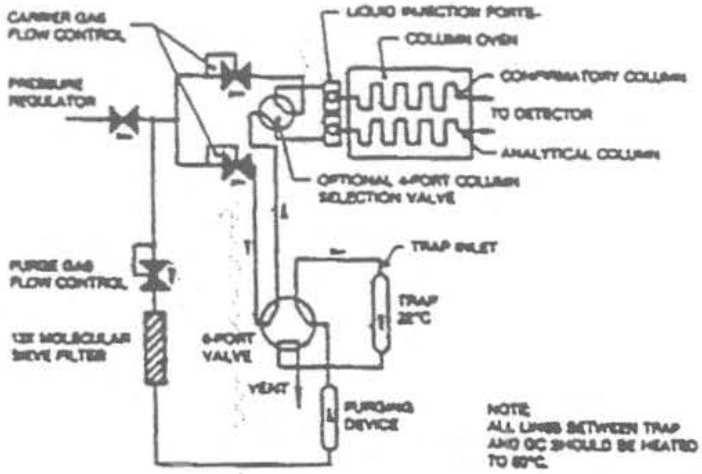


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

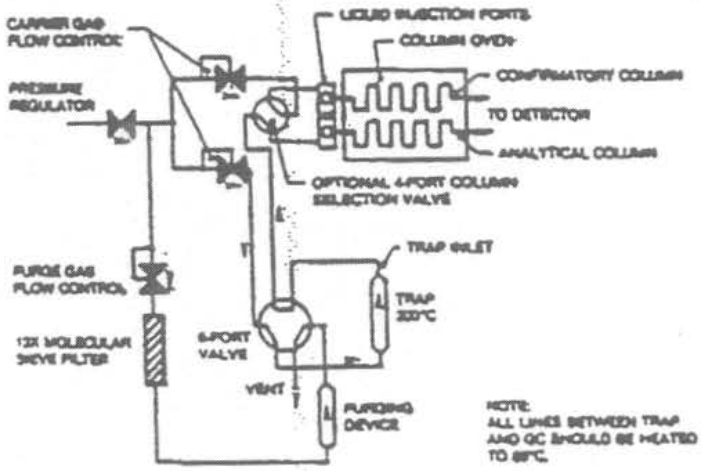


FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

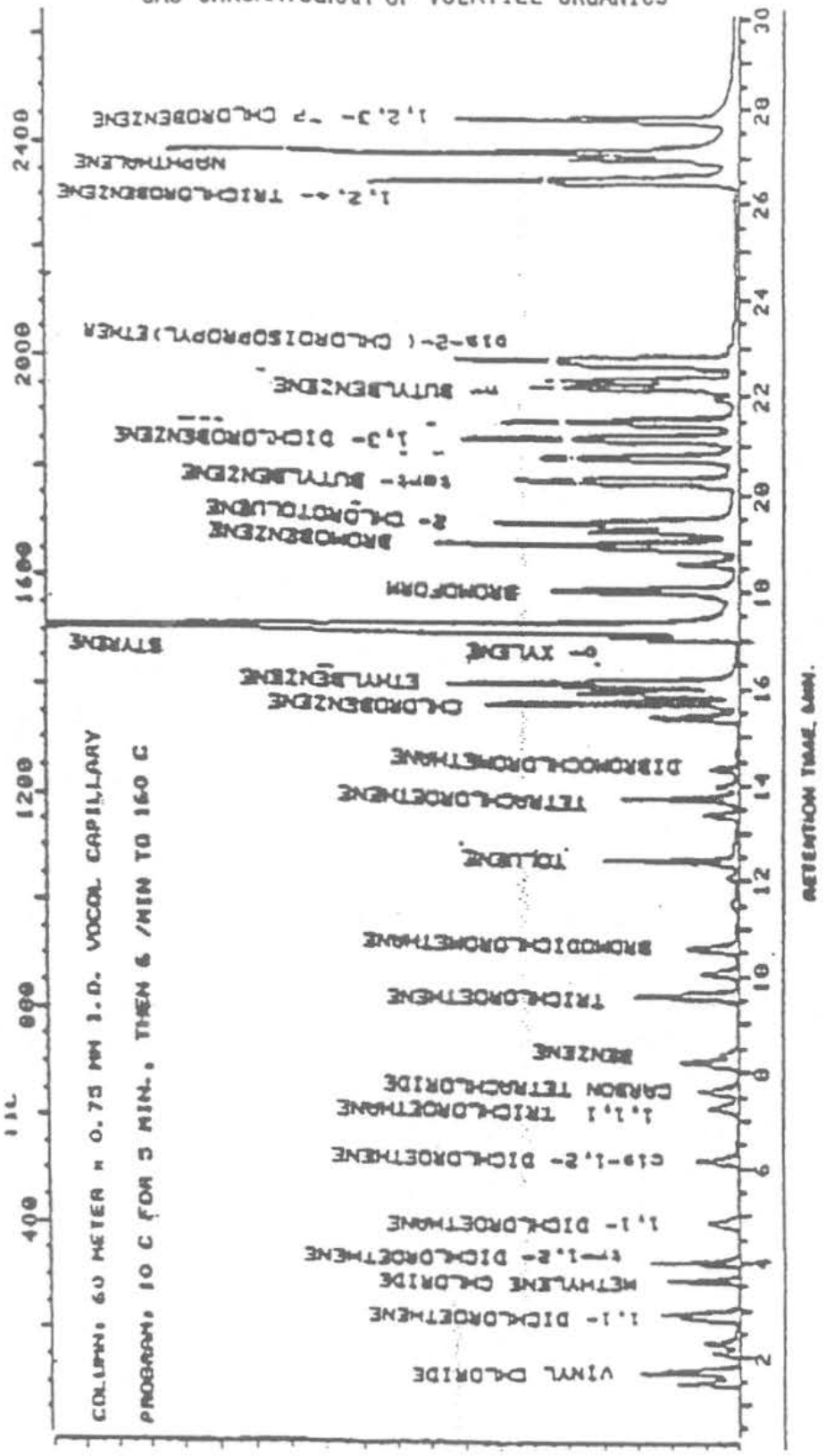


FIGURE 6.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

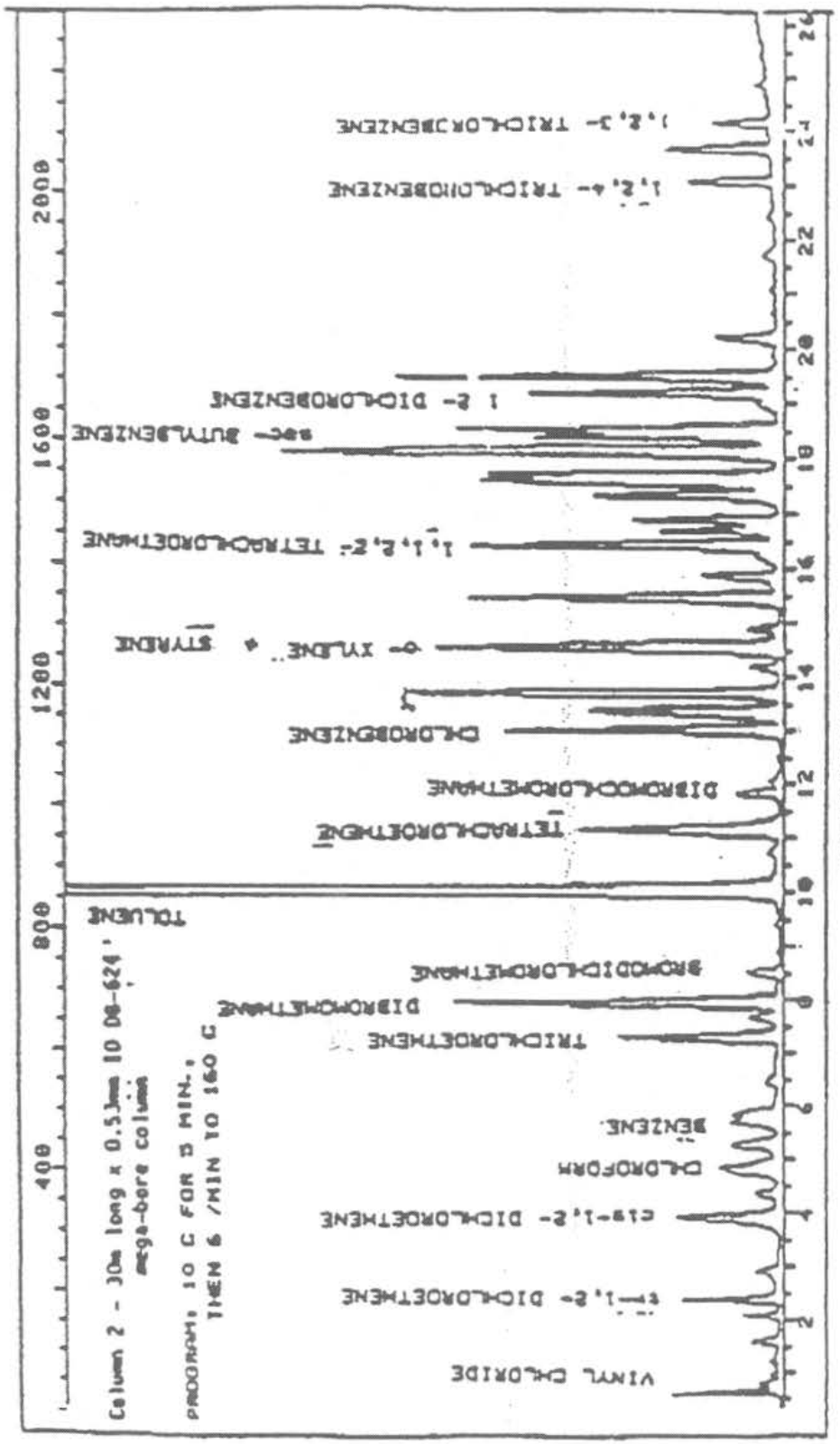


