Harding Lawson Associates

July 2, 1992

10495

Exxon Company, U.S.A
P.O. Box 4032
2300 Clayton Road
Concord, California 94524

Attention: Ms. Marla Guensler

Ladies and Gentlemen:

Work Plan
Offsite Groundwater Survey
Exxon Station 7-0104
Alameda, California

Harding Lawson Associates (HLA) has prepared this work plan for Exxon Company, U.S.A. (Exxon) for an offsite groundwater survey in the vicinity of Exxon Station 7-0104, 1725 Park Street, Alameda, California (site; Plate 1). This work plan has been prepared in response to a letter from the Alameda County Health Care Services Agency (County) dated May 11, 1992, requesting a work plan for the installation of offsite monitoring wells. This work plan addresses the first phase of the offsite investigation. HLA proposes to conduct the groundwater survey to select optimum locations for offsite monitoring well(s). Subsequent offsite work will be described in a separate work plan, if appropriate, following completion of the groundwater survey. It is HLA's understanding that Exxon will transmit copies of this work plan to the County and the California Regional Water Quality Control Board, San Francisco Bay Region.

BACKGROUND

HLA has conducted three phases of site characterization and presented the results to Exxon in reports dated June 24, 1988; March 21, 1989; and May 1, 1990, respectively. HLA has also been conducting monthly water-level monitoring and quarterly groundwater sampling programs at the site since June 1989. In February 1992, HLA conducted a file review and offsite reconnaissance to assess potential sources of petroleum hydrocarbons in the site vicinity. The following presents a summary of these investigations.

Site Hydrogeology

Site lithology consists of 1 to 5 feet of fill overlying interbedded sand, silty and clayey sand, and silt of the Merritt Sand and Posey formations. These units comprise the uppermost water-bearing zone. Confining clay strata of the underlying San Antonio formation occurs at depths greater than 38 feet in the site vicinity. Measured piezometric levels in onsite wells have ranged from 4.5 to 7.5 feet below ground surface. On the basis of measured piezometric levels, the apparent direction of groundwater flow in the upper water-bearing zone at the site is southeast.

Distribution of Petroleum Hydrocarbons in the Subsurface

Petroleum constituents have been detected in soil samples collected from all borings drilled at the site. Detected concentrations of total petroleum hydrocarbons (TPH) as gasoline have ranged from 0.6 to 2,600 milligrams per kilogram (mg/kg). The highest concentrations of TPH as gasoline were detected in soil samples collected near the tank field and in the downgradient, southeast corner of the site.

Free-phase petroleum hydrocarbon product has not been observed in onsite monitoring wells. However, concentrations of benzene in groundwater collected from all monitoring wells exceed the EPA Maximum Contaminant Level (MCL) of 1 microgram per liter (ug/l). The highest concentrations of benzene in groundwater were detected in wells adjacent to and downgradient of the tank field and dispenser islands.

Known and Potential Offsite Sources of Contamination

Within 0.15 mile of the site, HLA has identified 22 gasoline stations, car dealerships, and auto repair facilities that have potential to handle hazardous materials. Several of these facilities are known to operate underground storage tanks.

Review of County files indicates that there are two facilities within 0.25 mile of the site where petroleum hydrocarbons and oil and grease have impacted soil or groundwater quality. These facilities are Good Chevrolet, 1630 Park Street and Cavanaugh Motors, 1700 Park Street. Both facilities appear to be crossgradient of the Exxon station.

PURPOSE AND SCOPE OF WORK

The objectives of this investigation are to:

- Evaluate the horizontal extent of total petroleum hydrocarbons (TPH) as gasoline and benzene, toluene, ethylbenzene, and xylenes (BTEX) in groundwater within the limits of the study area (Plate 2), and
- Evaluate other potential sources of contaminants in the groundwater.

To achieve these objectives, HLA will perform a groundwater survey in the vicinity of the site. The scope of the investigation will include collecting groundwater samples from up-, cross-, and downgradient sampling locations, analyzing the samples for petroleum hydrocarbon constituents and purgeable halocarbons, and preparing a report. Prior to the start of work, HLA will obtain the necessary permits and will contact pertinent public and private entities to locate underground utilities in the site vicinity. All field work will be performed by an HLA geologist, hydrogeologist, or technician under the supervision of a California-registered geologist. The investigation will be performed by completing the tasks described below.

Task 1: Utility Clearance and Permitting

A utility clearance investigation will be conducted in the site vicinity. HLA will contact Underground Service Alert and arrange a field meeting to discuss proposed sampling locations. Additionally, HLA will contract a private utility clearance company to clear each proposed sampling location.

Prior to initiating the field investigation, HLA will obtain an encroachment permit from the City of Alameda for work performed in the City right-of-way. In addition, HLA will obtain a *Groundwater Protection Ordinance Permit* from the Alameda County Flood Control and Water Conservation District.

Task 2: Groundwater Survey

HLA will supervise the collection and analysis of groundwater samples in the site vicinity. Work will be performed adjacent to street gutters in the Eagle Avenue and Park Street right-of-ways. Traffic control in the vicinity of work activities will be coordinated by a subcontractor in accordance with California Department of Transportation and City of Alameda regulations.

Groundwater samples will be collected by Hydro Geo Chem, Inc., Tucson, Arizona, under contract to HLA. A detailed description of groundwater survey sampling and analysis methodology is provided as Attachment A.

Groundwater samples will be collected from temporary 1 $^3/_8$-inch-outer diameter galvanized steel probes, with hardened-steel disposable points. The probes will be pneumatically driven to an approximate depth of 8 feet below ground surface (approximately 2 feet below the groundwater table). To collect a representative groundwater sample, the probes will be purged of approximately three probe volumes of water prior to sample collection. After purging, a groundwater sample will be collected from each probe by lowering a stainless steel bailer through the probe into the groundwater. The groundwater samples will be decanted from the bailer into 40-milliliter volatile organic analysis (VOA) vials and one-liter amber glass jars, labeled, placed in a cooler with ice, and transported to Hydro Geo Chem's onsite laboratory or Pace Incorporated's (Pace's) fixed-base laboratory in Novato, California.

HLA proposes to collect groundwater samples from approximately 18 sampling points (Plate 2). Actual sampling locations may vary depending on site conditions, the results of the utility clearance, and field data gathered during the course of this investigation.

In order to minimize the possibility of cross contamination, all sampling equipment will be decontaminated prior to and after use. The probes and bailers will be steam cleaned or washed in a low-phosphorous soap solution and double rinsed with deionized water. Decontamination fluids will be contained in 55-gallon drums and temporarily stored at the Exxon station. A sample will be collected from the decontamination fluids and submitted for analysis. Upon receipt of analytical results, the water will be disposed in accordance with state and local regulations.

Following completion of groundwater sampling, the probe holes will be filled with a neat cement grout. The grout will be poured from the ground surface until the hole is completely filled. If samples are collected from paved areas, asphalt patch will be applied to the top several inches of the grout-filled hole.

Laboratory Analytical Program

The samples will be analyzed onsite by Hydro Geo Chem for TPH as gasoline, purgeable halocarbons, and benzene, toluene, ethylbenzene, and xylenes (BTEX) using EPA Test Methods 8015 (modified) and 502.2. Samples will also be analyzed by Pace for TPH as diesel using EPA Test Method 3550/8015 (modified).

Quality Assurance/Quality Control

Quality Assurance and quality control will be achieved through strict laboratory protocol. Chain of custody procedures will be initiated in the field and maintained until the samples are transferred to the analytical laboratories. All parts of the collection system that come into contact with a sample will be decontaminated before each use. A system blank and calibration run will be performed at the beginning of each day of mobile laboratory operation and after 10 samples have been collected.

Prior to each day's sampling, field blanks of the entire sampling apparatus will be taken and analyzed to check background contamination in the sampling system and cartridges. One field blank will be collected for each day of water sampling to ensure that proper groundwater sample collection procedures are being followed. Duplicate samples will be analyzed from 10 percent of the sample locations as a measure of reproducibility.

Task 3: Report Preparation

At the completion of all field work and upon receipt of laboratory analytical reports, HLA will prepare a written report summarizing the work performed and presenting conclusions regarding conditions within the study area.

We trust that this is the information you require at the present time. If you have any questions, please call us at 415/892-0821.

