Field Analysis of Groundwater for Volatile Organic Contaminants using On-Column Aqueous Injection Capillary Gas Chromatography

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PERFORMANCE SPECIFICATIONS

Fractovap Series 2150 Carlo Erba gas chromatograph

Dual detection (ECD,FID), on-column injection (direct aqueous), temperature programming capabilities

Method Detection Limit (MDL)

direct aqueous injections: ECD 1.0 $\mu g\ L^{-1}$ FID 25 $\mu g\ L^{-1}$

Linear Working Range: ECD MDL - 10 $mg\ L^{-1}$ FID MDL - >100 $mg\ L^{-1}$

Injection Precision (1.0 μL injections): 2.6%

Maximum Injection Size: 4.0 μL

Retention Time Variability (rt)

chart recorder at 10 $mm\ min^{-1}$: ± 0.05 mm

Working Attenuation Ranges: ECD 8-4096 FID 1-1024

Programming Capabilities: initial temperature/initial hold time
temperature ramp (single rate)
final temperature/final hold time

Analysis Capabilities:

lowest bp compounds	CH_2Cl_2	40°C
	C_5H_{12}	37°C
highest bp compounds	tetrachlorobenzene	254°C
	phenanthrene	212°C

INTRODUCTION

In the past five years, increased public awareness of environmental issues has focused attention on the problem of toxic waste dumpsites and toxic spill areas. This has resulted in a new generation of legislation which requires judicial assessment of health and environmental damages at these sites. The courts are responsible for awarding settlements, if any are warranted, and ensuring that cleanup is instituted by the offending party. This entire process is a costly one, to all the parties involved, in part due to the enormous costs incurred in obtaining the samples that establish guilt or innocence, and then having them analyzed by analytical laboratories using such techniques as gas chromatography-mass spectrometry (GCMS).

This report describes a gas chromatograph (GC) which combines technological advances in chromatographic column design and established GC methodologies into a field utilizable instrument. The capability of analyzing a sample every 20 minutes, making direct aqueous injections without sample pretreatment, and having the capacity to separate compounds using temperature programming are major advantages to this system. This makes the system particularly well suited for real time mapping of contaminant groundwater plumes and for directing the accurate placement of monitoring wells. Although not able to replace GCMS analyses and their resultant costs entirely, this system saves both time and money by targeting the samples that need more expensive analysis.

BACKGROUND

Several advances in the area of capillary gas chromatography have occurred in the last few years which suggest the suitability of this analytical instrumentation for quick on-site characterization of volatile organic contaminants in groundwater samples. First, use of fused silica capillary tubing with an exterior polyimide protective coating (Dandeneau et al., 1979) has resulted in particularly robust chromatographic columns suitable for use by nonspecialists and under rugged conditions such as might occur during field work. Next, as demonstrated by Grob and coworkers (1977, 1983) very thick stationary phase films can be used to accomplish improved analyses of mixtures of volatile organic analytes even at elevated oven temperatures. Coupled with the introduction of direct on-column aqueous injections (Grob, 1978; Grob and Habich, 1983), these thick film capillary columns can handle microliter water samples and resolve the water from volatile solutes such as methylene chloride, chloroform, or benzene. Finally, due to the recent introduction of cross-linking techniques which immobilize the stationary film during the preparation of capillary columns, relatively "dirty" samples can be injected onto these columns, their volatile contents assessed, and the column regenerated by washing with solvents without risking stationary phase removal (Grob et al., 1981; Grob and Grob, 1981). These chromatography advances applied together permit greatly improved on-site measurements of solvent and fossil fuel-derived contaminants in groundwater samples. The results are obtained within minutes rather than the weeks commonly associated with contract laboratory analyses. Also, chemical identities can be much more firmly assigned and many additional organic substances can be assessed than is currently possible using widely

available Foxboro-Century Model OVA-128 or Photovac Model 10A10 photoionization techniques (Barber and Leveson, 1980).

HARDWARE REQUIREMENTS

The gas chromatograph used in this project is an older model Carlo Erba GC (Model 2150, Haake Buchler Instruments, Inc., Saddle Brook, NJ) which was originally designed for glass capillary column use. The instrument's original equipment included temperature programming capabilities, heated injector/detector ports, and an FID controller. It has now been retrofitted to include the following features: air cooled, on-column injector; 50 meter, fused silica capillary column; vitreous silica, column effluent splitter; dual detectors operating in parallel (Electron Capture Detector and Flame Ionization Detector); and a dual channel strip chart recorder (see Figure 1). This retrofit necessitated a number of major modifications to the initial hardware configurations of the instrument. These changes are outlined below and should correspond to those needed to upgrade most GC's.