FIGURE 7.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

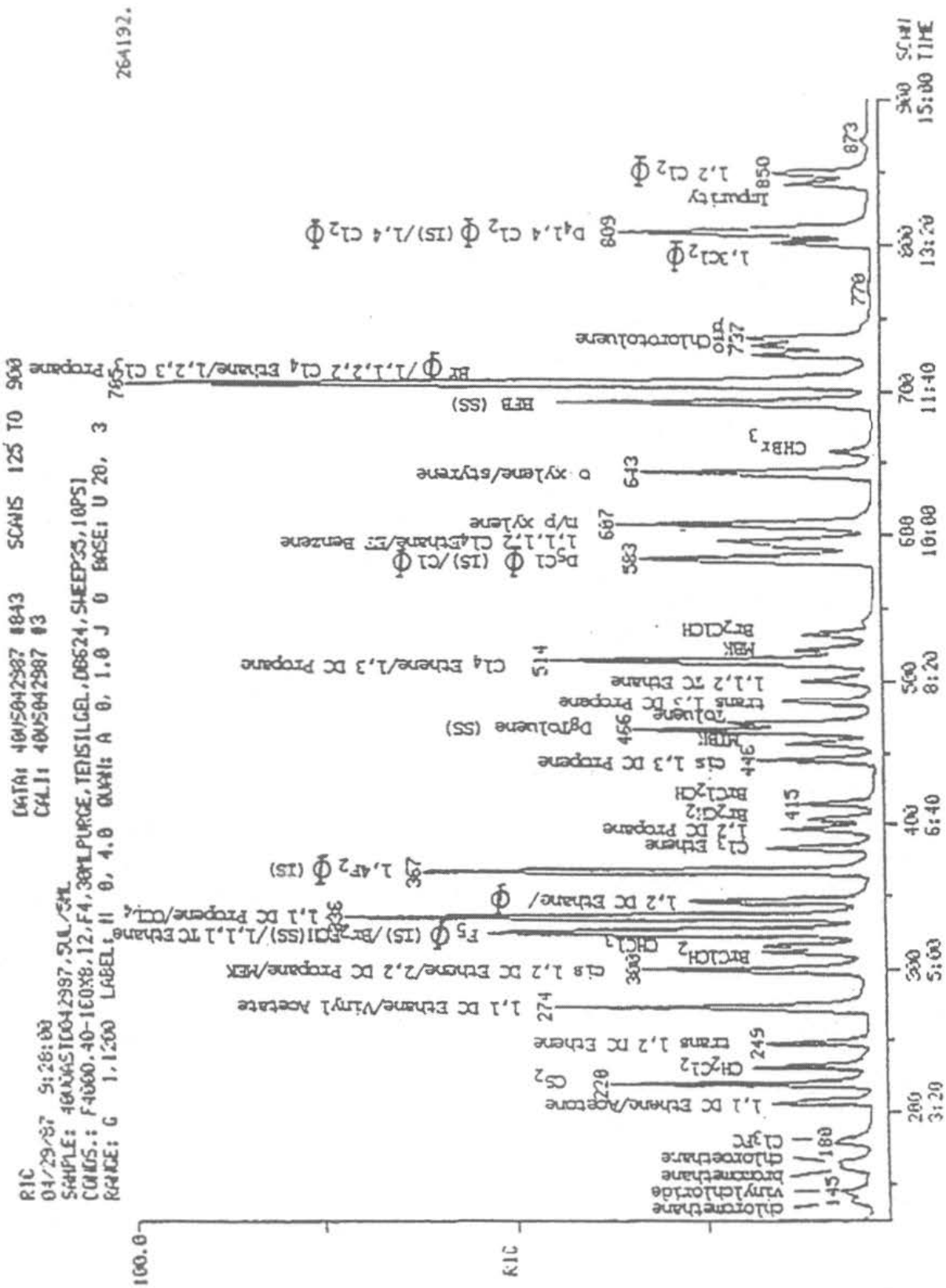


FIGURE 8.
GAS CHROMATOGRAM OF TEST MIXTURE

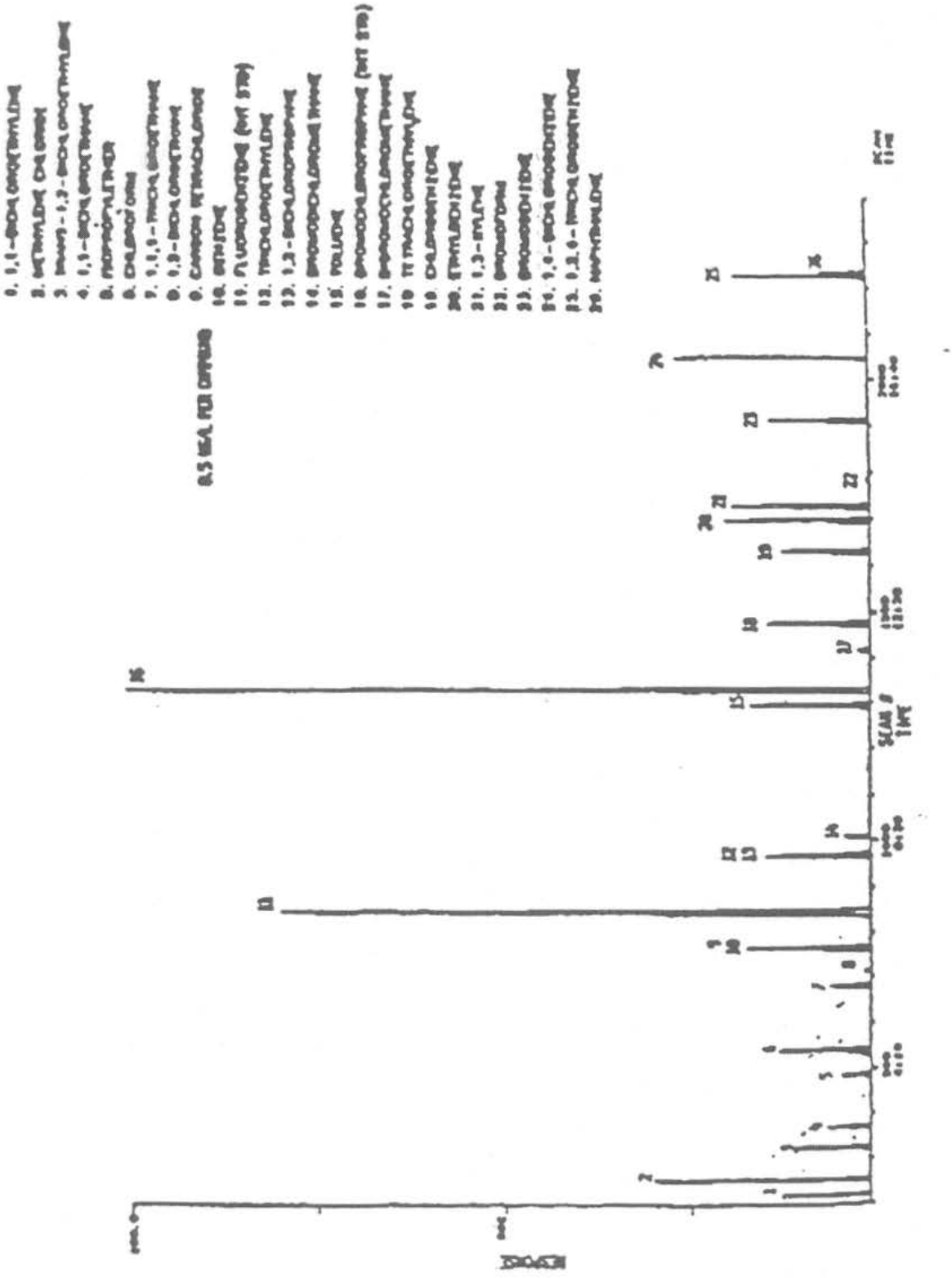
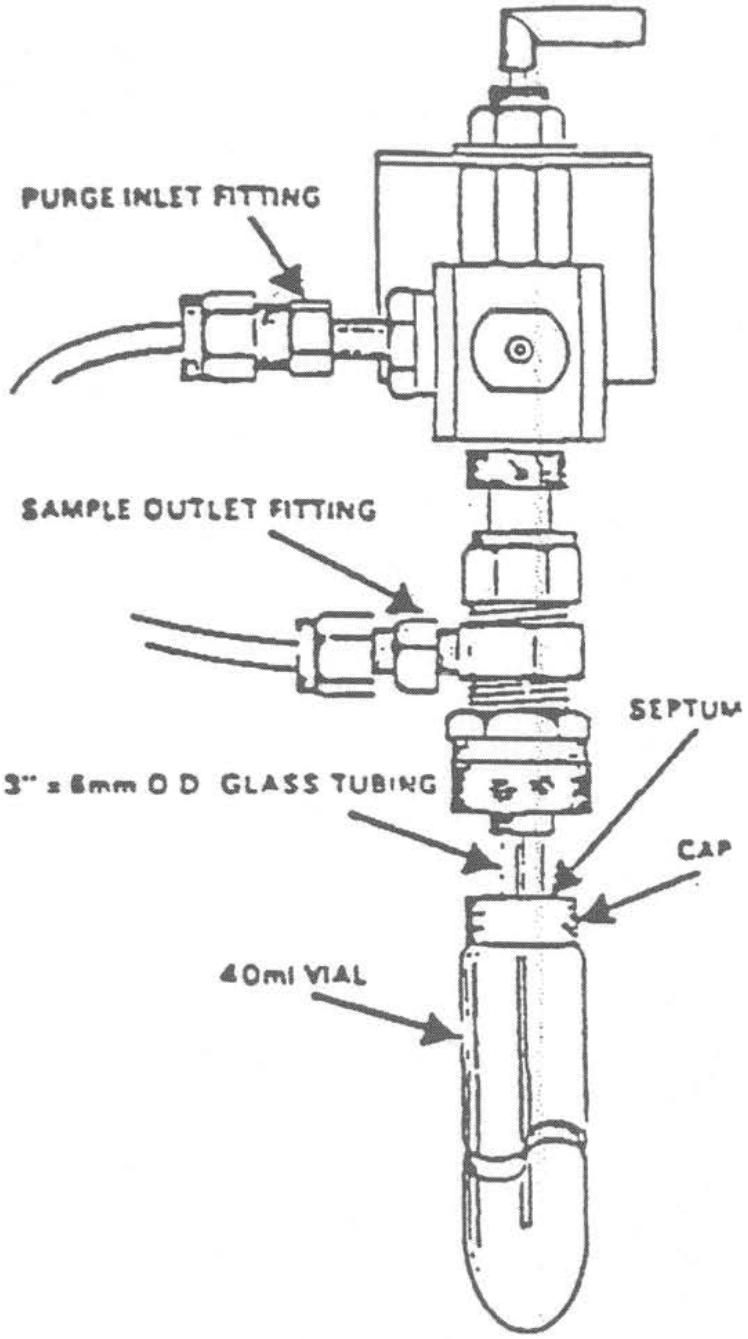
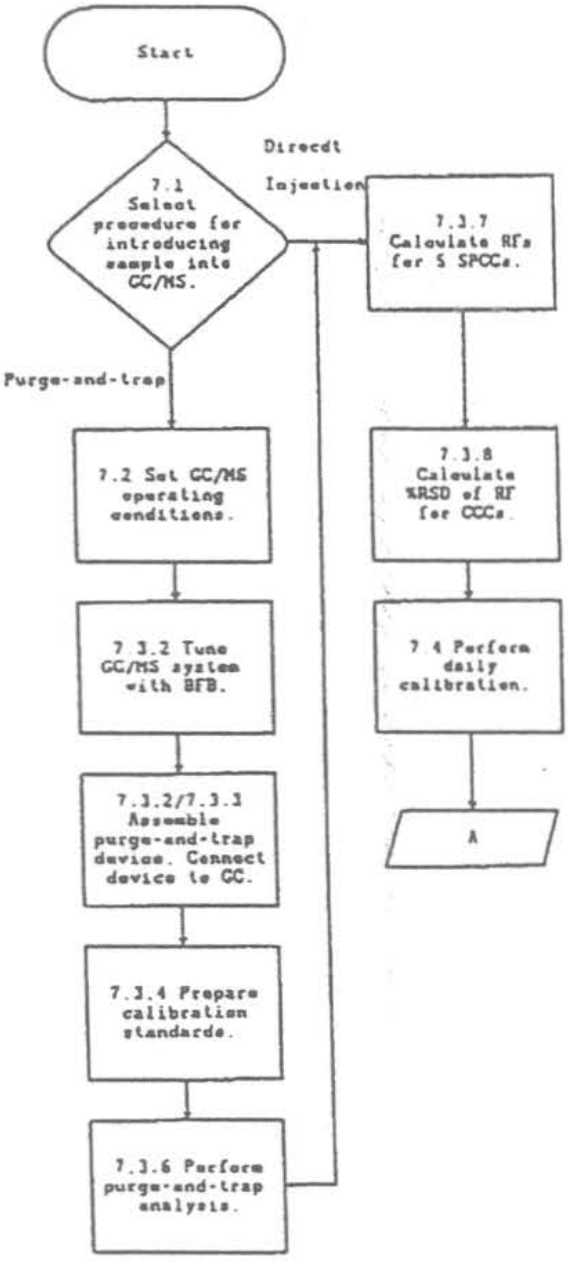
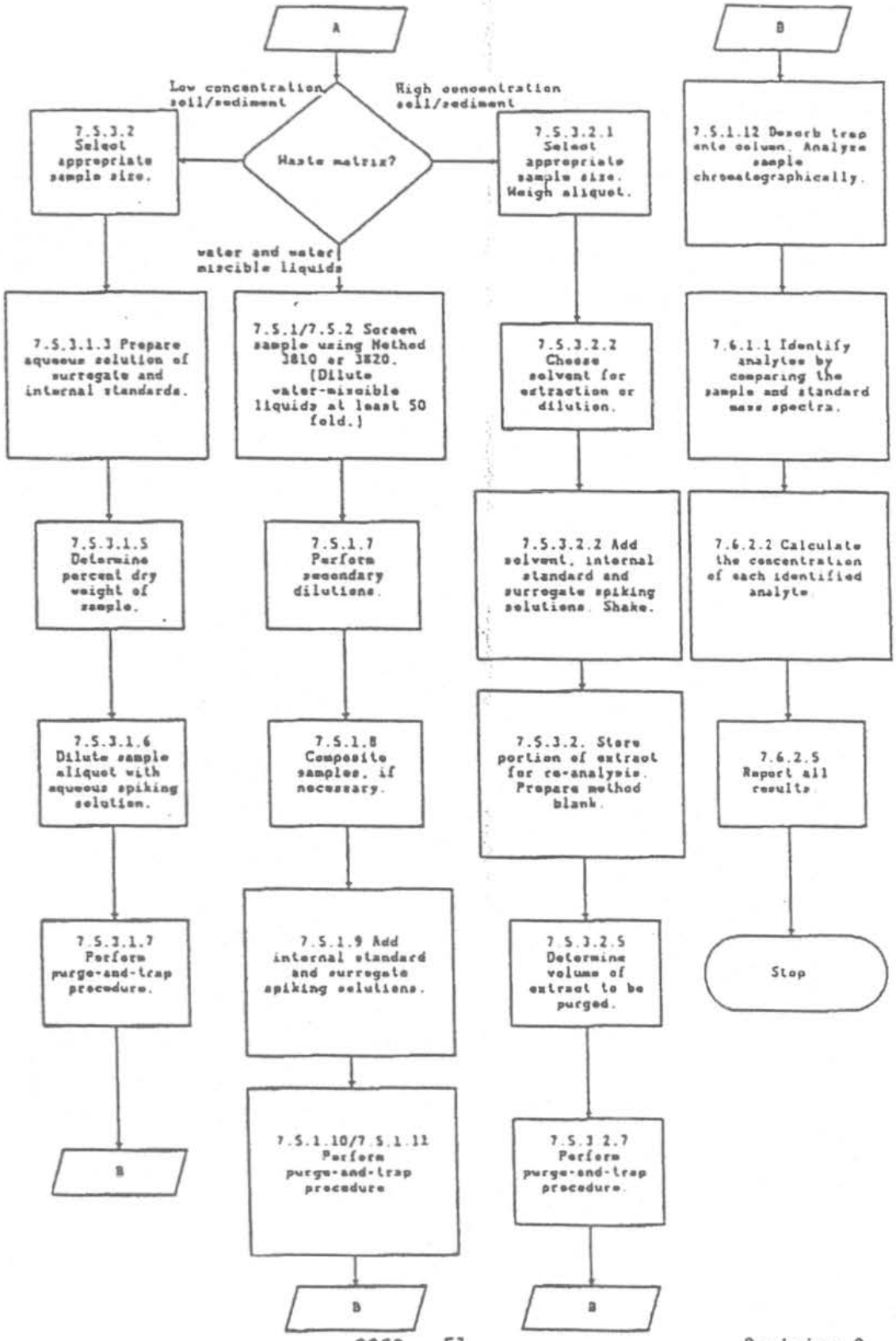