Yours very truly,

HARDING LAWSON ASSOCIATES

Mary Jo Heassler

Mary Jo Heassler
Project Geologist

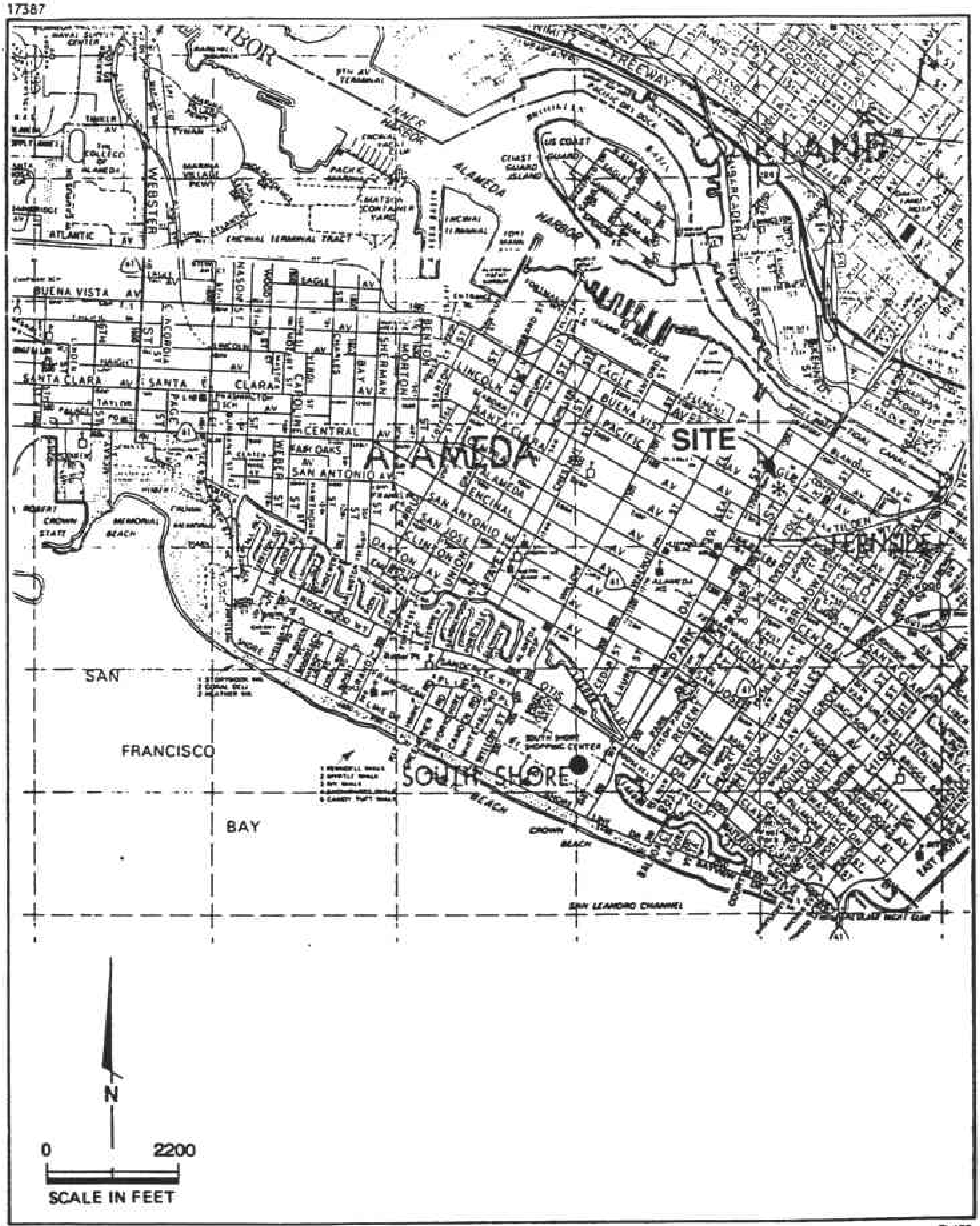
Michael Siembieda
Associate Geologist, R.G. 4007

MICHAEL L. SIEMBIEDA
No: 4007

Attachments: Plate 1 - Area Map
Plate 2 - Proposed Sampling Locations
Attachment A - Volatile Organic Sampling and Analysis

mjh\letter\exxon\workpln.doc

17387

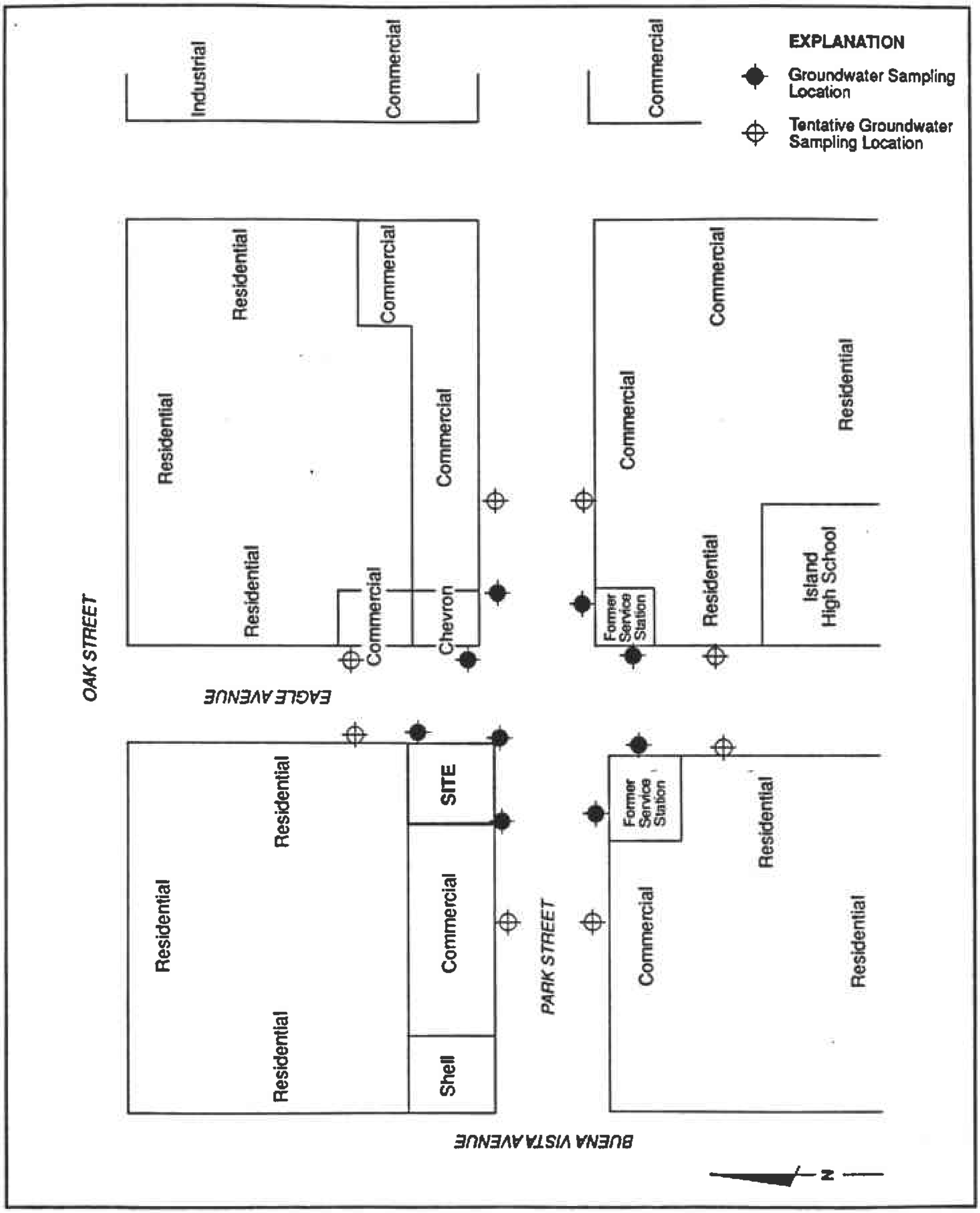


Harding Lawson Associates
Engineering and
Environmental Services

Area Map
Phase III Evaluation of Petroleum Hydrocarbons
Exxon Station #7-0104
Alameda, California

PLATE
1

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED	DATE
CVD		MJH	3/90		



Harding Lawson Associates
Engineering and
Environmental Services

Proposed Sampling Locations
Exxon Station #7-0104
Alameda, California

PLATE
2

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
LZc	10495 416	MJH	7/92	

ATTACHMENT A

VOLATILE ORGANIC SAMPLING AND ANALYSIS

VOLATILE ORGANIC SAMPLING AND ANALYSES IN SOIL GAS, SOILS, WATER, AND ATMOSPHERE BY MODIFIED EPA 8021 HYDRO GEO CHEM, INC.

Hydro Geo Chem, Inc.
1430 North Sixth Avenue
Tucson, Arizona 85705
(602)623-6981

TABLE OF CONTENTS

Page

List of Figures

Figure

Page

TABLE OF CONTENTS (CONTINUED)

List of Tables

Table

Page

VOLATILE ORGANIC SAMPLING AND ANALYSES IN SOIL GAS, SOILS, WATER, AND ATMOSPHERE BY MODIFIED EPA 8021

HYDRO GEO CHEM, INC.