On-Column Injector

The gas chromatograph had been initially equipped with a heated "Grob type" split/splitless injector which, by design, shared a common heating block with a detector base body that was adjacent to it. After removing the old injector and heating block, an on-column injector was mounted in its place (P.N. 299-020-00, Haake Buchler Instruments Inc.). An air channel was cut in the surrounding oven insulation and fitted with a metal tube (to decrease resistance to air flow). This allowed cooling air to be supplied to the injector by a fan (in our case, a motor and fan cannibilized from an old hair dryer) that was mounted on the back wall of the oven. We believe that air cooling of the injector is a more viable option for a field instrument than water cooling.

FIELD GAS CHROMATOGRAPH

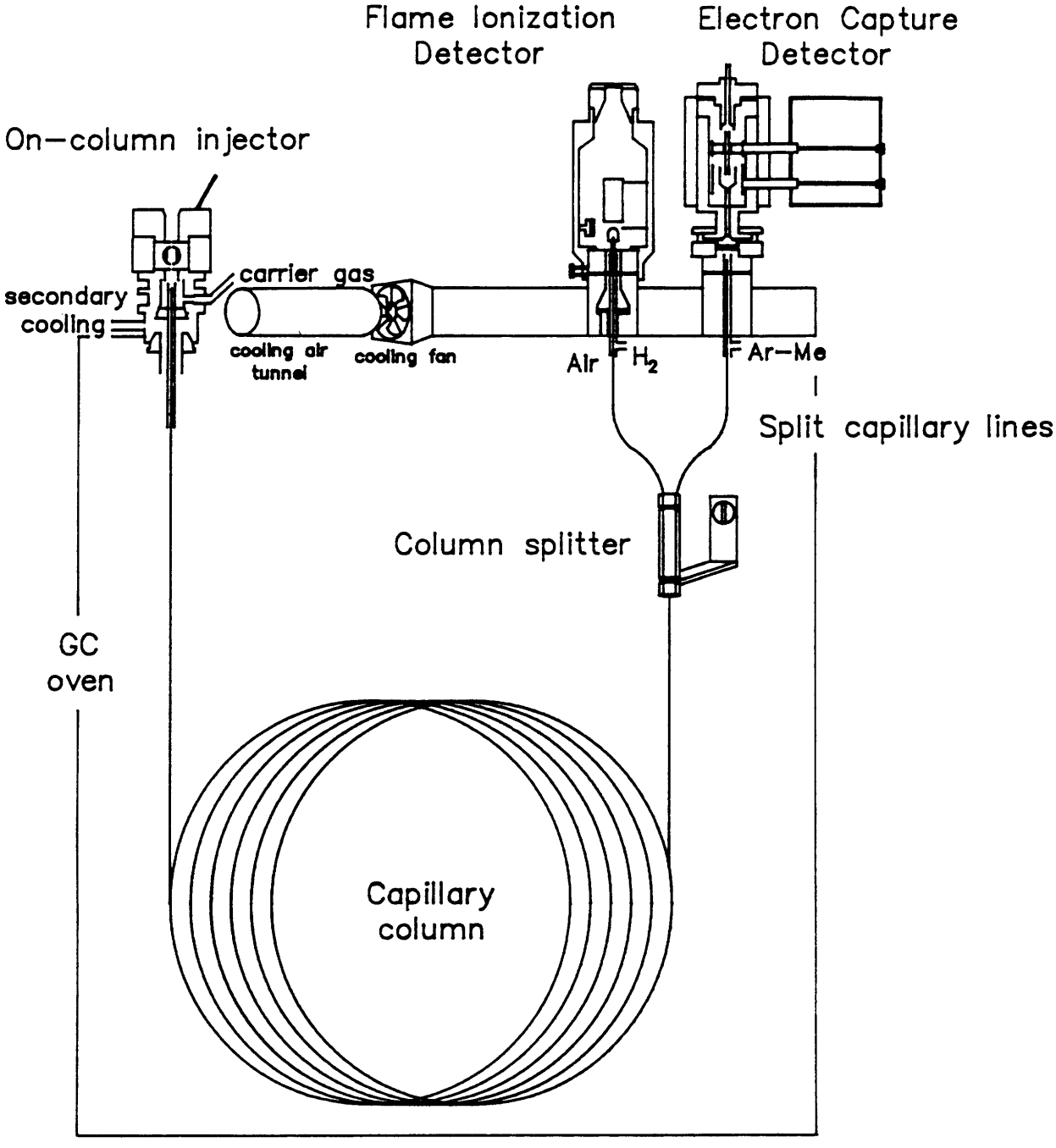


Figure 1

Detectors

Two options were available for modifying the single detector setup of the original instrument package. The GC manufacturer suggested that the detectors be run in series with the FID seated above the ECD using a special connector fitted with the appropriate gas lines. Although apparently the quickest and easiest solution, this configuration was not chosen for two reasons. First, the FID is inoperable in the presence of normal ECD makeup gas (95% Argon, 5% Methane). The system, therefore, would have had to have been used with a much costlier Argon-Carbon Dioxide mixture. Second, the sensitivity of the ECD decreases when Ar-CO_2 is used as the makeup gas. Consequently, a second detector base body (P.N. 247-038-01, Haake Buchler Instruments Inc.) was mounted to the roof of the oven adjacent to the one already there. An aluminum heating block was machined to fit around both detector bases and was also designed to accept the original heating element and sensor. With the injector and detector bodies in place, new insulation (2 inch thick, 3 lb. fiberglass board with SSK vapor barrier, General Insulation, Somerville, MA) was fitted to the oven roof and a new aluminum cover plate was made and installed.

Capillary Column