FIGURE 9.
LOW SOILS IMPINGER




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


A
B
Low concentration soil/sediment
High concentration soil/sediment
Waste matrix?
water and water miscible liquids
7.5.3.2 Select appropriate sample size.
7.5.3.2.1 Select appropriate sample size. Weigh aliquot.
7.5.1.12 Desorb trap onto column. Analyze sample chromatographically.
7.5.3.1.3 Prepare aqueous solution of surrogate and internal standards.
7.5.1/7.5.2 Screen sample using Method 3810 or 3820. (Dilute water-miscible liquids at least 50 fold.)
7.5.3.2.2 Choose solvent for extraction or dilution.
7.6.1.1 Identify analytes by comparing the sample and standard mass spectra.
7.5.3.1.5 Determine percent dry weight of sample.
7.5.1.7 Perform secondary dilutions.
7.5.3.2.2 Add solvent, internal standard and surrogate spiking solutions. Shake.
7.6.2.2 Calculate the concentration of each identified analyte.
7.5.3.1.6 Dilute sample aliquot with aqueous spiking solution.
7.5.1.8 Composite samples, if necessary.
7.5.3.2. Store portion of extract for re-analysis. Prepare method blank.
7.6.2.5 Report all results.
7.5.3.1.7 Perform purge-and-trap procedure.
7.5.1.9 Add internal standard and surrogate spiking solutions.
7.5.3.2.5 Determine volume of extract to be purged.
Stop
B
7.5.1.10/7.5.1.11 Perform purge-and-trap procedure
7.5.3.2.7 Perform purge-and-trap procedure.
B
B

RECOMMENDED QA/QC FOR EPA METHOD 8260
FOUND IN EPA METHOD 8000

METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of reagent water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^*}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm$15%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 **Internal standard calibration procedure:**

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent.

standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse products (i.e., PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis:

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 **Direct Injection:** Inject 2-5 uL of the sample extract using the solvent flush technique. Smaller (1.0-uL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.7.2 **Capillary columns:** Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 **Metal injector body:** Turn off the oven and remove the analytical column when oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations:

7.8.1 **External standard calibration:** The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Paragraph 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples:

$$\text{Concentration (ug/L)} = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

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

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

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.5 Required instrument QC:

8.5.1 Section 7.4 requires that the %RSD vary by <20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ±15% difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.6.2.

8.6.6.2 Beginning with Section 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.6.2.

8.7 The laboratory must, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC check sample (8.6.2) or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g., maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC check sample concentration (Section 8.6.2).

complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Section 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 Preparation of the QC check standard: For volatile organics, add 10 uL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 5 mL of reagent water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.7. Prepare the QC check standard for analysis following the guidelines given in Method 3500 (e.g., purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Section 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

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

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

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

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

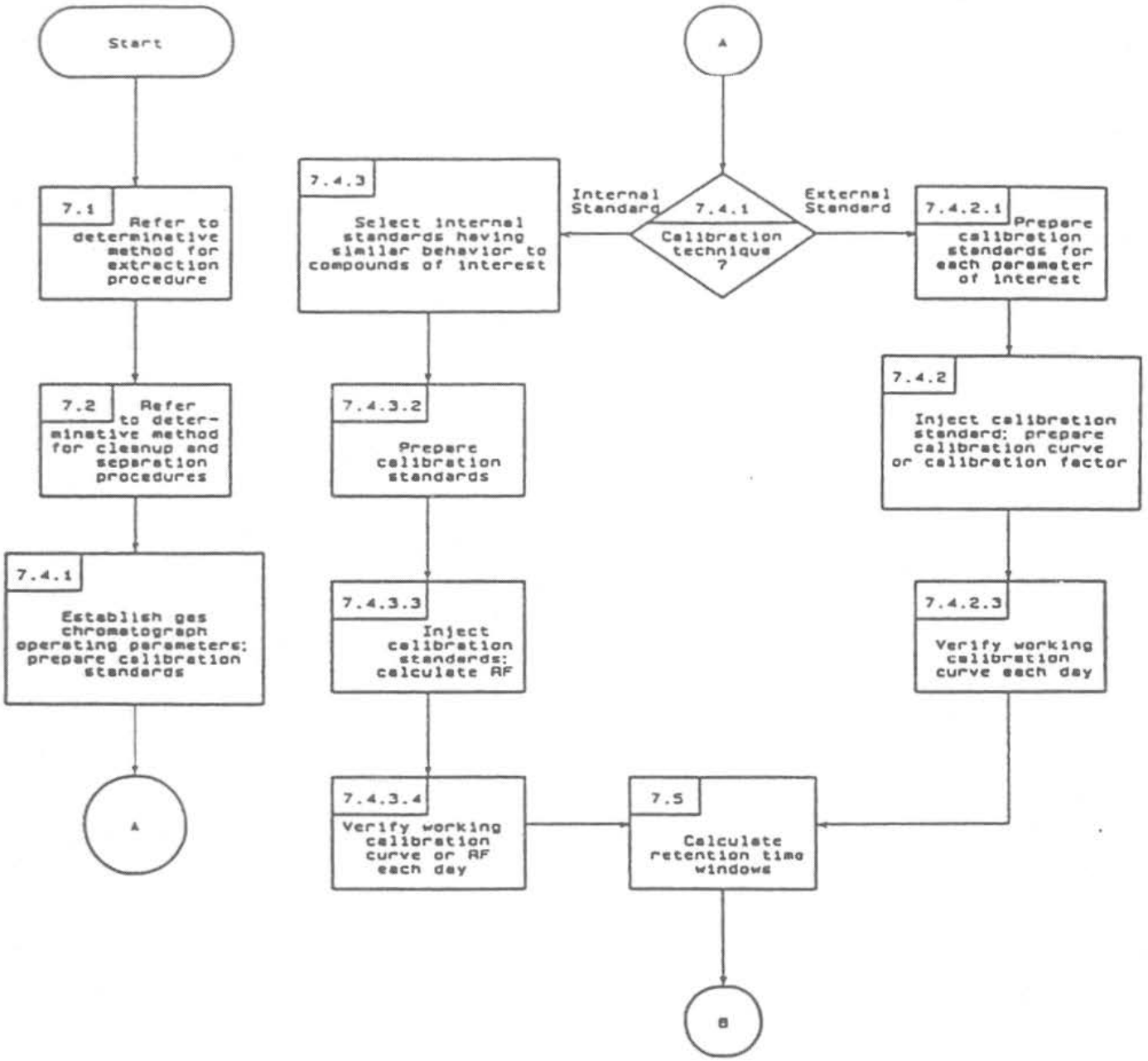
8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

10.0 REFERENCES

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

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

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.


Start
7.1 Refer to determinative method for extraction procedure
7.2 Refer to determinative method for cleanup and separation procedures
7.4.1 Establish gas chromatograph operating parameters; prepare calibration standards
A
A
7.4.1 Calibration technique ?
Internal Standard
External Standard
7.4.3 Select internal standards having similar behavior to compounds of interest
7.4.3.2 Prepare calibration standards
7.4.3.3 Inject calibration standards; calculate RF
7.4.3.4 Verify working calibration curve or RF each day
7.4.2.1 Prepare calibration standards for each parameter of interest
7.4.2 Inject calibration standard; prepare calibration curve or calibration factor
7.4.2.3 Verify working calibration curve each day
7.5 Calculate retention time windows
B

SELECTED ION MONITORING (SIM)
AND SIM QA/QC PROCEDURES

PHOENIX ANALYTICAL LABORATORIES, INC.
QC CRITERIA AND CORRECTIVE ACTION
MODIFIED EPA 8260
BENZENE, TOLUENE, ETHYL BENZENE, AND TOTAL XYLENES (BTEX) BY SELECTED ION MONITORING (SIM)

SEE THE FEB. 12, 1992 METHOD MODIFICATION FOR THE SPECIFIC PROCEDURE USED FOR THIS ANALYSIS.

GENERAL QC REQUIREMENTS ARE AS IN EPA 8260 (SW-846)

SPECIFIC CRITERIA:

SURROGATE RECOVERIES - SPIKING IS DONE AT 5 ug/L (WATER) AND 5 ug/Kg (SOIL)

SURROGATE	% REC. LOW/HIGH WATER	% REC. LOW/HIGH SOIL
Dibromofluoromethane	86-118	80-120
Toluene-d8	88-110	81-117
Bromofluorobenzene	86-115	74-121

CORRECTIVE ACTION:
If any surrogate is out, a rerun is performed. If the same surrogate is out, the results are flagged as estimates due to an apparent matrix effect. If the surrogates are in on the second run, those results are used. EXCEPTION: FOR BTEX ANALYSIS, DIBROMOFLUOROMETHANE IS REGARDED AS NOT REPRESENTATIVE. THEREFORE, NO ACTION IS TAKEN UNLESS ITS RECOVERY IS LESS THAN 50 % OR OVER 150%

MATRIX SPIKES - SPIKING IS NORMALLY DONE AT 5 ug/L (WATER) AND 5 ug/Kg (SOIL)

CONPOUND	% REC. LOW/HIGH WATER	%REC. LOW/HIGH SOIL
Benzene	78 - 117	71 - 123
Toluene	78 - 126	70 - 134
Ethyl benzene	74 - 124	65 - 133
Xylenes	82 - 126	75 - 133

The range for water is obtained from 3x the standard deviation for water recoveries, Table 7 in SW-846. For soil, four times the standard deviation is used.

CORRECTIVE ACTION: If any matrix spike recovery is out of limits, a duplicate matrix spike is run, and a QC spike is run. If the matrix spike is still out of limits, and the QC spike is within limits, the problem is considered to be due to a matrix effect. If the QC spike is also out of limits, the samples associated with this matrix spike must be rerun with another matrix spike.

PHOENIX ANALYTICAL LABORATORIES, INC.
QC CRITERIA AND CORRECTIVE ACTION
MODIFIED EPA 8260
BENZENE, TOLUENE, ETHYL BENZENE, AND TOTAL
XYLENES (BTEX) BY SELECTED ION MONITORING (SIM)

SEE THE FEB. 12, 1992 METHOD MODIFICATION FOR THE SPECIFIC PROCEDURE USED FOR THIS ANALYSIS.

BLANKS

Levels of targets in the blanks must be below the method detection limit. The only exceptions to this are the common solvents permitted in method 8260. For BTEX, benzene, toluene, ethyl benzene, and xylenes must all be below 0.2 ug/L.

Surrogate recoveries in blanks must always meet the criteria shown above for surrogate recoveries or the analysis cannot proceed.

TUNING CHECK

BFB is used as the tuning check compound. The criteria used are now as per CLP, 1990 contract. These are as follows:

m/e	ion abundance criteria
50	8% - 40% of mass 95
75	30 - 66 % of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	less than 2% of mass 95
174	50-120 % of mass 95
175	4 -9 % of mass 174
176	93 -101 % of mass 174
177	5 -9 % of mass 176

The tune check is accomplished by injecting 50 ng of BFB onto the GC column and obtaining the mass spectrum of the resultant GC peak. The tune is in force for 12 hours. If the tune does not meet the criteria above, the analysis cannot proceed until the situation is corrected.

CALIBRATIONS

An initial 5-point calibration is done at 1 ug/L, 5 ug/l, 10 ug/l, 15 ug/l, and 20 ug/L. The standard deviation of the response factors for all targeted analytes should be within +/- 30%, preferably within +/- 15%. Internal standards used for BTEX analysis are 1,4-difluorobenzene and chlorobenzene-d5.

PHOENIX ANALYTICAL LABORATORIES, INC.
QC CRITERIA AND CORRECTIVE ACTION
MODIFIED EPA 8260
BENZENE, TOLUENE, ETHYL BENZENE, AND TOTAL
XYLENES (BTEX) BY SELECTED ION MONITORING (SIM)

SEE THE FEB. 12, 1992 METHOD MODIFICATION FOR THE SPECIFIC PROCEDURE USED FOR THIS ANALYSIS.

Once the initial calibration is done, a daily calibration at 5/ ug/L is conducted on each working day, immediately after the BFB tune is met. The % difference between the response factor for the daily standard and the initial calibration should be within 25%, otherwise a new initial calibration needs to be conducted. This standard is good for 12 hours.

Any analytes that are detected under a daily calibration that does not meet the % difference criterion for those analytes should be flagged as estimates.

APPROVED; _____

John G. Huntington,
Laboratory Director
JGH:jh

Feb. 12, 1992

PHOENIX ANALYTICAL LABORATORIES, INC.
PROCEDURE MODIFICATION
MODIFIED EPA 8260
BENZENE, TOLUENE, ETHYL BENZENE, AND TOTAL
XYLENES BY SELECTED ION MONITORING (BTEX/SIM)

SUMMARY

EPA Method 8260 is a promulgated purge and trap gcms method for volatile organics, including benzene, toluene, ethyl benzene, and xylenes (BTEX). Detection limits for the method are 0.2-5 ug/L in water and 1-5 ug/Kg in soil depending on the amount of sample used. The method uses full-scan mass spectrometry for detection. In cases where considerable interference is present due to certain hydrocarbons or other organics, the detection limits can be much higher for the unmodified method.

This modification describes the use of selected ion monitoring (SIM), also known as selected ion detection (SID), to allow lower detection limits in clean matrices, or to allow better detection limits in samples with interference. Detection limits achievable are approximately a factor of 100 -1000 lower than those typically achievable using the unmodified method. In exchange one gives up the capability of detecting tentatively-identified compounds.