INTRODUCTION

On site analysis of volatile organic compounds (VOC) is increasingly important to environmental assessments. The ability to perform real-time chemical analysis during investigations of potentially contaminated soils, water, and air allows field decisions to be made regarding the depth and areal extent of the investigation.

The applications of on-site VOC analysis include: soil analysis for evaluation of subsurface spills and leaking tanks; atmospheric analysis for evaluation of VOC emissions from landfills, contaminated soils, and industrial facilities; water analysis for identification and definition of the vertical and areal extent of groundwater VOC plumes; and soil gas surveys in which VOC's in the soil atmosphere are sampled and analysed in order to determine the vertical and areal distribution of VOC's in site soils.

Because VOC's are readily transported in soils by diffusive and advective processes, soil gas surveys have proved to be a powerful technique for determining whether spills have taken place on the site, for locating these spills, and, if subsurface conditions are favorable, for finding and delineating groundwater VOC plumes by the presence of VOC's in overlying soils.

The analytical requirements for real-time mobile-laboratory analysis are different than the conventional VOC analyses prescribed by EPA protocols. The laboratory productivity, that is, the number of analyses required per unit time, must be much greater for the mobile facility. Otherwise, the value of using the data to modify the investigation is diminished.

Despite the need for greater productivity, the other analytical requirements for detection limits, variety of analytes, and freedom from laboratory contamination are, if anything, more stringent than those of fixed laboratory facilities.

The following sampling and analytical protocols have been adopted by Hydro Geo Chem to meet these stringent requirements of on-site VOC analysis.

Summary of Method

In summary, the analytical method consists of the recently approved EPA 8021 protocol, modified to allow greater throughput and to minimize the potential for laboratory contamination. These modifications include temperature programming and flow changes to reduce analytical time, the use of gas rather than water-solution standards, purging of VOA bottles (40 or 250 ml bottles sealed with a teflon septum) directly rather than using a conventional water purging apparatus (a technique recently independently developed and used in EPA Region 5 RI/FS studies), methanol solvent extraction of soils and subsequent stripping of a methanol-water solution; and splitting of the sample injection stream to allow simultaneous analysis on a separate column and detector of other compounds not analyzed by the 8021 protocol. Table 1 lists the compounds that can be analyzed using EPA 8021 protocol.

Table 1. Compounds EPA Method 8021 (Hall/PID Analysis)

- Benzene
- Bromobenzene
- Bromochloromethane
- Bromodichloromethane
- Bromoform
- Bromomethane
- n-Butylbenzene
- sec-Butylbenzene
- tert-Butylbenzene
- Carbon tetrachloride
- Chlorobenzene
- Chloroethane
- Chloroform
- Chloromethane
- 2-Chlorotoluene
- 4-Chlorotoluene
- Dibromochloromethane
- 1,2-Dibromo-3-chloropropane
- 1,2-Dibromoethane
- Dibromomethane
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- Dichlorodifluoromethane
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- 1,1-Dichloroethene
- cis-1,2-Dichloroethene
- trans-1,2-Diochloroethene
- 1,2-Dichloropropane
- 1,3-Dichloropropane
- 2,2-Dichloropropane
- 1,1-Dichloropropane
- Ethylbenzene
- Hexachlorobutadiene
- Isopropylbenzene
- p-Isopropyltoluene
- Methylene chloride
- Naphthalene
- n-Propylbenzene
- Styrene
- 1,1,1,2-Tetrachloroethane
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethene
- Toluene
- 1,2,3-Trichlorobenzene
- 1,2,4-Trichlorobenzene
- 1,3,5-Trichlorobenzene
- 1,1,2-Trichloroethane
- 1,1,1-Trichloroethane
- Trichlorofluoromethane
- 1,2,3-Trichloropropane
- 1,2,4-Trimethylbenzene
- 1,3,5-Trimethylbenzene
- Vinyl chloride
- o-Xylene
- m-Xylene
- p-Xylene

The sampling methods included in the protocol have been designed to allow accurate, contamination-free sampling of soils, water, atmosphere, and soil gas. These methods offer a detection limit of at least 0.1 µg/kg (soil), 0.01 µg/l (soil gas or water), and 0.001 µg/l (atmosphere) for any compounds listed in Table 1. Additional, simultaneous analysis is provided for total petroleum hydrocarbons, methane, and total chlorinated hydrocarbons. The following sections document the materials, apparatus, and procedures used.

1. SAMPLING

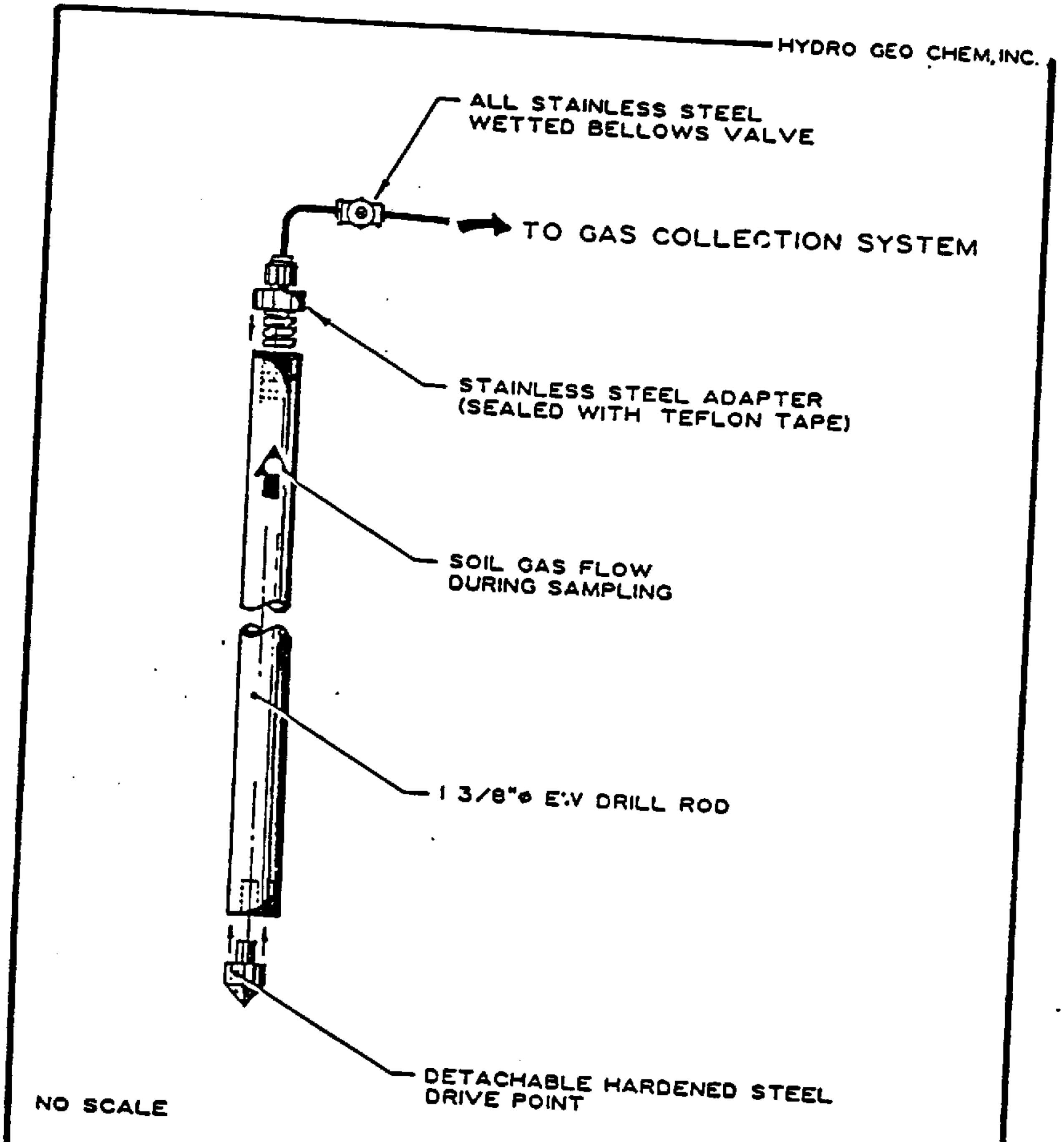
1.1 Scope and Application

This section covers the materials, equipment and procedures utilized by Hydro Geo Chem, Inc. for collecting soil gas, atmospheric, soil, and shallow groundwater samples in the field.

1.2 Sampling Equipment

1.2.1 Sampling Probes and Drive Point Rigs

Sampling probes consist of 5 foot sections of nickel plated $1^3/_8$" hardened EW drill rod with Acme threads. The high carbon steel points are left behind when the pipe is hydraulically pulled back to expose the formation to pumping. Figure 1 shows our probe design. The probes are driven to the sampling depth using a heavy duty hydraulic hammer mounted on Ford F-450 trucks. These rigs are capable of driving sampling pipe to a depth in excess of 50 feet under normal driving conditions. The drive point rigs are equipped with hydraulic outriggers, pipe racks and a steam cleaner. The probes are removed by the drive point rig using a hydraulically activated pulling dog. Latex gloves are worn during handling and assembling of the sampling apparatus.