Choosing the capillary column involved the following considerations. First, a thick film (5 μm), nonpolar phase was needed to minimize retention of water and maximize retention of the nonpolar contaminants of interest. Second, the column had to be long enough to separate the most volatile halocarbons of interest from the water peak without prolonging the analysis time unnecessarily. With this in mind we chose a 50 m x 0.32 mm, i.d. cross-linked SE 54 (5% vinyl-95% methyl-phenyl silicone) coated column (P.N. 007-2-50W-5.0F, Quadrex Corp., New Haven, CN).

Connecting the capillary column to the on-column injector requires precise alignment to ensure that the syringe needle enters the column smoothly (see Figure 2). This was achieved by using the following procedure. The column nut and graphite vespel ferrule (P.N. 290-334-60, Haake Buchler Instruments Inc. Saddle Brook, N.J.) were fitted on the column and tightened only until the column no longer slid through the ferrule. The on-column syringe was inserted at this point and confirmation was made visually that it extended down into the column. The column nut was then tightened, with the needle in place, until just leak tight (barely a 1/4 turn beyond finger tight). Two points need stressing here. First, due to the on-column design, specially designed syringes are required (P.N. 701SN, 32 ga, 7.5 cm, Pt. No. 3, Hamilton Co., Reno NV). These syringes have long, narrow bore needles which bend and kink very easily. It is imperative that operators use the syringe guide supplied with the injector for proper insertion and withdrawal from the column. Second being a "cold" injector, ferrules must be properly sized and in good condition in order to seal since no "flowing" of the ferrule material due to compression under elevated temperature is possible.

Splitter

The detector end of the column was somewhat more difficult to attach. Since the system was configured with parallel detectors, the column effluent needed to be split into two equal outputs. This was accomplished by mounting a stainless steel, butt connector (P.N. 123830, SGE Inc., Austin, TX) to a supporting brace in the oven centered below the two detector base bodies (see Figure 3). One end accepted the capillary column, the other, two lengths of deactivated vitreous silica, connected by means of a two-hole ferrule. Properly installing this "splitter" required a good deal of patience and a delicate