PRINCIPLE

In full-scan mass spectral detection, the masses formed in the ionizing chamber of the mass spectrometer are detected over a specific mass range. A mass range of 35 amu - 300 amu is fairly typical for volatile analysis. This scan of the masses in this range occurs in 1 second in a typical arrangement. For this example, then, the detector would have approximately 0.0038 seconds to detected each mass in the scan. With selected ion monitoring, one limits the detector to only a few masses. For example, for benzene one could scan m/z (mass/charge ratio) 78, the parent ion, and m/z 52, a fragment ion. If one has the detector spend the whole time on these to ions only, then in one second each would receive 0.5 seconds of attention. Thus, sensitivity of the instrument would be enhanced by 0.5/0.0038, for a factor of 133. Therefore, if the full-scan detection gave a detection limit of 1 ug/L, the SIM detection limit would be 0.0076 ug/L under the same conditions. For a more complete description of this well-known technique, one can consult any one of many references, including numerous papers by EPA and others describing environmental applications. A useful review of mass spectrometry, which describes this method, is "Gas Chromatography/Mass Spectrometry Operation", by S.T.F. Lai, Realistic Systems, Inc., East Longmeadow, Massachusetts, /1988.

PHOENIX ANALYTICAL LABORATORIES, INC.
PROCEDURE MODIFICATION
MODIFIED EPA 8260
BENZENE, TOLUENE, ETHYL BENZENE, AND TOTAL
XYLENES BY SELECTED ION MONITORING (BTEX/SIM)

METHOD MODIFICATIONS

The general approach of the method is identical to EPA 8260 except for several changes. These are, in summary:

1. Initial calibration standards are run at 0.05, 0.2, 1, 1.5, and 2 ug/L.
2. The daily calibration is run at 1 ug/L.
3. Extreme care is required with blanks, because of the low levels of analysis needed. The daily blank may have to be run twice, and great care is needed to prevent low-level carryover between samples. The blank should have BTEX at less than the PQL of the analysis.
4. The surrogates used are toluene-D8 and bromofluorobenzene.
5. The internal standards used are 1,4-difluorobenzene and chlorobenzene-d5.
6. The SIM is set up as follows:
   - SET 1, for benzene.
     - Mass 78, 20-40 counts
     - Mass 52, 20-40 counts
   - SET 2, for toluene
     - Mass 114 (I.S.), 5-10 counts
     - Mass 98 (S.S.), 5-10 counts
     - Mass 92, toluene 20-40 counts
     - Mass 91, toluene 20-40 counts
   - SET 3, for ethylbenzene/xylenes
     - Mass 117, (I.S.), 5-10 counts
     - Mass 174, (S.S.), 5-10 counts
     - Mass 106 (ethyl benzene + xylenes), 20-40 counts
     - Mass 91 (ethyl benzene + xylenes), 20-40 counts
7. Identifications are made as follows:
   a. A relative retention time window is established as described in EPA 8260.
   b. Candidate peaks in that window must have the correct masses, and the ratio of masses must be within 25% of the ratio determined in the standard runs.
8. All other quality control, such as detection limit measurement, blanks, surrogate recoveries, matrix spikes, QC spikes, etc., are as per EPA 8260.

APPROVED: _____

John G. Huntington, Ph.D.
Laboratory Director

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-GWS016

TITLE: GROUNDWATER SAMPLE COLLECTION FROM MONITORING WELLS - TRILOC PUMPS

DATE: August 11, 1993 Revision: 2

PURPOSE:

To provide representative samples of groundwater from monitoring wells using a "Triloc Pump". This Standard Operating Procedure is designed specifically for wells where the primary interest is volatile organics and a floating hydrocarbon may exist.

MATERIALS REQUIRED:

1. Equipment to measure water levels and floating hydrocarbons
2. Triloc pump of suitable length, including inner and outer tubes, check valves, pump foot, pump head, holding dog, and extra o-rings.
3. Decontamination equipment (ie., steam cleaner - see DEC019)
4. Distilled water
5. Plastic sheeting
6. Personal safety equipment
7. Bucket/barrel
8. Short length of hose or tubing

PROCEDURE:

Wells without floating product.

1. Measure water level in well (see GWM002)

2. Decontaminate Triloc pump (see DEC003) and lay on new plastic sheeting.

3. Install outer tube in five foot sections. Inspect condition of O-rings and check-valve during installation. Check-valve is installed on the bottom-most outer tube.

4. When the bottom of the outer tube has been installed to the desired sampling depth, hang the tube on the well casing, using the "holding dog" supplied by the pump manufacture.

5. Install the inner rod. The first section to be installed must contain a check valve (pump foot). Inspect condition and operation of check valve. Inspect condition of O-rings during installation.

6. Install pump head onto outer tube and over the inner rod.

7. Using inner rod, pump water from well at comfortable rate. Depending upon the governing requirements, remove either three well volumes or remove water until the pH, conductivity, and temperature have stabilized.

8. Pump additional water volume to fill sample containers.

9. Remove the Triloc pump in reverse order as described above.

Wells with floating product (At least 3 days lead time is required between pump installation and sampling).

1. Follow steps 1-3, as described above.

2. Prior to reaching the fluid level, fill the outer tube with distilled or deionized water. The check valve should seat, allowing the tube to be filled. As each additional five foot section is added, add additional water to maintain the check valve in a closed position. The height of distilled water within the outer tube must be greater than the column of water in the well (between the bottom of the pump and the water surface) in order to insure that the check valve remains closed.

3. As described above, when the end of the tube is at the sampling depth, secure with a "holding dog" and install the inner rod.

4. After the pump is completely installed, allow at least 3 days before sampling the groundwater. The "wait" time is designed to allow hydrocarbons which may have adhered to the outside of

the tube time to float back to the surface.

5. Sample as described above. However, it is particularly important to pump at a slow enough rate so that hydrocarbons are not dragged down the annular space and into the pump. The well efficiency, formation permeability, and sampling depth should all be considered in determining a safe pumping rate.

CALIBRATION:

No calibration is required.

QUALITY ASSURANCE:

QA/QC samples are designed to help identify potential sources of sample contamination and evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled with QA/QC identification numbers and sent to the laboratory with the other samples for analyses.

Rinsate Samples

An equipment rinsate sample of sampling equipment is intended to check if decontamination procedures have been effective. For the well sampling operation, a rinsate sample will be collected from the decontaminated sampling equipment or filter equipment before it is used to obtain the sample. Deionized water will be rinsed over the decontaminated sampling apparatus and transferred to the sample bottles. The sample parameters that are being analyzed in the groundwater samples will be analyzed in the rinsate samples. The rinsate sample is assigned a QA/QC sample identification number, stored in an iced cooler, and shipped to the laboratory on the day it is collected. One rinsate sample will be collected in every sample round, sample day or one for every 10 samples, based on whichever approach provides for the greatest number of rinsate samples..

Duplicate Samples

Duplicate samples are samples collected side-by-side to check for the natural sample variance and the consistency of field techniques

and laboratory analysis. For the groundwater sampling a duplicate sample will be collected at the same time as the initial sample. The initial sample bottles for volatiles analyses will be filled first, then the duplicate sample bottles for volatiles and so on until all necessary sample bottle for both the initial sample and the duplicate sample have been filled. The duplicate groundwater sample will be handled in the same manner as the primary sample. The duplicate sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory on the day it is collected. One duplicate sample will be collected for every 10 water samples.

Field Blanks

Field blanks check for contamination of samples due to factors at the well site. For a field blank, a sample bottle is taken empty to the field and filled at the well site with organic-free deionized water at the time the well is sampled. The sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory with the other samples. One field blank will be collected for every 10 water samples.

Trip Blanks

Trip blanks are normally provided by the analytical laboratory. They consist of preprepared samples that accompany the coolers to the field. The trip blanks are never opened and test the integrity of storage, handling and transport and serve to detect contamination introduced by the laboratory. A trip blank accompanies the samples as though it was already collected. Each cooler containing samples will include a trip blank.

Matrix Spikes

Matrix spikes are used to determine long-term precision and accuracy of the analytical method on various matrices. For this procedure duplicate samples are collected at a well and spiking is done by the lab. Samples are labelled as matrix spikes for the lab. It is useful to collect both the matrix spike and duplicate at the same well. One matrix spike and one duplicate will be taken for every 10 water samples.

REPORTING:

Field Sampling Data

Field sampling data for groundwater extraction well samples will be noted in the field notebook at each sampling location. If items do not apply to a specific location, the item will be labeled as not applicable (NA). The data include the following:

- Well number
- Date and time of sampling
- Person performing sampling
- Volume of water evacuated before sampling
- Time samples are obtained
- Number of samples taken
- Sample identification number
- Preservation of sample
- Record of any QC samples from site
- Any irregularities of problems which may have a bearing on sampling quality
- Temperature (measured in field)
- pH (measured in field)
- Conductivity (measured in field)

Field Notes

Field notes shall be kept in a bound field book. The following information will be recorded using waterproof ink:

- Names of personnel
- Weather conditions
- Date and time of sampling
- Location and well number
- Condition of the well
- Decontamination information
- Analytes of interest

DISCUSSION:

If a wait time of 3 days is not possible between the time of setting the pump and sampling, the procedures can be modified to improve the likelihood of obtaining representative samples. A

double thickness of plastic food wrap can be placed tightly over the end of the bottom Triloc outer tube and secured with a rubber band. Gather two of the corners of the plastic wrap and carefully secure each with a string of suitable strength (ie., mason's cord). The outer tube is then installed as described above, while holding the strings at the surface. When the pump is in position, the strings can be gently pulled until the plastic tears and the plastic, rubber band, and strings pulled to the surface.

REFERENCES:

No references are available on this procedure.

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-DEC019

TITLE: DECONTAMINATION - Volatile Organics

DATE: September 16, 1991 Revision: 0

PURPOSE:

To provide for representative samples, miniminzing the risk of cross contamination between sample sites.

MATERIALS REQUIRED:

The following is a list of equipment that may be needed to perform decontamination:

- Brushes
- Wash tubs
- Buckets
- Scrapers
- Steam cleaner or high-pressure sprayer
- Disposal drums
- Sponges or paper towels
- Methanol
- Potable tap water
- Deionized or distilled water
- Graden type water sprayers
- Clean plastic sheeting and/or trash bags

PROCEDURE:

1. Equipment will be steam-cleaned, insuring all surfaces have been in contact with the steam jet. After and during steam-cleaning, decontaminated equipment must be kept off the ground and any other source of potential contamination.

2. Inspect equipment for deep scratches or other irregular surfaces which may contain foreign material.

3. Using sprayer, rinse all equipment surfaces with methanol.

4. Using sprayer, rinse all equipment surfaces with deionized water.

5. Equipment sensitive to steam cleaning will be cleaned with soap and water and then rinsed as described above.

CALIBRATION:

None.

QUALITY ASSURANCE:

Rinsate samples should be collected as specified in the field sampling plan to verify the effectiveness of the decontamination procedures.

REPORTING:

Sampling personnel will be responsible for documenting the decontamination of sampling and drilling equipment. The documentation will be recorded with waterproof ink in the sampler's field notebook with consecutively numbered pages. The information entered in the field book concerning decontamination should include the following:

- Decontamination personnel
- Date and start and end times
- Decontamination observations
- Weather conditions

DISCUSSION:

REFERENCES:

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-SAM020

TITLE: PACKAGING AND SHIPPING OF SAMPLES - LIQUIDS (Volatiles)

DATE: September 16, 1991 Revision: 1

PURPOSE:

To provide for safe, secure transfer of samples from the field site to the laboratory.

MATERIALS REQUIRED:

- Sample bottles
- Labels
- Permanent marker
- Bubble wrap
- Ice chest
- Blue ice or ice
- Seals
- Shipping tape
- Chain of custody forms

PROCEDURE:

1. Fill prelabeled glass jars or 40 ml glass VOA bottles to the top and immediately slip teflon cap liner onto bottle, excluding any headspace.

2. Screw on cap and check for any air bubbles by inverting bottle. If air bubbles exist, remove cap and cap liner and refill bottle and repeat procedure.

3. Once bottle is properly filled, fill out label completely, place in bubble wrap, place in cooler, and pack in ice.

4. After all samples have been collected (within the time limit of the specified holding time), fill out chain of custody form. Seal ice chest (initialed paper seal) and tape shut.

5. Transport cooler to the laboratory, insuring that the samples remain iced during transportation, and completing chain of custody forms as samples are relinquished.

6. Submit cooler to laboratory, making sure again to properly complete the chain of custody form.

CALIBRATION:

None

QUALITY ASSURANCE:

As specified in the field sampling plan. QA may include field blanks and trip blanks.

REPORTING:

Record all procedures and variances in procedures in field notebook. All other relevant information will be recorded on the chain of custody form.

DISCUSSION:

REFERENCES:

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-AIR022

TITLE: COLLECTION OF AIR SAMPLES - TENEX TUBES

DATE: May 1, 1992 Revision: 0

PURPOSE:

The purpose of this SOP is to provide representative samples of air which may contain volatile hydrocarbons, using a syringe-type sampler and Tenex Tubes. This SOP is designed specifically for sampling air which is under positive or negative pressure where the primary interest is volatile organics.

MATERIALS REQUIRED:

1. Air sample device with proper fittings for sample ports
2. Tenex Tubes with rubber caps
3. Labels
4. Permanent marker
5. Shipping container
6. Padding
7. Chain of custody form
8. Field notebook

PROCEDURE:

It is important that the air sampling equipment be stored and used in a clean manner because at this time, the equipment can not be easily decontaminated in a field setting. Contact with liquids should be avoided at all times. Avoid at all times connecting the sampler to devices with air pressures which might exceed 30 psi. Pressures in excess of 30 psi will burst the glass syringe and could result in injury.