SOIL GAS SAMPLING PROBE

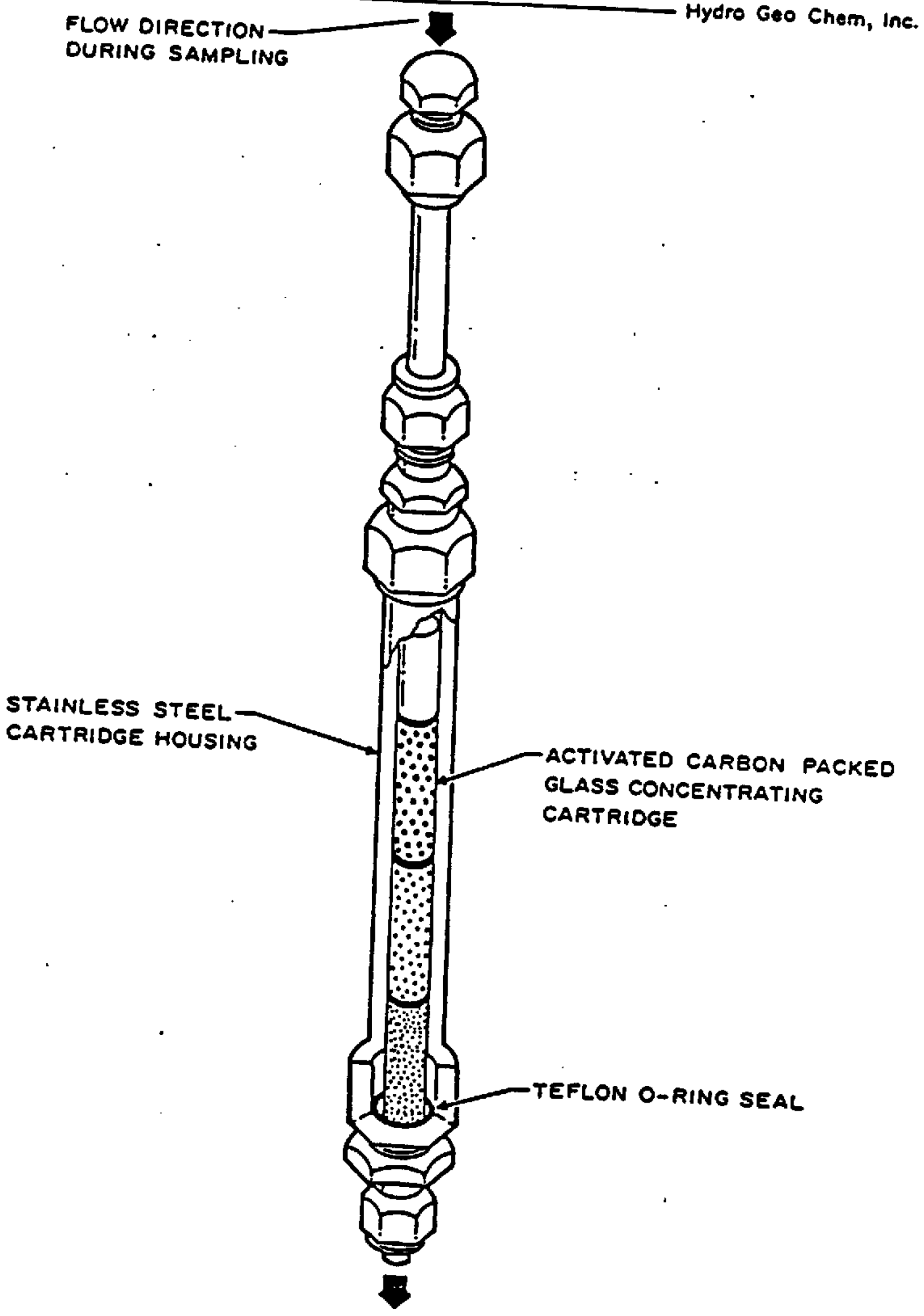
FIGURE 1

1.2.2 Sampling Adaptors

Soil gas samples are collected from the probes via adaptors constructed of stainless steel pipe caps welded to stainless steel tubing connected to an inline stainless steel bellows valve.

1.2.3 Soil Gas Cartridges

Atmospheric or soil gas samples are collected in stainless steel cartridges housing a glass tube (Supelco) filled with a three layer packing of various types of adsorptive hydrophobic carbon (see Figure 2). The soil gas is passed through these layers, the first, Carbotrap, absorbing "heavy" volatiles such as dichlorobenzene, the second, Carbopack B, the lighter volatiles such as TCE and DCE, and the third, Carbosieve III, the ultralights such methylene chloride or vinyl chloride. The most mobile constituent, vinyl chloride, has a breakthrough volume of 158 liters (vinyl chloride detected at the tube outlet after 158 liters of 25 ppb vinyl chloride are passed through the cartridge). These cartridges are therefore rated to absorb at least 158 liters of soil gas or atmospheric gas before breakthrough of any of the priority pollutants listed in EPA method 8021. Table 2 shows some breakthrough volumes for the types of carbon sorbents making up the adsorption cartridge. Thus the sampling capacity of this technique far exceeds that of syringe collection. The high capacity is necessary to meet the wide range of specified detection limits encountered in site investigations.



SOIL GAS SAMPLE HOUSING

Figure 2

Table 2

Breakthrough Volumes (in Liters) for Selected Hydrocarbons on the Carbosieve™ S-III/Carbopack B/Carbotrap C Thermal Desorption Tube

Hydrocarbon	Carbosieve S-III (125 mg)	Carbopack B (200 mg)	Carbotrap C (300 mg)
Vinyl Chloride	158		
Chloroform		1.1	
1,2-Dichloroethane		0.4	
1,1,1-Trichloroethane		2.7	
Carbon tetrachloride		4.7	
1,2-Dichloropropane		6.8	
Trichloroethylene		2.5	
Bromoform		1.7	
Tetrachloroethylene		2.2	
Chlorobenzene		316	
n-Heptane		262	
1-Heptene		284	
Benzene		2.3	
Toluene		130	
Ethylbenzene		4060	12.9
p-Xylene			11.2
m-xylene			11.0
o-xylene			11.0
Cumene			27.8

1.2.4 Groundwater Samples

Groundwater is sampled through the $1^3/_8$ inch EW drill rod using $^3/_8$" stainless steel bailers.