ON-COLUMN INJECTOR

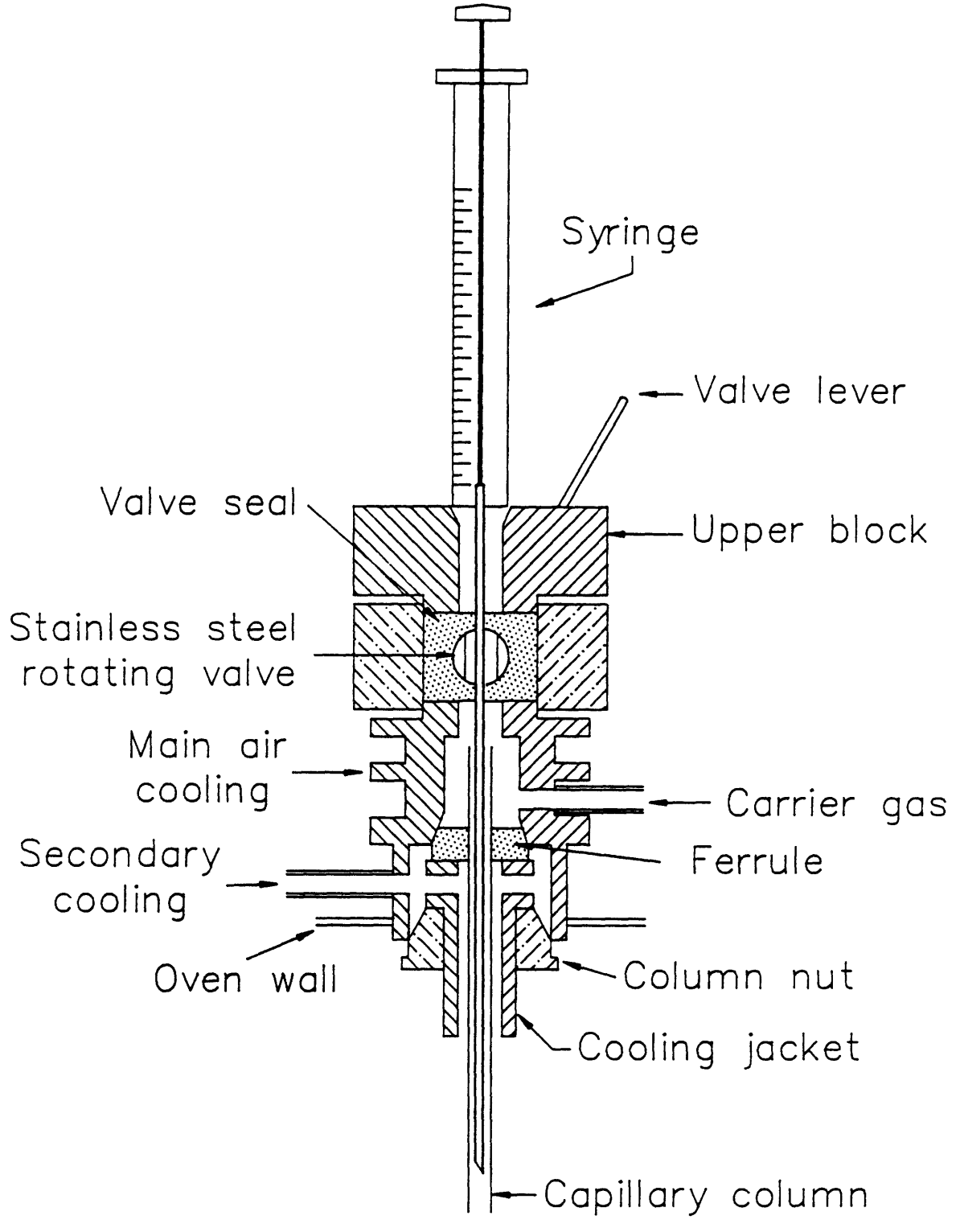
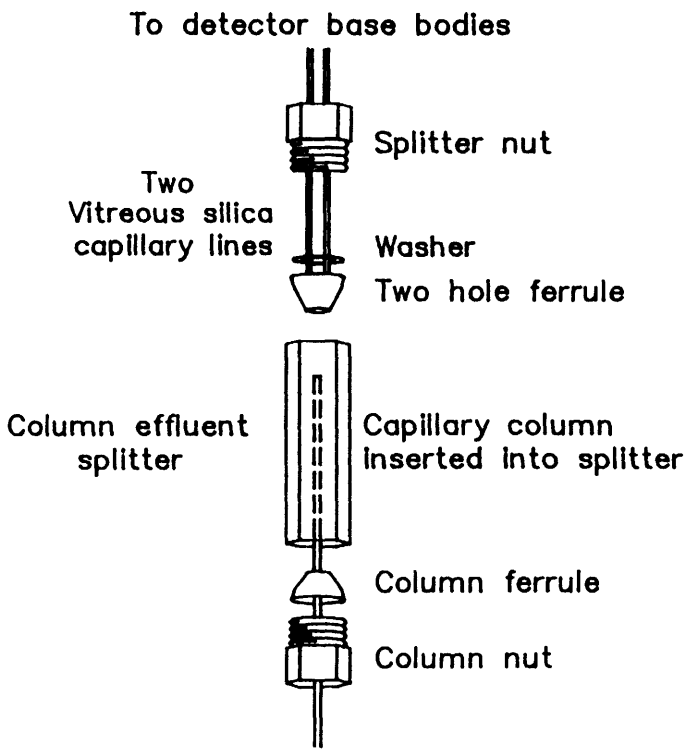