1. Inspect the sampling equipment to make sure all fittings are tight and surfaces are clean.

2. Inspect the check valves to determine the direction of air flow that will pass each valve. The sampler end with "inward"

pointing arrow should be connected to the sampling port of the device to be sampled. Make sure the connections are secure. The end of the sampler with the "outward" pointing arrow is for exhaust or purge during the sampling process.

3. After connecting the proper sampler end to the device to be sampled, connect the glass syringe to the syringe port and open stainless steel valve at end of syringe.

4. Slowly withdraw air from the sample location by pulling back on the syringe. When full, expel the air to purge the sampler. This process should be repeated at least three times to insure that the total volume of the sampler has been purged.

5. After purging, fill syringe and close valve on syringe.

6. Disconnect the syringe from the sampler. Fill out and place label on Tenex Tube. The label may have to be placed on "flag" fashion because of the size of the tube.

7. Break glass ends of a Tenex Tube and place the correct end into the adaptor. The correct end can be identified by the membrane which is located approximately 2/3 the distance from input end of the tube. The longer portion of Tenex material (as divided by the membrane) is the correct end for input of the sample.

8. The compression nut on the tube adaptor should be tightened by hand only. The tube should not be able to be pulled out if tightened sufficiently. Connect adaptor to the syringe.

9. Expel 50 cc of air into the Tenex Tube (record volume actually expelled into the tube on the label). Quickly remove the tube from the adaptor and place rubber caps over each end of the tube and store in a padded, dry, cool place.

10. After sampling is completed, insure all tubes are sufficiently padded and ship to the laboratory.

CALIBRATION

None

QUALITY ASSURANCE

Because of the sensitivity of the Tenex Tubes to hydrocarbon contamination in the general environment, QA procedures are essential. The exact QA requirements for each sampling period will be established before sampling begins. The minimum which will usually be required are field and trip blanks. The trip blank will consist of an unaltered Tenex Tube which is transported from the lab, is carried into the field, and is returned to the lab. The field blank will consist of a Tenex Tube which has been opened at the sampling site and capped with the rubber caps. The field blank should be treated exactly as the actual sample tubes, but without the air sample.

REPORTING

All procedures, sampling locations and numbers, variations in procedures, and air volumes should be recorded in a standard field book. A chain of custody form will also be required to accompany the samples.

DISCUSSION:

REFERENCES:

None

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-SLS023

TITLE: SPLITSPOON SAMPLING OF SOIL FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

DATE: May 21, 1992 Revision: 0

PURPOSE:

Collect representative soil samples from the subsurface using a splitspoon sampling device for the purpose of grain-size distribution, stratigraphic correlations, and/or chemical analysis of volatile organic compounds.

MATERIALS REQUIRED:

The materials required for the performance of this SOP are:

1. One or two splitspoon samplers of the required length and diameter (sampler length and diameter are determined by both the available drilling equipment and the volume of sample required).
2. Platform for disassembly of splitspoon and obtaining the soil sample (usually a pipe stand is provided by the drilling company).
3. Brass sleeves (6-inches long, 2-inch diameter and 6-inches long, 1.5-inch diameter) plastic caps, and teflon liners.
4. Decontamination equipment (See SOP-DEC019).
5. Labels and permanent markers.
6. Field log book.
7. Chain of custody forms.

PROCEDURE:

1. Determine the sampling interval (ie., one splitspoon every five feet, continuous, every other two feet, etc.) which will suit the sampling needs of the specific project and will be consistent with the project budget.

2 Determine the exact length of the splitspoon samplers, inner rods, and augers (hollow-stem auger drilling is assumed in this SOP).

3. Fill the splitspoon sampler with three 6-inch long brass sleeves, using the 2-inch diameter sleeves above the water table and the 1.5-inch diameter sleeves below the water table.

4. At the specified sampling depth, the driller will remove the inner bit and install a decontaminated splitspoon sampler and lower to the bottom of the drilled interval.

5. The splitspoon can either be pushed or driven the full length of the sampler. If geotechnical information is required or the formation is sufficiently hard, the sampler will be driven with a standard weight "hammer" while counting the number of "blows" required to move the sampler a given distance. The "blow-count" is provided in number of blows per length driven. If the sampler can be pushed and geotechnical information is not needed, the rig hydraulics are used to push the sampler its full length.

6. The sampler is removed from the hole and the splitspoon placed on the platform, where the end-pieces are loosened or removed by the rig personnel. Precautions regarding sample handling are contained in the project-specific Site Safety Plan.

7. The top brass sleeve is then used to log the interval, the middle brass sleeve is used for observation and PID measurements (See SOP-SLS035), and the bottom sleeve becomes the sample.

8. Place the teflon lining over the exposed ends of the bottom brass sleeve and then place the plastic caps over the ends. Immediately place the sealed units into a ice chest cooled to 4°C.

9. Describe any soil material left in the splitspoon and the sample in the container (without reopening the container) (See Discussion section).

10. The auger rig will advance the augers to the next sample point, using both the auger bit and an inner bit to keep soil

material from filling the hollow-stem augers. At the next sample point, the inner bit is removed and a decontaminated splitspoon lowered into place and the process repeated.

11. Usually two splitspoons are used to avoid delays due to the decontamination process. The spoons are alternated in the sampling process.

CALIBRATION:

None required.

QUALITY ASSURANCE:

Rinsate samples should be collected from the decontaminated splitspoon samplers during the sampling process.

REPORTING:

Notes regarding sample intervals, sample descriptions, variances in the SOP procedures, and other comments should be recorded in the field book.

DISCUSSION:

Stratigraphic Logging

Borehole stratigraphy will be logged by examination of the sample cuttings, or undisturbed split barrel samples (in soil). The data will be recorded in the field book and will include the following information:

- Project name and number
- Drilling company name
- Date drilling started and finished
- Type of bit and size
- Casing sizes and depths
- Well completion details
- Driller's name
- Name of field geologist or engineer
- Type of drill rig
- Boring number
- Surface elevation (if available)
- Sample depths and times
- Sample characteristics with depth, such as lithology, grain size, sorting, texture, structure, bedding, color, moisture content, and the Unified Soil Classification (if in

unconsolidated geologic materials)
- Water levels
- Geophysical or video logs run (if any)
- Drilling observations
- Other pertinent information

Cuttings will be collected at a minimum of 5-foot intervals, or at changes in lithology, and described by the field geologist or engineer. A portion of each sample will be archived in sealed and labelled plastic bags, if samples are not collected for other purposes.

REFERENCES:

None

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-SAM-039

TITLE: SAMPLING OF OPERATING GROUNDWATER EXTRACTION WELLS

DATE: August 11, 1993 Revision: 3

PURPOSE:

The purpose of this document is to define the standard procedure for collecting a groundwater sample for analysis of volatile hydrocarbons.

MATERIALS REQUIRED:

- 5-gallon bucket
- Plastic sheeting
- Appropriate sample bottles
- Appropriate sample preservatives
- Bottle labels
- Permanent markers
- Field book
- Cooler with ice

PROCEDURE:

This section outlines the step-by-step procedures used to collect a groundwater sample from an operating extraction well that is equipped with a valve at the wellhead that opens to atmosphere.

Well Purging

Well purging is not necessary in the case of operating groundwater extraction wells as long as the well has been in operation greater than the amount of time required to remove at least three well volumes at the given pumping rate.

Preparation for Sample Collection

Before the sample is collected, the following steps must first be executed:

- Place clean plastic sheeting around the well.
- Open the valve and collect approximately five gallons of water. This ensures that any stagnant water in the valve arm is purged before sampling.
- Prepare sample bottles with preservative and appropriate labels.

Collect Water Samples

After the preparation is complete, open the valve to a flow not more than 0.5 gpm and collect the sample. Be sure the samples are zero headspace and place in the cooler. SEE SOP-SAM020 FOR PACKAGING AND SHIPPING OF SAMPLES.

CALIBRATION:

No calibration is required for this procedure.

QUALITY ASSURANCE:

QA/QC samples are designed to help identify potential sources of sample contamination and evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled with QA/QC identification numbers and sent to the laboratory with the other samples for analyses.

Rinsate Samples

An equipment rinsate sample of sampling equipment is intended to check if decontamination procedures have been effective. For the well sampling operation, a rinsate sample will be collected from the decontaminated sampling equipment or filter equipment before it is used to obtain the sample. Deionized water will be rinsed over the decontaminated sampling apparatus and transferred to the sample bottles. The sample parameters that are being analyzed in the

groundwater samples will be analyzed in the rinsate samples. The rinsate sample is assigned a QA/QC sample identification number, stored in an iced cooler, and shipped to the laboratory on the day it is collected. One rinsate sample will be collected in every sample round, sample day or one for every 10 samples, based on whichever approach provides for the greatest number of rinsate samples.

Duplicate Samples

Duplicate samples are samples collected side-by-side to check for the natural sample variance and the consistency of field techniques and laboratory analysis. For the groundwater sampling a duplicate sample will be collected at the same time as the initial sample. The initial sample bottles for volatiles analyses will be filled first, then the duplicate sample bottles for volatiles and so on until all necessary sample bottle for both the initial sample and the duplicate sample have been filled. The duplicate groundwater sample will be handled in the same manner as the primary sample. The duplicate sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory on the day it is collected. One duplicate sample will be collected for every 10 water samples.

Field Blanks

Field blanks check for contamination of samples due to factors at the well site. For a field blank, a sample bottle is taken empty to the field and filled at the well site with organic-free deionized water at the time the well is sampled. The sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory with the other samples. One field blank will be collected for every 10 water samples.

Trip Blanks

Trip blanks are normally provided by the analytical laboratory. They consist of preprepared samples that accompany the coolers to the field. The trip blanks are never opened and test the integrity of storage, handling and transport and serve to detect contamination introduced by the laboratory. A trip blank accompanies the samples as though it was already collected. Each cooler containing samples will include a trip blank.

Matrix Spikes

Matrix spikes are used to determine long-term precision and accuracy of the analytical method on various matrices. For this procedure duplicate samples are collected at a well and spiking is done by the lab. Samples are labelled as matrix spikes for the lab. It is useful to collect both the matrix spike and duplicate at the same well. One matrix spike and one duplicate will be taken for every 10 water samples.

Sample Handling

Sample containers and preservatives are specified in SOP SAM005, Sample Handling, Documentation and Analysis. Samples will be labeled and handled as described in SOP SAM005. The parameters for analysis are also specified in the FSP.

REPORTING:

Field Sampling Data

Field sampling data for groundwater extraction well samples will be noted in the field notebook at each sampling location. If items do not apply to a specific location, the item will be labeled as not applicable (NA). The data include the following:

- Well number
- Date and time of sampling
- Person performing sampling
- Volume of water evacuated before sampling
- Time samples are obtained
- Number of samples taken
- Sample identification number
- Preservation of sample
- Record of any QC samples from site
- Any irregularities of problems which may have a bearing on sampling quality
- Temperature (measured in field)
- pH (measured in field)
- Conductivity (measured in field)

Field Notes

Field notes shall be kept in a bound field book. The following information will be recorded using waterproof ink:

- Names of personnel
- Weather conditions
- Date and time of sampling
- Location and well number
- Condition of the well
- Decontamination information
- Analytes of interest

REFERENCES:

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-TWS040

TITLE: TREATED WATER SAMPLING FROM KN ENERGY INJECTION WATER SUMP

DATE: August 11, 1993 Revision: 1

PURPOSE:

To outline the sampling procedure followed when sampling treated water from the stripping tower at the KN Facility.

MATERIALS REQUIRED:

Sample bottles with preservatives will be obtained from the analytical laboratory.

Equipment that may be used during the sampling:

- Sample bottles
- Bottle labels
- Permanent marker
- Cooler with ice
- Preservatives for samples
- Latex gloves
- Eye protection
- Bubble wrap

PROCEDURE:

This section gives step-by-step procedures for collecting treated water samples from the injection water side of the sump.

With proper eye protection, latex gloves and using a 40-ml VOA bottle, reach into the treated water side of the sump and collect a water sample. After it has been collected, and before capping, add the appropriate preservative. Cap the sample such that there is zero headspace. Label the sample location, time, date, person who collected the sample, and analytes of interest. Wrap the sample in bubble wrap to prevent breakage and place into the ice chest in order to maintain the temperature below 4°C.

Follow SOP SAM005 for Sample Handling, Documentation & Analsis.

CALIBRATION:

No calibration necessary for this procedure.

QUALITY ASSURANCE:

QA/QC samples are designed to help identify potential sources of sample contamination and evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled with QA/QC identification numbers and sent to the laboratory with the other samples for analyses.

Rinsate Samples

An equipment rinsate sample of sampling equipment is intended to check if decontamination procedures have been effective. For the well sampling operation, a rinsate sample will be collected from the decontaminated sampling equipment (bailer) or filter equipment before it is used to obtain the sample. Deionized water will be rinsed over the decontaminated sampling apparatus and transferred to the sample bottles. The sample parameters that are being analyzed in the groundwater samples will be analyzed in the rinsate samples. The rinsate sample is assigned a QA/QC sample identification number, stored in an iced cooler, and shipped to the laboratory on the day it is collected. One rinsate sample will be collected for every 10 water samples.