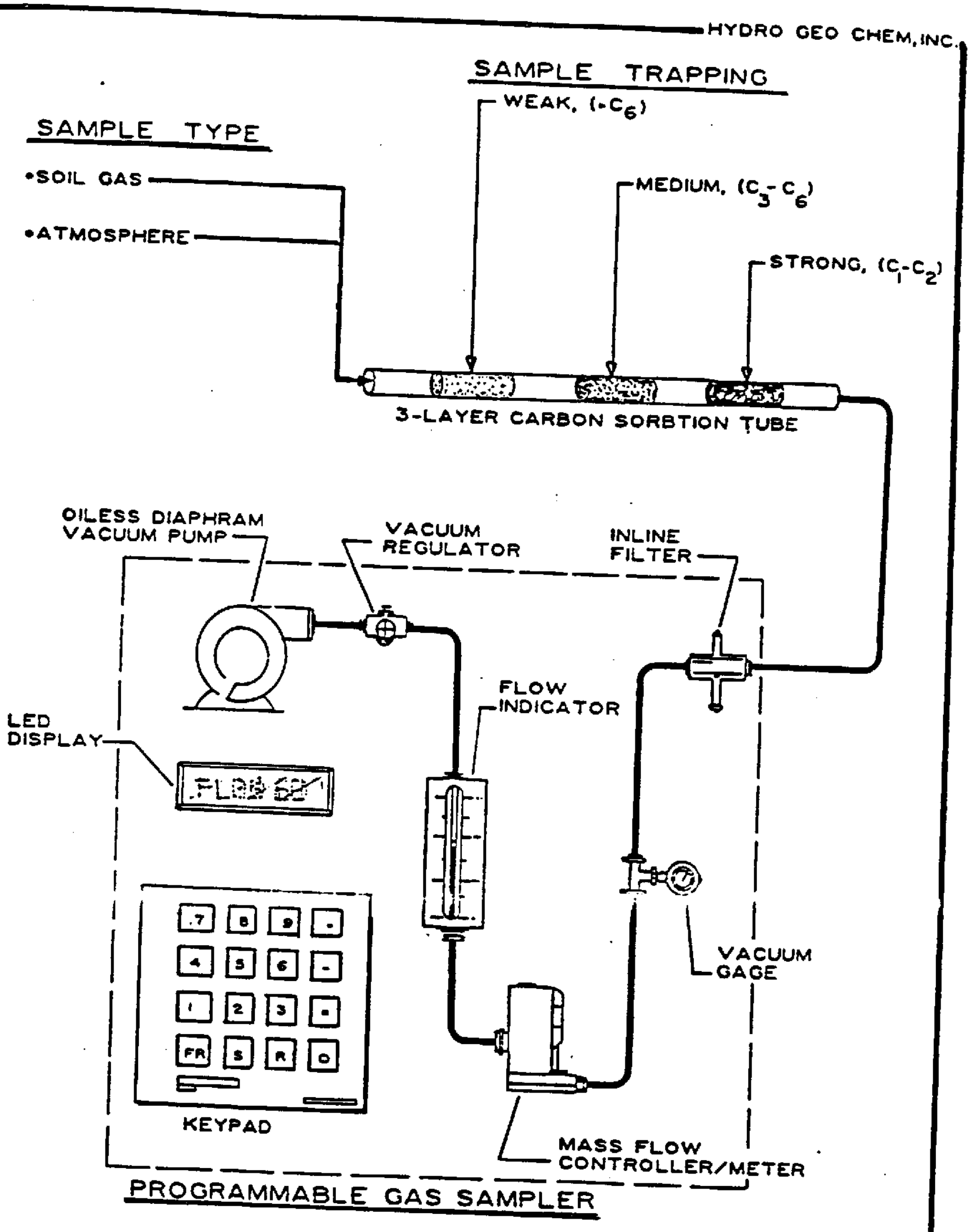
1.2.5 Soil Samplers

Soil is sampled at specified intervals using a 1 inch diameter by 12 inch length ring-barrel sampler containing multiple stainless steel sleeves.

1.3 Sample Collection

1.3.1 Soil Gas Sampling

After purging 3 probe volumes from the sampling train, the bellows valve on the adaptor is shut off and the stainless steel sample cartridge housing is attached in line using Swagelok compression fittings. The cartridge inlet leads to the adaptor and the outlet to a programmable mass flow controller equipped with a vacuum regulated oilless diaphragm vacuum pump (see Figure 3). The flow controller is typically programmed to pump 200 ml of soil gas at a flow rate of 100 ml/min. When the specified flow volume has been obtained, a



SOIL GAS SAMPLE COLLECTION

Figure 3

solenoid valve is automatically closed and the sample collection is complete. The mass flow meter delivers sample volumes between 20 and 5000 standard ml with less than 2% error independent of temperature and vacuum conditions.

1.3.2 Atmospheric Sampling

Atmospheric samples are collected by positioning the probe in the area of interest, and programming the mass flow controller to the appropriate pumping rate and total sample volume. If desired, the probe can be moved through a sampling volume at a specified rate to collect an integrated sample. No purging is necessary for atmospheric samples.

1.3.3 Soil Sampling

Soil samples are collected using 1" ring samplers equipped with three 4" stainless steel sleeves. The $1^3/_8$" sampling probe is first equipped at its end with a retrievable point and emplaced to depth. The sampling probe is then fully extracted and the retrievable point is replaced with the 1" ring sampler. The sampling probe is then run back into the original hole and the sampler is driven 12" beyond the hole bottom. The sampling probe is extracted again and the 1.0" ring sampler detached. No liquids (i.e., drilling mud, water, foam) are used during the probe placement or sampling procedure. All soil samples to be analyzed or sent out for analysis are retained in the stainless steel tubes (1.0 inch diameter, 4 inches long). Immediately following removal of the stainless steel sleeves from the sampler, the center tube is capped with aluminum foil and plastic slip caps. The slip caps are then duct taped to the stainless steel sleeves to maintain a proper seal. Samples are labeled and placed in a zip lock plastic bag and stored in a cooler.

1.3.4 Water Sampling

Groundwater samples are collected using $^3/_8$" stainless steel bailers. The bailers are lowered down the inside of the probe using a nylon cord that is replaced before each sampling. The water sample is carefully poured in 40 ml VOA vials in a manner not to allow air bubbles to pass through the water sample. The liquid full vials are then immediately capped with a teflon-lined septum cap and delivered to the mobile lab for analysis.

1.4 Decontamination of Equipment

1.4.1 Prior to each use and reuse, each soil sampler, stainless steel sleeve, sampling probe, point and bailer are steam cleaned and stored in clean storage in clean storage areas on the drive point rigs. Care is taken with this equipment to eliminate both soil-surface and cross-hole contamination. Vinyl or latex surgical gloves are worn during handling and assembly of the sampling apparatus.

1.4.2 Adaptors, stainless steel bottles, and stainless steel cartridge holders are heated to 120°C using a convection oven and held for 1 hour at that temperature. Carbon packed desorption cartridges are purged at 400°C with helium for 8 minutes.

1.4.3 Separate storage areas are provided for used and cleaned equipment. No equipment is reused without cleaning.

2. ANALYSIS

2.1 Scope

This section covers the equipment, materials, and procedures used to determine the concentrations of various volatile organic compounds in the soil gas, atmospheric, soil, and shallow groundwater samples.

2.2 Detection Limits

Method detection limits (MDL's) are matrix dependent. The MDL for soil gas samples is 0.01 µg/l, 0.01 µg/l for water and 0.1 µg/kg for soils. The MDL for atmospheric samples is 0.001 µg/L. The applicable concentration range of this method is influenced by sample size and instrument limitations.

2.3 Apparatus and Equipment

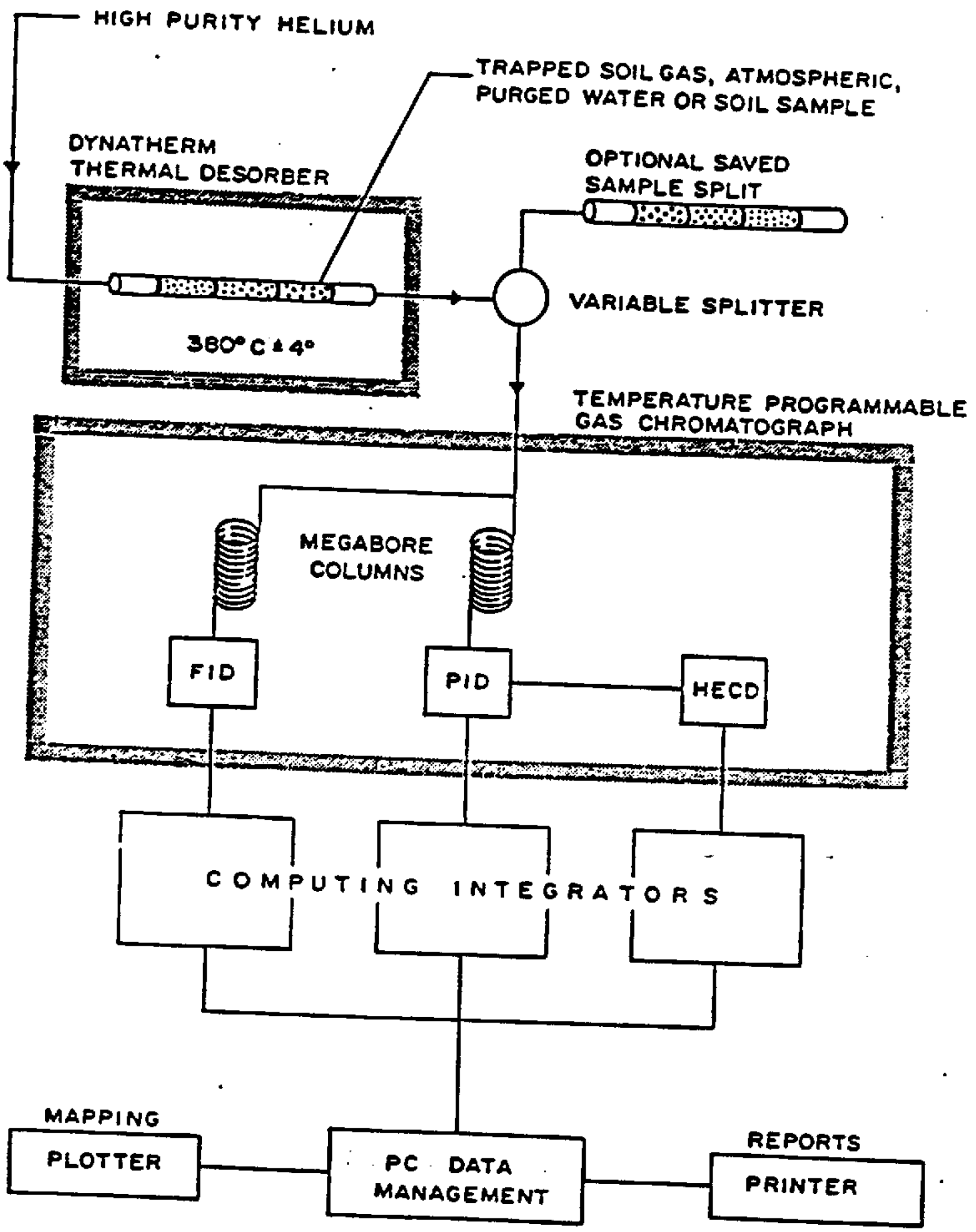
2.3.1 Gas Chromatographs

Hydro Geo Chem's mobile laboratories, used to provide on-site analyses, are housed in 18 foot custom built non-motorized trailers. The mobile laboratories are stand-alone vehicles that operate separately from the drive point rig, thereby allowing efficient operation of both. Each mobile lab has a Varian 3400 temperature programmable gas chromatograph (GC) equipped with cryogenics capable of cooling the column to below 0°C using carbon dioxide. The chromatograph is connected to an Envirochem thermal desorber (Model 850) which accepts the glass sorption tubes used to collect the soil gas, atmospheric, or the purged water or soil samples. Figure 4 is a schematic of the analytical apparatus. Helium flow is opposite to the flow direction of sample collection. The thermal desorber rapidly heats the sample sorption tube to 380 ± 4°C in 26 ± 2 seconds releasing the volatile organic compounds from the activated carbon. The released compounds are transferred from the desorber unit to the analytical columns via heated (250°C) nickel lines. The compounds are held in the cooled columns (cryofocused) at the start of the chromatographic run.

The carrier gas is ultra high purity helium at 10-20 ml/minute. The carrier gas flow is augmented with an additional 25 ml/minute helium before entering the photoionization detector (PID) to optimize response of both PID and Hall electrolytic conductivity (Hall) detectors.

2.3.2 GC Columns

A DB 624 Megabore column, 30 m x 0.53 mm (J&W Scientific) is used in the Varian 3400 chromatograph. The helium flow rate is adjusted to approximately 7.0 ml/minute. The temperature program varies with the client needs. A typical temperature program is as follows: the column temperature is held at 2°C for 3 minutes, then



MOBILE LABORATORY
ANALYTICAL SCHEMATIC

Figure 4

programmed to 35°C at 15 C°/minute, no hold time, to 145°C at 8 C°/minute, no hold, to 230°C at 35 C°/minute.

Additional columns are available for the analysis of pesticides and classes of hydrocarbons other than aromatic and halogenated. Columns available include DB-WAX, 30m x 0.53mm, DB-5, 30m x 0.53mm, and DB 608, 15m x .53mm. All columns are obtained from J&W Scientific.

The GC is also equipped with a 1/8" x 18" Carbosphere column, 60/80 mesh, used to analyze for nonsorbable gases, such as methane, by direct injection. This column is operated at ambient temperatures.

2.3.3 Detectors

2.3.3.1 A photoionization detector (PID) equipped with a 10.2ev lamp (Tracor Model 703) is used.

2.3.3.2 A Hall electrolytic conductivity detector (HECD) (Tracor Model 700A) is also used. Operation conditions are as follows:

Reaction tube:	Nickel 1/16" OD
Reactor temperature:	900°C

Reactor base temperature: 250°C
Electrolyte: n-propyl alcohol
Electrolyte flow rate: 0.7 ml/min
Reaction gas: hydrogen at 35 ml/min.
Carrier gas plus make up: helium at 32 ml/min.

2.3.3.3 Hydro Geo Chem also has available an Electron Capture Detector, ECD (Varian).

2.3.3.4 A Flame Ionization Detector, FID (Varian), is also provided for total hydrocarbon analyses.

2.3.4 Integrators

The mobile laboratories are equipped with Spectra Physics dual channel integrators (Model 4400) and Varian integrating printer/plotters.

2.3.5 Purge and Trap Apparatus

An in-house designed and built purging apparatus (Figure 5) is used in the analysis of soil and water samples. High purity, inert (He

PURGE APPARATUS FOR SHALLOW WATER SAMPLES

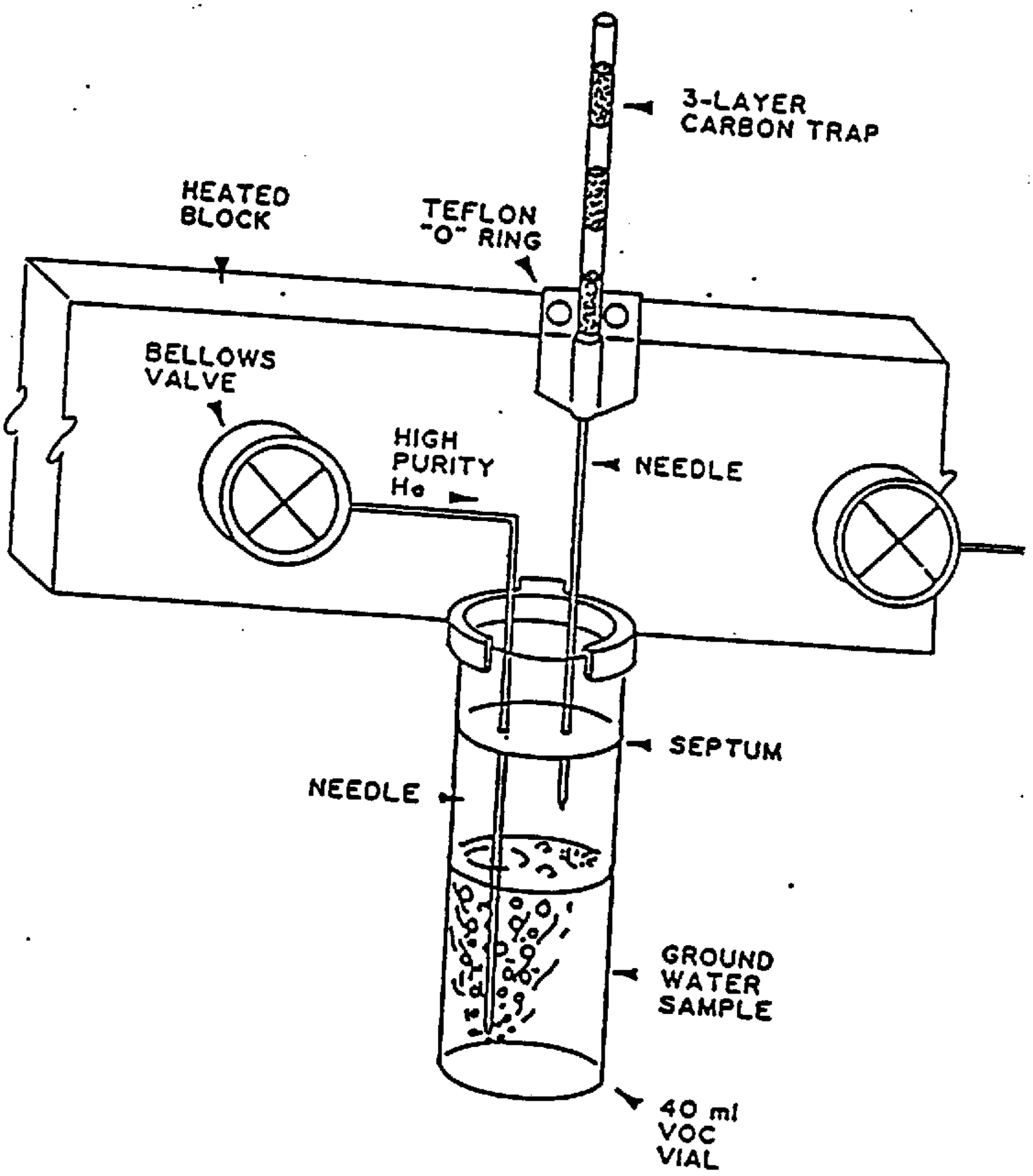


Figure 5

or N_2) gas is bubbled through the sample at 200 ml/min for 15 minutes. In addition, a temperature programmable Dynatherm Thermal Dynamic Stripper is also used for purging both soil and water samples. Purged sample components are trapped in activated carbon cartridges.

2.3.6 Standards and Reagents

2.3.6.1 Standards are obtained from certified gas mixtures or prepared from stock mixtures of neat reagent grade compounds. Stock mixtures are prepared by adding a measured aliquot of each compound to be analyzed to a preweighed septum sealed vial. The actual mass of each compound added is determined by weighing the vial. An aliquot volume of the final mixture is then weighed to establish density (weight/volume). Weighing is done on a 0.1 mg Mettler balance calibrated according to manufacturers guidelines with weights traceable to NBS standards. Certified mixtures include vinyl chloride in nitrogen, and methane in nitrogen purchased from Matheson Gas Products, Cucamonga, California.