Duplicate Samples

Duplicate samples are samples collected side-by-side to check for the natural sample variance and the consistency of field techniques and laboratory analysis. For the groundwater sampling a duplicate sample will be collected at the same time as the initial sample. The initial sample bottles for volatiles analyses will be filled first, then the duplicate sample bottles for volatiles and so on until all necessary sample bottle for both the initial sample and the duplicate sample have been filled. The duplicate groundwater sample will be handled in the same manner as the primary sample. The duplicate sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory on

the day it is collected. One duplicate sample will be collected for every 10 water samples.

Field Blanks

Field blanks check for contamination of samples due to factors at the well site. For a field blank, a sample bottle is taken empty to the field and filled at the well site with organic-free deionized water at the time the well is sampled. The sample will be assigned a QA/QC identification number, stored in an iced cooler, and shipped to the laboratory with the other samples. One field blank will be collected for every 10 water samples.

Trip Blanks

Trip blanks are normally provided by the analytical laboratory. They consist of preprepared samples that accompany the coolers to the field. The trip blanks are never opened and test the integrity of storage, handling and transport and serve to detect contamination introduced by the laboratory. A trip blank accompanies the samples as though it was already collected. Each cooler containing samples will include a trip blank.

Matrix Spikes

Matrix spikes are used to determine long-term precision and accuracy of the analytical method on various matrices. For this procedure duplicate samples are collected at a well and spiking is done by the lab. Samples are labelled as matrix spikes for the lab. It is useful to collect both the matrix spike and duplicate at the same well. One matrix spike and one duplicate will be taken for every 10 water samples.

Sample Handling

Sample containers and preservatives are specified in SOP SAM005, Sample Handling, Documentation and Analysis. Samples will be labeled and handled as described in SOP SAM005. The parameters for analysis are also specified in the FSP.

REPORTING:

Field sampling notes for sample collection will be maintained in the field notebook of the individual performing the sampling. The data included in the field notebook will include:

- Date and time of sampling
- Person performing sampling
- Time samples are obtained
- Number of samples taken
- Sample identification number
- Preservation of sample
- Record of any QC samples from site
- Any irregularities of problems which may have a bearing on sampling quality
- Temperature (field measurement)
- pH (field measurement)
- Conductivity (field measurement)

DISCUSSION:

Since the function of the stripping tower is to fully aerate the water, no precautions are necessary to avoid sample aeration during sample collection except to cap the sample as soon as possible after collection and addition of the preservatives.

REFERENCES:

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-SAM041

TITLE: PACKAGING AND SHIPPING OF SAMPLES -- Soil (Volatiles)

DATE: June 28, 1993 Revision: 1

PURPOSE:

To provide for safe, secure transfer of samples from the field site to the laboratory.

MATERIALS REQUIRED:

- Brass sleeves
- Teflon sheets
- Plastic caps
- Labels
- Permanent marker
- Ice chest
- Blue ice
- Seals
- Shipping tape
- Chain of custody forms

PROCEDURE:

1. Remove the brass sleeves from the splitspoon sampler and immediately cover the ends with teflon sheeting and cap with plastic end caps.

2. Once the brass sleeve is properly prepared, fill out the sample label completely, place the sample in bubble wrap, place the sample in the cooler, and pack in blue ice.

3. After all samples have been collected (within the time limit of the specified holding time), fill out chain of custody form. Seal ice chest (initialed paper seal) and tape shut.

4. Transport cooler to the laboratory, insuring that the samples remain iced during transportation, and completing chain of custody forms as samples are relinquished.

5. Submit cooler to laboratory, making sure again to properly complete the chain of custody form.

CALIBRATION:

None

QUALITY ASSURANCE:

As specified in the field sampling plan. QA may include field blanks.

REPORTING:

Record all procedures and variances in procedures in field notebook. All other relevant information will be recorded on the chain of custody form.

DISCUSSION:

REFERENCES:

STANDARD OPERATING PROCEDURE . . . . . NUMBER: SOP-SAM042

TITLE: PACKAGING AND SHIPPING OF SAMPLES - Air (Volatiles)

DATE: June 28, 1993 Revision: 1

PURPOSE:

To provide for safe, secure transfer of samples from the field site to the laboratory.

MATERIALS REQUIRED:

- Tenex tubes
- Rubber caps
- Labels
- Permanent marker
- Ice chest
- Blue ice
- Seals
- Shipping tape
- Chain of custody forms

PROCEDURE:

1. Inject 50 ml of sample air into the tenex tube using a calibrated, clean syringe.

2. Cap the ends of the tube with the rubber caps.

2. Once the tenex tube is properly prepared, fill out the sample label completely, place the sample in bubble wrap, place the sample in the cooler, and pack in blue ice.

3. After all samples have been collected (within the time limit of the specified holding time), fill out chain of custody form. Seal ice chest (initialed paper seal) and tape shut.

4. Transport cooler to the laboratory, insuring that the samples remain iced during transportation, and completing chain of custody forms as samples are relinquished.

5. Submit cooler to laboratory, making sure again to properly complete the chain of custody form.

CALIBRATION:

None

QUALITY ASSURANCE:

As specified in the field sampling plan. QA may include field blanks.

REPORTING:

Record all procedures and variances in procedures in field notebook. All other relevant information will be recorded on the chain of custody form.

DISCUSSION:

REFERENCES:

APPENDIX C

PHOENIX ANALYTICAL LABORATORIES QA/QC FOR ORGANIC ANALYSIS BY GCMS

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QA/QC FOR ORGANICS ANALYSIS BY GCMS

SEMIVOLATILES ANALYSIS

I. Instrument Tune

A. Objective

The instrument tune criterion is established to make sure mass spectra obtained will have correct mass assignment and will properly match library spectra. The approach also establishes minimum sensitivity requirements to do the test work.

B. Requirements

Every gcms system used for semivolatiles analysis must be tuned at the beginning of every 12 hour shift to meet the ion abundance limits set by the EPA CLP program. The tuning compound is DFTPP (decafluorotriphenylphosphine), and is introduced to the instrument through the column to be used for the analysis. A 50 ug/ml solution of this compound in methylene chloride is used for this purpose, and 1 ul of this solution is injected. This gives a 50 ng charge to the analytical system.

When the compound has eluded from the column and been detected by the mass spectrometer, a hard copy of the bar graph spectrum is produced, and a mass listing. The DFTPP tune form is filled out. If the tune is not in compliance, the situation must be corrected prior to the beginning of analysis. The form and documentation are stored in the instrument tune book kept at each instrument workstation.

C. Expanded DFTPP Criteria

The CLP has published expanded DFTPP criteria, and has issued several publications on this matter. This is because some of the ion abundances have been shown not to be critical. We have chosen to abide by the most recent EPA publication in this area (J.R. Donnely, R.K. Mitchum, Yves Tondeur, et.al., Biomedical and Env. Mass Spec., vol 15, 429-439 (1988)). Their recom-

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mended criteria are shown in Table 1, compared to standard criteria.

Table 1 1988 Recommended DFTPP Criteria

m/z	Recommendation	1975 Criteria
51	15-75% of m/z 198	30-60% of 198
68	< 2% if m/z 69	<2% of 69
70	<2% of m/z 69	<2% of 69
127	15-60% OF m/z 198	40-60% of 198
197	<1% of m/z 198	<1% of 198
198	>30% of m/z 442 if 442 is base peak	
198 or 442	Base Peak	198 must be base; 442 > 40% of 198
199	4.5-9% of m/z 198	5-9% of 198
275	10-60% of m/z 198	10-30% of 198
365	>0.5% of m/z 198	>1% of 198
441	Delete criterion	Present, < 443
442	>40% of m/z 198 if 198 is base peak	
443	15-24% of m/z 442	17-23% of 442

Because the EPA has not made specific official recommendations, we will adhere to the 1975 criteria under normal conditions, and use the 1988 recommended criteria under the following conditions:

1) RUSH work

2) If client turnaround needs conflict with meeting the 1975 criteria

3) If needed to meet holding time requirements

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II. Calibration of the GCMS System

A. Objective

The calibration of the system is conducted with known standards of the compounds targeted for analysis. The purpose is to establish the sensitivity of the system toward each target compound relative to internal standards (response factors), and to insure that these response factors fall within acceptable limits to achieve quantification at an acceptable level of accuracy.

B. Requirements

Prior to any sample analysis, and after DFTPP tune has been met, the GCMS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response for the target analytes. This calibration must be verified each 12- hour shift with a continuing calibration check before analysis can proceed.

For semivolatile compounds, initial calibration is conducted with 20, 50, 80, 120, and 160 total nanograms injected. This is accomplished by the injection of 1 ul of standards prepared at concentration of 20, 50, 80, 120, and 160 ug/ml (ng/ul). Ten compounds: benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2- nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, pentachlorophenol, and benzidine are not considered to be detectable below 50 ng, so that only the higher 4 points are used in the calibration for these compounds.

Each of the standard solutions will also contain the surrogate compounds to be analyzed at the concentration of the standard, and will contain internal standards at a concentration of 40 ug/ml. The normal surrogates are 2-fluorophenol, phenol-d5, 2,4,6-tribromophenol, d-5 nitrobenzene, 2-fluorobiphenyl, and terphenyl-d14. New standards will be prepared at least every 6 months, and more frequently if degradation is suspected. Standards will be maintained in the standards refrigerator. When a new standard is prepared, it must be checked against an EPA reference standard by gcms analysis.

The quantitation is conducted as described by the EPA CLP protocol, using internal standards. The internal standards used

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are normally 1,4- dichlorobenzene-d4, naphthalene-d8, acnaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12.

For each initial calibration, an Initial Calibration Data, form is prepared. All criteria set forth on that form must be met for analytical work to continue. In addition, PAL requires that the peak areas for the internal standards must be within a factor of 2 of one another, and the relative retention times must be within 0.06 relative retention time units for each analyte.

III. Continuing Calibration of the GCMS System

A. Objective

The continuing calibration check is intended to show that the analytical system is performing as it has during the initial calibration within acceptable limits.

B. Requirements

After DFTPP tune has been met, and after an initial calibration has been performed, the procedure is follows for each 12-hour shift. First, the DFTPP tune is met. Second, a continuing calibration check is made by analyzing the 50 ug/ml standard solution. The continuing calibration check form must be filled out, and all criteria met before analyses are conducted. The form is to be filled out completely and kept in the instrument QC book at each instrument workstation.

In cases where the full list of analytes are not targeted (such as analysis for polynuclear aromatics only), a somewhat different set of calibration criteria may be required.

If the calibration check does not meet the established criteria, then corrective action must be taken. After the action, the standard is again analyzed: if it now meets the criteria, and if a 12- hour period has not elapsed, the analysis may proceed. If this does not work, it may be necessary to replace the column, or the mass spectrometer may require cleaning and maintenance. If such action is taken, the DFTPP must be run before the calibration check is again attempted.

If the calibration check meets all criteria except the difference for each CCC, then a new 5-point initial calibration must be run prior to analysis. This will generally occur when a new column is

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used, or when a major maintenance is conducted on the mass spectrometer. In addition, a new 5-point plot must be obtained each time new standards are prepared. In effect, this means that a new plot is obtained at a minimum of once every 6 months.

IV. Semivolatiles Reagent Blank Analysis

A. Objective

The reagent blank is intended to demonstrate the level of laboratory and reagent contamination, and to insure that that level is low enough or controlled enough to allow meaningful results to be obtained from the analytical data.

B. Requirements

A reagent blank for semivolatile analyses must be performed once each case, where a case is a group or set of samples collected from a particular site over a given period of time. It must be performed with every 20 samples of a similar concentration or sample matrix, or whenever samples are extracted. The more frequent blank analysis is the one of choice.

The reagent blank is prepared in exactly the same fashion as is the sample, with surrogates added in the same concentration, and carried through the whole analysis in the same manner. For waters, laboratory purified water is used, and for soils, the sodium sulfate used for the soils extraction provides the matrix. If alumina column cleanup or other preparation variations are required, the blank must be treated to these procedures. The results for the blank are to be retained in a permanent record and also to be reported to the client explicitly.

If the blank does not meet the criteria established for the analysis, the entire set of samples to which it applies must be reextracted and a new blank prepared.

A reagent blank should contain no more than two times the EPA-mandated detection limit of any common phthalate ester. It must not contain more than five times the detection limit of any phthalate ester. For all other target compounds, the reagent blank must contain less than the EPA-mandated detection limit of any single target analyte.

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The results for the reagent blank will be reported as a sample, with uncorrected concentrations reported on the PAL semivolatiles report form (see attachments). Surrogate recoveries will also be reported explicitly for the reagent blank, and should meet the same criteria as those required for the sample. In addition to target compounds, any tentatively-identified compounds will be reported.

V. Surrogate Spike Analysis for Semivolatiles

A. Objective

The addition of surrogate spikes to every sample and blank is intended to show that the matrix and the analysis of the chemical characteristics represented by the surrogates to be detected and quantified within acceptable limits.

B. Requirements

Surrogate spike compounds are added to all samples and blanks prior to extraction, and the surrogates are recovered and reported in every analysis. For semivolatiles, the surrogate spiking solution is prepared in methylene chloride with the same frequency as the standard, at a concentration of 100 ug/ml for base- neutral surrogates, and a concentration of 200 ug/ml for acid surrogates. One ml of this solution is added to the sample before extraction, so that the concentration in the final extract would be 100 and 200 ug/ml if 100% recovery were achieved.

The surrogate compounds used for this analysis are nitrobenxene-d5, 2-fluorobiphenyl, terphenyl-d14, phenol- d5, 2-fluorophenol, and 2,4,6-tribromophenol. Additional surrogates, such as pyridine-d5, anthracene-d10, or perdeuteracridine, may be used for special requirements, but are not a part of the standard method. When they are used, their concentration will be 100 ug/ml or 200 ug/ml depending on the type of compound.

The surrogate recoveries required for water or soils are mandated by the EPA Contract Lab Program, and are shown below. These may change as new contracts are issued. We will notify our clients if we decide to use the newer criteria.

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Surrogate Compound	Recovery range acceptable %	
	water	soil
nitrobenzene-d5	35-114	23-120
2-fluorobiphenyl	43-116	30-115
terphenyl-d14	33-141	18-137
phenol-d5	10-110	24-113
2-fluorophenol	21-110	25-121
2,4,6-tribromophenol	10-123	19-122

Generally speaking, the laboratory will try to adhere to recovery limits for soils in the case of oily wastes; however, because of the limited amount of work on these complex matrices, such recoveries may occasionally be infeasible. If the recovery is not within this range on such a material, a reextraction and reanalysis will be attempted. If the recovery can still not be achieved and the results for the associated blank are acceptable, then the problem will be assumed to be a matrix effect. In any event, all surrogate recovery data will be explicitly reported to the client.

All surrogate recovery data will also be maintained in a permanent record at the laboratory so that the history of recoveries can be traced.

VI. Matrix Spikes and Matrix Spike Duplicates

A. Objective

Matrix spikes are added to samples in order to assess the accuracy of the method as applied to the particular matrix at hand.

B. Requirements

Matrix spike samples will be run with every 10 samples and matrix spike duplicates with every 20 samples of a similar matrix. This will be done with no additional charge to the client. If a client has a smaller sample suite, the laboratory will charge for matrix spikes and matrix spike duplicates at the same rate as the analytical charge. However, even if the client does not elect to have matrix spikes conducted, the laboratory will prepare a matrix spike extract with every sample matrix change. The analysis of the extract will be an option of the client or the laboratory. PAL may

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elect to analyze the matrix spike extract for its own internal QC purposes. However, with 10 more samples, the analysis of the matrix spike extracts is not optional.

The standard matrix spike solution for semivolatiles includes 1,24-trichlorobenzene, acenaphthene, 2,4- dinitro- toluene, di-n-butyl phthalate, pyrene, n-nitroso-di-n- propylamine, 1,4-dichlorobenzene, pentachlorophenol, phenol, 2-chlorophenol, 4-chloro-3-methylphenol, and 4- nitrophenol. The spiking solution is prepared in methylene chloride at 100 ug/ml for the base-neutrals and at 200 ug/ml for the phenols. Normally, 1.0 ml of the solution is added to the sample prior to extraction, along with the normal surrogate spike solution. The extraction is conducted normally, and the recoveries of the matrix spike compounds obtained after subtraction of the separately-measured sample result.

The normal recovery limits are set by the EPA CLP program, and are shown below for the semivolatile matrix spike compounds. Normally, we will adhere to the recovery limits for soil and sediment for oily wastes, unless we have shown that the matrix effect precludes such recoveries.

MATRIX SPIKE RECOVERY LIMITS*			
Fraction	Matrix Spike Compound	Water	Soil/Sediment*
BN	1,2,4-Trichlorobenzene	39-98	38-107
BN	Acenaphthene	46-118	31-137
BN	2,4-Dinitrotoluene	24-96	28-89
BN	Di-n-butyl Phthalate	11-117	29-135
BN	Pyrene	26-127	35-142
BN	N-Nitroso-Di-n-Propylamine	41-116	41-126
BN	1,4-Dichlorobenzene	36-97	28-104
Acid	Pentachlorophenol	9-103	17-109
Acid	Phenol	12-89	26-90
Acid	2-Chlorophenol	27-123	25-102
Acid	4-Chloro-3-Methylphenol	23-97	26-103
Acid	4-Nitrophenol	10-80	11-114

Please note that these limits are advisory. There is not action required by the EPA if they are not met. Rather, they are to be

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used in assessing trends of accuracy. For instance, consistently low values might be taken as an indication that actual concentrations are higher than measured.

2. VOLATILES ANALYSIS

I. Instrument Tune

A. Objective

The instrument tune criterion is established to make sure mass spectra obtained will have correct mass assignments and will properly match library spectra. The approach also established minimum sensitivity requirements to do the test work.

B. Requirements

Every gcms system used for volatiles analysis must be tuned at the beginning of every 12-hour shift to meet the ion abundance limits set by the EPA CLP program. The tuning compound is BFB (4-bromofluorobenzene), and it is introduced to the gcms through the column to be used for the analysis. A 50 ug/ml solution of this compound in methanol is used for this purpose, and 1 ul of this solution is injected.

When the BFB has eluded from the column and been detected by the mass spectrometer, a hard copy of the bar graph spectrum is produced, and a mass listing. The BFB tune form is filled out. If the tune is not in compliance, the situation must be corrected prior to the beginning of any analyses. The form and documentation are stored in the instrument tune book.

BFB KEY IONS AND ABUNDANCE CRITERIA	
Mass	Ion Abundance Criteria
50	15.0-40.0 percent of the base peak
75	30.0-60.0 percent of the base peak
95	100 percent relative abundancebase peak
96	5.0-9.0 percent of the base peak
173	less than 1.00 percent of the base peak
174	greater than 50.0 percent of the base peak
175	5.0-9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

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II. Calibration of the GCMS System

A. Objective

The calibration of the system is conducted with standards of the compounds targeted for analysis. The purpose is to establish the sensitivity of the system toward each target compound relative to internal standards (response factors), and to insure that these response factors fall with in acceptable limits to achieve quantification at an acceptable level of accuracy.

Prior to any sample analysis, and after BFB tune has been met, the GCMS system must be initially calibrated at the minimum of five concentration to determine the linearity of response factors for the target analytes. This calibration must be verified each 12-hour shift with a continuing calibration check before analysis can proceed.

For volatile compounds, initial calibration is conducted with 20, 50, 100, 150, and 200 ug/l standards in water. This results in 100-1000 total ng of each analyte being determined. Three separate calibration must be produced. One is for analysis of water at the standard purge temperature, one is for analysis of soils at 40 degrees C, and one is for medium-level analysis of soils at 40 degrees C with the appropriate amount of methanol in the standards.

Each of the five concentrations of standards will also contain the surrogate compounds to be analyzed at the concentrations of the standard, and must contain internal standards at a concentration of 50 ug/l. The surrogates to be used are normally 1,2-dichloroethane- d4, toluene-d8, and bromoflurobenzene (BFB). The internal standards to be used are normally bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d5. All standards are prepared in purge and trap quality methanol, and must be prepared at minimum once every three months, more often if signs of degradation are observed. Standards are to be kept in the VOA standards refrigerator.

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The quantitation is conducted as described by the EPA CLP protocol, using the internal standard method. For each initial calibration, the EPA form for Initial Calibration Data on volatile organics must be prepared. All criteria set forth on that form must be met for analytical work to continue. IN addition, PAL requires that the peak areas for the internal standards from run to run must be within a factor of 2.

The attachments show the ions to be used for quantitation of each analyte, and also the analytes assigned to each internal standard. Variations from this procedure must be according to client-accepted rules. Details of the calculations are given in the attachments.

At times, the standards may be prepared using additional surrogate compounds or target compounds. Acetonitrile-d3, acetone-d3,j and pyridene-d5 are sometimes used when accurate quantitation of these analytes is required.

III. Continuing Calibration of the GCMS System

A. Objective

The continuing calibration check is intended to show that the analytical system is performing as it was during the initial calibration within acceptable limits.

B. Requirements

After BFB tune has been met, and after an initial calibration has been performed, the procedure is as follows for each 12-hour shift. First, the BFB tune is met. Second, a continuing calibration check is made by analyzing the 50 ug/l standard. The continuing calibration check form is filled out, and all criteria met before analysis is to proceed. The form must be filled out and retained in the instrument QC book.

In case where the full list of analytes are not targeted (such as analysis for BETX only), a somewhat different set of calibration criteria may be required. This will be established prior to the analysis by the method supervisor or the project manager, and recorded on the calibration check form. the form should be signed and dated by the individual assigning these additional criteria.

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If the calibration does not meet requirements, then corrective action must be taken. The mass spectrometer may need to be cleaned, the standards may need to be replaced, or the column may need to be repacked. Whatever changes are made, BFB must be rerun and the calibration check conducted again. If the criteria are met, the analysis may proceed. If all criteria are met but for the % differences for the CCC, then a new 5- point calibration must be conducted.

IV. Volatiles Reagent Blank Analysis

A. Objective

The reagent blank is intended to demonstrate the level of laboratory and reagent contamination, and to insure that that level is low enough or controlled enough to allow meaningful results to be obtained from the analytical data.

B. Requirements

A reagent blank for volatiles analysis must be performed every 12 hours, once per case, or with every 20 samples of similar concentration and/or sample matrix, whichever is more frequent. In practice, at the beginning of each 12-hour shift, once BFB tune has been conducted, a reagent blank is run which reflects the nature of the samples to be run that shift. That is, it contains all the reagents to be used in the samples, including methanol, surrogate compounds, etc. No analysis may proceed until this is done and the results are acceptable.

A reagent blank for volatile analysis should contain no more than 2 times the EPA CLP-mandated detection limit of methylene chloride, acetone, benzene, toluene, and methyl ethyl ketone. It must not contain greater than 5 times the detection limit of those compounds. For any other HSL compound, the blank must contain less than the detection limit.

The results for the reagent blank will be reported as a sample, with uncorrected concentrations reported in the PAL volatiles report form. Surrogate recoveries will be explicitly reported, and should meet the same criteria as those required for the samples. In addition to target compounds, any tentatively\identified compounds will be reported.

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VI. Matrix Spikes and Matrix Spike Duplicates

A. Objective

Matrix spikes are added to samples in order to assess the accuracy of the method as applied to the particular matrix at hand.

B. Requirements

Matrix spike samples will be run with every 10 samples and matrix spike duplicates with every 20 samples of a similar matrix. This will be done at no additional charge to the client. If a client has a smaller sample suite, the laboratory will charge for matrix spikes and matrix spike duplicates at the same rate as the sample analysis charge. PAL may in some cases elect to conduct matrix spike analysis when the client does not wish to have the results on such small sample sets. this will be a decision of the method supervisor or the project manager. In such cases the results are not reported to the client, but retained by the laboratory as supporting documentation for the case.

The standard matrix spike solution for volatiles includes 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. For specific requirements, occasionally other compounds may be added to the matrix spike test; for instance, if the client is particularly interested in tetrachloroethene, the method supervisor or project manager may elect to use this as an additional matrix spiking compound. Recoveries or the matrix spike compounds are calculated after correction for the sample result.

The normal recovery limits are set by the EPA CLP, and are shown below. Normally we will adhere to the soil limits for oily wastes, except in cases where we have shown that the matrix effect precludes such recoveries.

Please note that these limits are advisory. There is not action required by the EPA if they are not met. Rather, they are to be used in assessing trends of accuracy. For instance, consistently low values might be taken as an indication that actual concentrations are higher than measured.

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MATRIX SPIKE RECOVERY LIMITS*			
Fraction	Matrix Spike Compound	Water	Soil/Sediment*
VOA	1,1-Dichloroethene	61-145	59-172
VOA	Trichlorethene	71-120	62-137
VOA	Chlorobenzene	75-130	60-133
VOA	Toluene	76-125	59-139
VOA	Benzene	76-127	66-142

V. Surrogate Spike Analysis for Volatiles

A. Objective

The addition of surrogate spikes to every sample and blank is intended to show that the matrix and the analysis will allow analytes of the chemical characteristics represented by the surrogates to be detected and quantified within acceptable limits.

Surrogate spike compounds are added to all samples and blanks prior to purging, and the surrogates are recovered and reported in the analysis. For volatiles, the surrogate compounds are normally 1,2-dichloroethane- d4, toluene-d8, and bromofluorobenzene (BFB). The sample or blank is made to 50 ug/l in these surrogate compounds and recoveries are reported based on this concentration.

Additional surrogates, such as acetonitrile-d3, acetone-d5, pyridine-d5, or others, may be used when they are appropriate to evaluate the recovery of such analytes. The concentration of these additional surrogates will be set by the project manager or the method supervisor.

The surrogate recoveries required for water or soils are mandated by the EPA CLP, and are shown below. These may change as new contracts are issued. We will notify our clients if we decide to use the newer criteria.

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Surrogate Compound	% Recovery Range Acceptable	
	water	soil
1,2-dichloroethane-d4	76-114	70-121
4-bromofluorobenzene	86-115	59-113
toluene-d8	88-110	84-138

Generally speaking, the laboratory will try to adhere to the soil recovery limits in the case of oily wastes. However, a specific oily matrix may make such recoveries infeasible. If the recovery is not within the range on such material, a reanalysis will be attempted. If the recovery is still not within these limits while being acceptable for the blank, the problem will be assumed to be a matrix effect. In any case all surrogate recoveries and reruns will be explicitly reported to the client.

All surrogate recovery data will be maintained in a permanent laboratory record so that histories can be traced.

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GENERAL DATA VALIDATION

10-4-91

COLORADO DEPARTMENT OF HEALTH

4210 East 11th Avenue
Denver, Colorado 80220-3716
Phone (303) 320-8333

Main Building/Denver
(303) 322-9076

Ptarmigan Place/Denver
(303) 320-1529

First National Bank Building/Denver
(303) 355-6559

Grand Junction Office
(303) 248-7198

Pueblo Office
(719) 543-8441

ROY ROMER
Governor

JOEL KOHN
Interim Executive Director

September 30, 1991

Ellen Drew
PHOENIX ANALYTICAL LABORATORIES
3401 Industrial Lane
Broomfield, Colorado 80020

Lab I.D. CO067

STATUS UPGRADE

Ms. Drew:

Based on addition PE-sample audit data, the laboratory, located at 3401 Industrial Lane, Broomfield, Colorado, is being upgraded to certified for the parameters listed.