2.3.6.2 A spiking solution containing two compounds to be used as internal standards are prepared as described in Section 2.3.6.1. The internal standards are selected such that they do not interfere with the compounds of interest. Typical compounds used as internal standards are fluorobenzene, 2-bromo-1-chloropropane, bromochloromethane, 1-chloro-2-bromobutane, and 4-bromo-fluorobenzene. The internal standard is added to the calibration standards or samples and carried through the analytical procedure. The amount of internal standard is selected such that its concentration is 3 to 5 times greater than the expected range of concentrations found in the actual samples.

2.3.6.3. VOC-free water used in purging soil samples is prepared from distilled water degassed by boiling >1 hour.

2.3.6.4 Purge and Trap or HPLC grade methanol is used when analyzing soil samples.

2.4 Calibration

2.4.1. Calibration

2.4.1.1 For daily soil gas calibration standards, a measured volume of the standard mixture is injected into a nitrogen-filled 1-liter glass, gas bottle through a septum side port. After heating the bottle to achieve volatilization and mixing of the standards, measured volumes are extracted with a gas syringe and injected into a 200 ml/min helium gas stream leading to a carbon packed sorption cartridge. Internal standards, if utilized, will also be injected at this time. After 2 minutes, this cartridge is inserted into the thermal desorber and analyzed exactly as the samples.

2.4.1.2 Standards used for soil and water analysis are prepared by injecting an aliquot of the stock mixture into methanol. An aliquot of the methanol solution will be injected into a 10.0 ml volume of water and purged in the same manner as soil or water samples. The aliquot of stock standard and methanol solution will depend on concentrations anticipated in the samples.

The amount of the standard stock solution used are dependent upon the required mass of analyte.

The standard will be injected at least three times at the beginning of the day to verify the instrument response. If the response varies by greater than ±20% appropriate measures will be taken to correct the circumstances causing the variability. Continuing calibration checks are performed after every tenth sample.

2.4.1.3 Spectra Physics calculates response factors when the external standard method is used as follows.

$$RF = A/C$$

where A = area of analyte to be measured

C = concentration of analyte, µg/l

Varian 3400 calculation of RF

$$RF = C/A \times 10000$$

2.4.1.4 The Spectra Physics calculates response factors when internal standards are used as follows.

$$RF_S = \frac{C_S}{A_S} \times \frac{A_{IS}}{C_{IS}}$$

where RF_S = response factor of components

A_S = area of components peak

C_S = amount of component used in the calibration sample, µg

A_{IS} = Area of the internal standard peak

C_{IS} = amount of internal standard used in the calibration sample, µg

2.4.1.5 Acceptable retention time window is ±0.10 minutes from the average retention time derived from the daily calibration analyses.

2.5 Quality Control

2.5.1 System Bank

A randomly selected sampling cartridge is analyzed daily to detail interferences from cartridges or the analytical system. If interference is found at unacceptable levels, an unpacked cartridge is analyzed to determine whether the interference is due to the cartridge or to the analytical system. Appropriate measures are taken to eliminate such interferences.

2.5.2 Reagent Blanks

At the beginning of each day that soil or water samples will be analyzed, the chemist fills a sampling container with reagent water/methanol and proceeds to handle it as an actual sample is handled in order to demonstrate that the system, methanol, and water are interference-free. If VOC's are detected, a water blank will be analyzed to determine if the interferences are in the water or the methanol. Appropriate measures will be taken to eliminate the interferences.

2.5.3 Field Blanks

2.5.3.1 Soil Gas

Prior to each day's soil gas or atmospheric sampling, field blanks of the entire sampling apparatus are taken and analyzed to check background contamination in the sampling system and cartridges. Sampling cartridges are attached to both the inlet and outlet end of a sampling probe. The sample collected in the discharge end cartridge is representative of sampling train contamination only while the intake cartridge provides a measure of the atmospheric concentrations. Additional field blanks are collected prior to any reuse of recleaned sampling equipment.

2.5.3.2 Water

A sampling container will be filled with interference-free water in the field in the same manner as water samples are collected. This sample, now designated as a field blank, is returned to the laboratory for analysis. If VOC's are detected, sample collection procedure will be reviewed. If necessary, sampling equipment will be thoroughly decontaminated. One field blank will be collected and analyzed on each day that water samples are collected.

2.5.3.3 Soil

Collection of field blank soil samples is not feasible due to the nature of the matrix and because interference-free soil is ordinarily not available.

2.5.4 Duplicate Samples

Duplicate soil gas, atmospheric, or shallow groundwater samples are collected from each sampling location. Duplicate analyses are performed on at least 10% of the samples collected. Duplicate analyses are not performed on soil samples because it would require homogenization of the sample, tend to release volatiles from the sample, and therefore, limit the accuracy of the results. Duplicate analyses may be performed on extract aliquots of soil samples. Duplicate analyses must have relative percent differences (RPDs) of less than ± 20%.

2.5.5 Trip Blanks

2.5.5.1 Soil Gas

An unused sample cartridge is transported into the field with the sampling equipment. The trip blank cartridge is handled in the same manner as a sample, but a sample is not collected through this cartridge.

The trip blank is returned to the lab with the other samples and analyzed. If VOC's are detected, sample handling and transport procedures are subsequently reviewed.

2.5.5.2 Water

A sampling container is filled with water determined to be interference-free and taken into the field. The trip blank container is handled in the same manner as other water samples. The trip blank is then returned to the laboratory for analysis with the other samples. If VOC's are detected, sample handling and transport procedures are reviewed and sampling equipment is decontaminated as necessary.

2.5.5.3 Soil

Trip blanks for soil sampling are not used because uncontaminated soils without background levels of organics are not available and the trip blank procedures are not feasible.

2.5.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

2.5.6.1 Soil Gas

During each standard calibration procedure for soil gas analysis, an activated carbon collection cartridge is directly spiked with standards in the vapor phase and thermally desorbed. This is equivalent to a matrix spike.

2.5.6.2. Water

Once a day a duplicate field sample is spiked with a calibration standard of known concentration. This spiked sample is then processed and analyzed in the same manner as all samples. The acceptable MS recovery will be within the range 50 to 150 percent. Matrix spike duplicates will be analyzed at a frequency of 1 in 10. Matrix spikes and matrix spike duplicates should have RPD of less than ±20% to be within control limits.

2.5.6.3. Soil

Soil sample matrix spikes are performed at a frequency of 1 in 10 on purged soil samples by injecting a compound of known concentration directly into the vessel containing methanol extract of the soil. The soil sample is then purged and trapped onto the carbon cartridges for thermal desorption analysis to evaluate purging efficiencies. Acceptable recovery limits are 50 to 150 percent. A matrix spike duplicate will be analyzed at a frequency of 1 in 10. Control limits are less than ±20% RPD.

2.5.7 Chromatographic Information

2.5.7.1 System Parameters

On the first page of each day's chromatograms, the following system parameters are noted:

A) Gas flows for H_2, He, N_2, and air

B) Tank pressures for H_2, He, N_2, and air

C) Temperatures

1. Injector
2. Columns
3. Detector
4. Thermal desorber oven
5. Thermal desorber transfer lines
6. Thermal desorber desorption temperature and duration

D) Integrator parameters

1. Attenuation
2. Peak markers
3. Baseline offset

E) Column(s)

1. Type
2. Length and diameter
3. Packing material
4. Temperature

F) Operator

G) Date

If any system parameters change, the changes shall be noted.

2.5.8 Internal Quality Control

All chromatograms are reviewed internally by a chemist other than the chemist performing the analysis.

2.5.9 Outside Quality Control Audits

Samples are periodically sent to independent laboratories for analysis as a quality assurance check.

2.5.10 Sample Chain of Custody

All samples are labeled with the following information:

1) Sample identification number

2) Date and time of sample collection

3) Name of sampler

In addition to labeling the samples, a field data/chain of custody form is completed for each sample (Figure 6). At the time of sample collection, the field sampler signs the custody form and records the date, time and sampling conditions. The sample is then transferred to the laboratory, where the individual receiving the sample for analysis signs the original custody form and records the date and time. This Soil Gas Field Data Sheet (Chain of Custody Form) is then filed in a notebook with the hard copy of the analytical results and eventually becomes part of the final report.

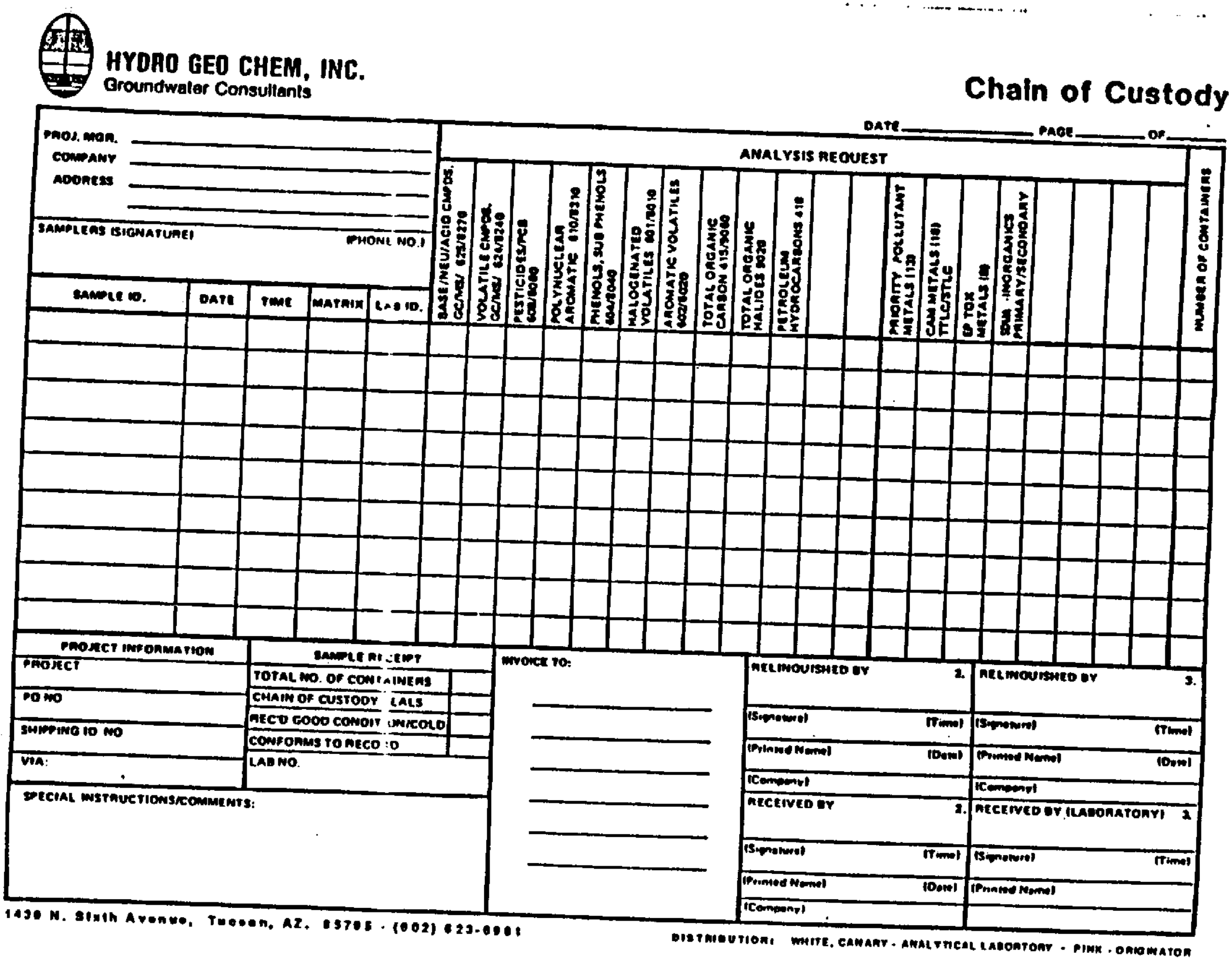
2.6 Procedures

2.6.1 Typical chromatographic equations are summarized in Section 2.7.

2.6.2 The system is calibrated daily as described in Section 2.4.1.

2.6.3 Soil Water Samples

A representative fraction, typically 20 ml of each cooled soil water sample will be transferred to a tared 40.0 ml VOC vial. The remaining volume is stored at less than 4°C. If less than 20 ml of the



HYDRO GEO CHEM, INC.
Groundwater Consultants

Chain of Custody

DATE ______ PAGE ______ OF ______

PROJ. MGR. ______
COMPANY ______
ADDRESS ______

SAMPLERS (SIGNATURE) (PHONE NO.)

SAMPLE ID.	DATE	TIME	MATRIX	LAB ID.	BASE/NEU/ACID CMPDS. GC/MS/ 625/8270	VOLATILE CMPDS. GC/MS/ 624/8240	PESTICIDES/PCB 608/8080	POLYNUCLEAR AROMATIC 610/8310	PHENOLS, SUB PHENOLS 604/8040	HALOGENATED VOLATILES 601/8010	AROMATIC VOLATILES 602/8020	TOTAL ORGANIC CARBON 415/9060	TOTAL ORGANIC HALIDES 9020	PETROLEUM HYDROCARBONS 418			PRIORITY POLLUTANT METALS (13)	CAM METALS (18) TTLC/STLC	EP TOX METALS (8)	SDWA INORGANICS PRIMARY/SECONDARY					NUMBER OF CONTAINERS

PROJECT INFORMATION
PROJECT
PO NO
SHIPPING ID NO
VIA:

SAMPLE RECEIPT

TOTAL NO. OF CONTAINERS	
CHAIN OF CUSTODY SEALS	
REC'D GOOD CONDITION/COLD	
CONFORMS TO RECORD	
LAB NO.	

INVOICE TO:

SPECIAL INSTRUCTIONS/COMMENTS:

RELINQUISHED BY 1.
(Signature) (Time)
(Printed Name) (Date)
(Company)

RECEIVED BY 2.
(Signature) (Time)
(Printed Name) (Date)
(Company)

RELINQUISHED BY 3.
(Signature) (Time)
(Printed Name) (Date)
(Company)

RECEIVED BY (LABORATORY) 3.
(Signature) (Time)
(Printed Name)

1430 N. Sixth Avenue, Tucson, AZ. 85705 · (602) 623-6981

DISTRIBUTION: WHITE, CANARY - ANALYTICAL LABORTORY - PINK - ORIGINATOR

Figure 6

soil water sample is used, the volume will be brought to 25 ml with VOC-free reagent water prior to purging. Any surrogate or spiking mixture will then be introduced by piercing the septum and injecting the mixture below the water surface. Following any additions, needle sparging will be carried out for 15 minutes under ambient lab temperatures using a purge gas flow rate of 200 ml/minute. The purged volatile compounds will then be trapped on a packed cartridge which is held at 40°C to minimize carry-over of water.

2.6.4 Soil Samples

Five grams of each soil will be transferred to a 40 ml VOC vial. Immediately following, five milliliters of HPLC-grade methanol will be added and the vial sealed. Any surrogate or spiking mixture will then be added by piercing the septum and injecting the mixture below the methanol surface. Following any additions, the soil/methanol mixture will be agitated to fully wet the soil with the extracting solution. After allowing the soil/methanol mixture to settle so that a particulate free layer forms, a measured aliquot will be transferred to a second 40.0 ml VOC vial containing 25 ml of VOC-free reagent grade water. The second vial will then be needle sparged for 15 minutes under ambient laboratory temperatures using a purge gas flow rate of 200 ml/minute.

The purged volatile compounds will then be trapped on a packed cartridge which will be held at 40°C to minimize carry-over of water.

2.6.5 Gas Samples

The thermal desorption tubes on which the samples are collected are placed in the thermal desorber and heated to 380 ±4°C with a helium flow of 20 ml/min. at the same time that the GC temperature program is initiated and data acquisition started. The trapped materials are desorbed and carried through the heated transfer lines to the GC columns where separation occurs (Figure 4).

2.7 Calculations

2.7.1 Each analyte in the sample chromatogram is identified by comparing the retention time of the suspect peak to retention times generated by the calibration standards on the appropriate detector. When applicable, the relative response of the alternate detector to the analyte is determined. The relative response should agree to within 20% of the relative response determined from the standards.

2.7.2 Quantitation is usually performed on the detector which exhibits the greater response if all detectors respond to an analyte. In cases where greater specificity or precision would result, the analyst uses his/her professional judgement in determining the alternate detector.

2.7.3 The concentration of the unknowns is determined by using the calibration curve or by comparing the peak height or area of the unknowns to the peak height or area of the standards as follows for external standards:

External Standards:

$$C = (A/RF)(1/SA)$$

or $$C = (A \times RF/10000)(1/SA)$$

where C = concentration of the analyte in sample in µg/L

SA = sample amount in L or kg

RF = relative response factor

Internal Standards:

$$C_{\mu g/l} = \left(\frac{IS}{SA}\right)\left(\frac{RF_S A_S}{RF_{IS} A_{IS}}\right)$$

where C µg/L = concentration of the component of interest present in the sample

SA = sample volume or mass (L or kg)

IS = the amount of the internal standard added to the samples

RF_s = response factor of component's determined by calibration

A_S = area count of the components in the sample analysis

RF_{IS} = response factor of the internal standard is 1 by definition

A_{IS} = the area of the internal standard in the sample analysis run

2.7.4 The results for the unknown samples are reported in µg/L. The results are rounded off to the nearest 0.01 µg/L or 2 significant figures.