Status	Parameters
Certified	Trace Metals
Certified	Tot. Trihalomethanes
Certified	Volatile Organic Chemicals
Certified	Pesticides/Herbicides

This certification status is valid for these parameters as long as the laboratory:

1. Continues to use SDWA approved methodology.
2. Performs acceptably on performance evaluation studies.
3. Provides appropriate information to the State Certifying Officer when requested and/or required.
4. Passes an on-site inspection at least every three years (next inspection due 1st quarter, 1994), or more frequently if changes arise that may effect the quality of the analytical data and
5. Laboratory wishes to retain certification.

Clarence E. Lott, Jr.

Clarence E. Lott, Jr.
Sr. Chemist/QA Officer

printed on recycled paper

REPORT CHECKLIST ROUTING PROCEDURES

Each report generated at PAL receives a detailed check before it leaves the laboratory. There are different checklists for the various types of tests we perform.

It is the responsibility of every chemist to be trained in checking as many types of analyses as possible. All chemists need to check the "Checklist Vertical Files" in the instrument lab frequently. It is important that all checking be done in order of time priority for the client. Check the due dates.

In all cases, it is the responsibility of the person checking each section of the report to personally verify that each item in the section they are checking has been reviewed by signing off for each item on the list.

The clerical and client support sections of the checklist are reviewed for clerical and client support needs by staff members trained to check the specific sections of the report.

The reporter will attach the appropriate checklist to the front of the report folder behind the draft invoice. The reporter is responsible for seeing that the report is checked in a timely fashion.

Reporter Review Section

This section of the report is checked by the chemist preparing the report. The reporter will verify that all data is present, correct and consistent. Each reporter should have a copy of "Reporting Responsibilities" in their possession and this gives a detailed explanation of what is expected of the reporter in most reporting situations.

When this section is completed, the report is routed to the "Checklist Vertical Files" in the instrument lab for the Technical Review.

General and Detailed Technical Review Section

This section is checked by a chemist, other than the reporter, who is trained to review the various types of analyses.

This section includes a detailed review of the data by the chemist for clarity, accuracy and consistency.

When the chemist has completed his "technical review", he will sign the report summary in the space marked "Reviewed by" and the report is then routed to the "Checklist Files" in the client support office. Please note if report needs to be "Rushed" or "Faxed" at this time.

Clerical Review Section

This section is checked by clerical staff. The report is reviewed for clerical accuracy, completeness, legibility and to assure that all data is present and correct.

The clerical staff will fax/deliver reports as requested and as noted on the draft invoice.

The clerical reviewer will forward the report to the CST staff when the clerical review is complete.

CST REVIEW SECTION

This section of the report is checked by the client support staff for client needs, overall appearance, correct pricing and verification that all corrections are completed, and that the report is "Quality Acceptable" for client needs.

After this review, the report is routed back to the clerical staff for invoicing and delivery.

After the report is invoiced, the invoice is checked and the report is prepared for delivery per provided instructions.

After the report is completed and mailed or delivered, the project folder is routed back through the CST office, logged as complete and filed in the file cabinets in the sample custodial area.

pw\shirley\checklist

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REPORTING RESPONSIBILITIES

Cover Letter

1. Consistent Format
   A. Client project name and number consistent with client needs. (NA if unavailable)
2. Note:
   A. Date received
   B. Method #'s (correlate to client needs)
   C. Full analyses description (If you know the analyses is Mod. please note this)
   D. Missed Hold Times and possible consequences (See protocol for missed hold times.)
   E. If rerun
   F. Sample substitution
   G. Modifications (Any)
   H. Any QC outliers and implications.

SUMMARY ANALYTICAL SHEETS

1. Same information as the cover letter.
   A. Consistent format.
   B. Client project number and name (Na if unavailable)
   C. Method numbers consistent with client requests and actual analyte lists used.
   D. Enecotech - Date Sampled
      Date Received
      J.P. Walsh- Date Sampled
      Date analyzed
      1. Note: Logins will have the date sampled if available and will be logged in by similar dates sampled.
      2. Note: If there are major deviations from the expected, this should be discussed in detail on an ANALYTICAL MODIFICATIONS sheet. For now, this sheet ca be prepared from TOTSUM form.

DATA SHEETS

1. All pertinent information--date run
   time run
   date analyzed etc.
   A. These must be the same as all other pieces of supporting documentation.

LIBRARY SCANS

1. Same as above

TURNAROUND TIMES

1. The agreed upon Turnaround Times per CLIENT REQUEST will be generated on Friday afternoons for the next week. These dates are FIRM.
2. One week notice to client support if unable to meet P.A.L. established Turnaround Times.

3. Normal Turnaround Times:
   A. 2-3 weeks - VOA
   B. 2-3 weeks - GC
   C. 3-4 weeks - GC + Prep
   D. 3-4 weeks - SVOA
   E. 3-4 weeks - METALS
   F. 2-3 weeks - WET CHEM

HOLD TIMES

1. VOA - Run in 7 days from date of sampling
   TCLP - extract in 14 days from date of sampling.
2. SVOA - Extracted in 7 days from date of sampling
   TCLP - extract in 7 days from date of sampling. 40 days
3. GC + PREP - Extract in 7 days from date of sampling.
   TCLP - extract in 7 days from date of sampling.
4. WET CHEM - Dependant upon appropriate method guidelines and preservatives.
5. METALS - 6 months (with preservation) except for Hg which is 28 days.
   TCLP - 6 months (with preservation) except for HG which is 28 days.
6. AIR Samples-being looked into

HOLD TIMES - IF MISSED

1. Immediate CST notification - NO EXCEPTIONS - even if samples were received with the hold times missed.
2. Note in the cover letter the particular circumstances and the possible data implications. Include No Charge statement as well as an offer to resample. (See CSP for wording as they have conversed with the client when this first occurred.)

CHANGES TO ANY HARDCOPY

1. BY ANALYST - Changes done by the analyst need only have a single line drawn through plus the analyst's initials
2. BY ANYONE OTHER THAN ANALYST - Changes done by anyone other than the analyst must have the following:
   A. Single line drawn through
   B. Initials
   C. Date
   D. P.A.L.
3. Changes made to any form must be correlated by that analyst to the original. Technical and Clerical review cannot completely review each data package in its entirety every time a single change is made to an already completed data package.

RUSH REPORTS-

1. Bring reports to the Client Services office and place in the top box next to the door (marked RUSH). We will FAX to the client immediately based on client preferance for draft or technically checked reports.

TECHNICAL REVIEW CHECKLIST REPORT DATE_____

BTEX 8260_____GCMS_____ or BTEX/TPH_____

PROJECT NO._____CLIENT NO._____REPORTED BY____

INITIALS	DATE	REPORTER	CLERICAL	TECHNICAL	CST

REPORTER REVIEW

1. _____ _____All formats are consistent.
2. _____ _____Cover letter addresses unique situations
3. _____ _____All pertinent info. on every sheet.

GENERAL TECHNICAL REVIEW

1. _____ _____Blank results within acceptable limits.
2. _____ _____Report complete - Letter, summary, data sheets, chromatograms, blanks, standards and matrix spikes (if applicable).
3. _____ _____Data matches data sheets to summaries.

DETAILED TECHNICAL REVIEW

1. _____ _____Randomly check 5% of analyte concentration calculations.
2. _____ _____Check all dilution factors.
3. _____ _____Randomly check 5% of surrogate calculations.
4. _____ _____Chromatogram is properly labeled, standards, target compounds and numbers under the unknown.
5. _____ _____Analyte spectra present and labeled.
6. _____ _____Correct EPA number is present and is checked against client request.
7. _____ _____Check comparisons between analyses where appropriate.
8. _____ _____Check results for reasonableness (i.e. concentration range.)
9. _____ _____Data interpretations clearly separated from analytical results. Interpretation simple & clear, not overstated (proper qualification mode.)
10. _____ _____EPA data qualifiers are correct, and consistent data reports to summaries.

ANY ADDITIONAL CORRECTIONS REQUIRED?_____

pw\Shirley\BTEX8260

CLERICAL REVIEW

1. Draft Invoice

A. _____ _____ All applicable information noted. Includes quote no., PAL no., Client nos.', Sample receipt date, report date, project name, and client contact.

2. Cover Letter

A. _____ _____ EPA method matches summary
B. _____ _____ All spelling correct; letter matches summary.
C. _____ _____ Letter has been signed.
D. _____ _____ Client name, nos., PAL nos. correct.

3. Log In to Summary Pages

A. _____ _____ PAL project number correct.
B. _____ _____ Client numbers correct.
C. _____ _____ Analyses requested\Method numbers ok.
D. _____ _____ Dates-sample, receipt, report-All correct.
E. _____ _____ All samples requested run & checked on log in.
F. _____ _____ Verify that all sample ID. No.s are correct.
G. _____ _____ Summaries signed; Spelling correct.

4. Summary to Data Packages - Cover Sheet

A. _____ _____ Sample I.D.s' must match log in sheet.
B. _____ _____ PAL project number correct.
C. _____ _____ Client numbers correct.
D. _____ _____ Matrix-Soil or Water-Matches Log in.
E. _____ _____ Sample concentrations-units consistent.
F. _____ _____ MTBE shown on all VOA summary sheets.
G. _____ _____ Matrix Spikes - if applicable & present numbers are correct.

5. Data Sheets Only

A. _____ _____ Matrix/Concetration units correct.
B. _____ _____ Blanks-All noted are present/dates match.
C. _____ _____ Surrogates-Present;In or out;noted if out and corrected if required.
D. _____ _____ Legibility/Reproducibility CLEAR
E. _____ _____ Run/analyzed date matches Data Sheet to first chromatogram.
F. _____ _____ Run numbers present all data sheets.
G. _____ _____ Sample Qtys. match/ran all requested.
H. _____ _____ All sample ID.s are correct.

CST REVIEW

1. Overall Review

A. _____ _____ Discrepancies corrected/checked off
B. _____ _____ All client needs/requests met.
C. _____ _____ Everything legible/Graphics output ok
D. _____ _____ Draft invoice-prices checked with price list/quotes; discounts noted?
E. _____ _____ Holding times met? Turnaround time ok?
F. _____ _____ Method/Delivery Time

2. Final Invoice

A. _____ _____ All numbers are correct.
B. _____ _____ Matches draft invoice numbers/etc.
C. _____ _____ All spelling is correct.

CSI CHECKLIST

1) COVER LETTER

A) _____ _____ Methods match log-in & summary.
B) _____ _____ Date received matches log-in.
C) _____ _____ Any special pertinent info. addressed in cover letter (Hold times, surrogates, items detected,etc.)

2) COMPLETE REPORT

A) _____ _____ Hold times,T.A.times,cust.due dates met.
B) _____ _____ All client needs met.
C) _____ _____ All discrepancies corrected/re-checked.
D) _____ _____ Report legible - Graphics output ok.
E) _____ _____ Delivery time and method noted.

2) SUMMARY

A) _____ _____ Methods match log-in and cover letter.
B) _____ _____ Dates: Rec'd,Analyzed,Extracted,Sampled, reported match -log-in to data package.
C) _____ _____ Test data #'s match Data Package #'s.

3)(DATA PACKAGE

A) _____ _____ Date extracted/analyzed within hold time.
B) _____ _____ Check surrogate #'s with handwritten #'s.
1)Surrogates to library - consistency
2)compounds and conc. to library.
C) _____ _____ Standards/Blanks checked - Tune #'s consecutive-dates match analyzed date.
D) _____ _____ Items detected - check handwritten #'s with typed data package #'s
E) _____ _____ Compare compounds found to summary with concentrations and qualifiers if needed.
F) _____ _____ Compounds - consistency of spelling.
G) _____ _____ Compounds & conc. data sheet to list.
H) _____ _____ Cross outs initialed.
I) _____ _____ First sheet of library stamped by chemist
J) _____ _____ All TIC's listed with concentration.
K) _____ _____ Chromatograms - All compounds and TIC's labeled or stamped (Ask Chemist).
L) _____ _____ All back-up paperwork appropriately labeled. (i.e. - Benzene or #1 for TIC)
M) _____ _____ Each data pkg. - headers legible, handwritten info. initialed & dated.

4) DRAFT INVOICE/BILLING

A) _____ _____ Verify prices, discounts,-check f/quotes.
B) _____ _____ All necessary/special info. on draft inv.

YES_____ NO_____ PROJECT COMPLETE

F:Shirley\CSIcheck\pw

ADRIAN BROWN CONSULTANTS, INC.

CHAIN OF CUSTODY RECORD

CLIENT NAME....:_____

PROJECT I.D....:_____

SAMPLER(S) ....:_____
(signature)

Page _____ of _____

Date _____

Sample I.D.	Date Sampled	Time Sampled							Remarks	Lab I.D.

<<<<<<<< Relinquished By (Signature) >>>>>>>>

Name _____ Date/Time ____/____
Organization _____

Name _____ Date/Time ____/____
Organization _____

Name _____ Date/Time ____/____
Organization _____

<<<<<<<< Received By (Signature) >>>>>>>>

Name _____ Date/Time ____/____
Organization _____

Name _____ Date/Time ____/____
Organization _____

Name _____ Date/Time ____/____
Organization _____