Figure 2


To detector base bodies
Splitter nut
Two
Vitreous silica
capillary lines
Washer
Two hole ferrule
Column effluent
splitter
Capillary column
inserted into splitter
Column ferrule
Column nut

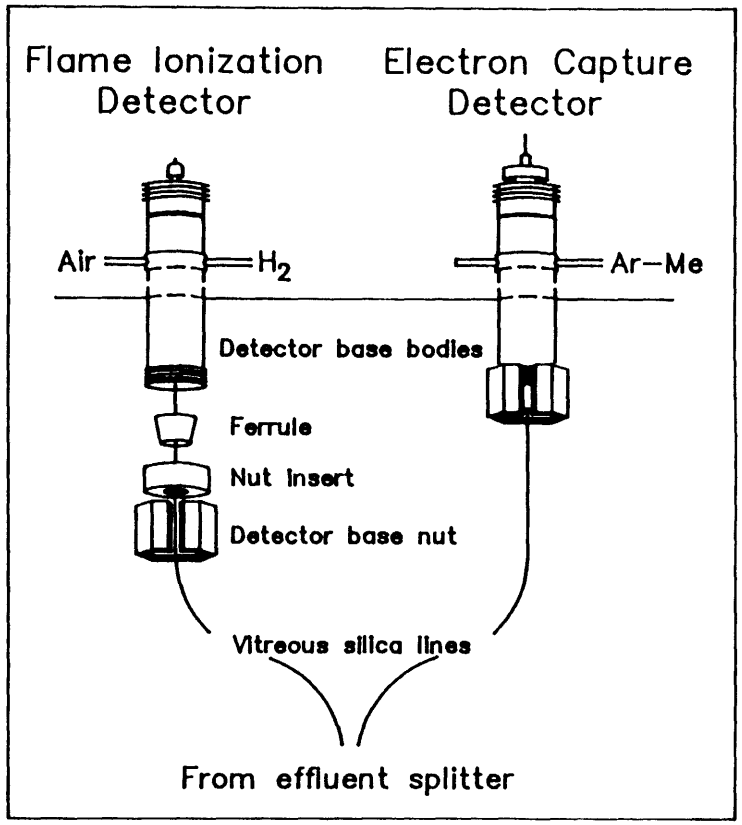

Flame Ionization
Detector
Electron Capture
Detector
Air
H_2
Ar–Me
Detector base bodies
Ferrule
Nut insert
Detector base nut
Vitreous silica lines
From effluent splitter

Figure 3

touch. The two vitreous silica lines did not tolerate much rotational strain; therefore, they had to be connected in the following manner. Both the detectors and their inserts (FID flame jet and ECD nozzle) were removed. The vitreous silica lines, joined at one end by a two-hole ferrule, washer (for reducing rotational strains during tightening) and splitter nut, and having ferrules in place for attachment to the base bodies, were carefully threaded through their respective detector bases from inside the oven to the appropriate height for attachment to the butt connector (the other ends of the silica lines had to be 1-2 inches above the tops of the detector bases in order to allow proper trimming once the FID flame tip and ECD nozzle were replaced). The silica lines were then attached to the detector bases by gently hand tightening the detector base nuts over the previously placed ferrules. The split lines were then attached to the butt connector fitting by carefully screwing the fitting into the ferrule (this also helps to minimize rotational stress). The capillary column was then threaded into the butt connector and tightened, creating a zero dead volume fit. Once the detector base nuts were retightened against leaks, the vitreous silica lines were trimmed to their proper lengths with the detector inserts in place (FID: even with the flame jet tip; ECD: 2 mm above the nozzle) and the detectors reinstalled.

STRUCTURAL MODIFICATIONS

Changing the GC injector and detector also meant modifying the plumbing of the gas lines required by each. The on-column injector required a carrier gas line (ca. 2 mL min^{-1}), a main cooling air source (external), and a secondary cooling air line (internal). The FID required a makeup H_2 gas line (30 mL min^{-1}) and a combustion air line (300 mL min^{-1}). The ECD required an argon-methane makeup gas line (30 mL min^{-1}). The gas chromatograph was originally equipped with three gas controllers which are now being used for controlling the column flow and the two FID gas requirements. The Ar-CH_4 controls for the ECD (all supplied by Haake Buchler Instruments Inc.) were added by installing a suitable pressure gauge (P.N. 367-16004), metal bellows type pressure controller (P.N. 425-07100), and a calibrated restrictor (P.N. 245-04300) onto the top of the GC oven. The secondary cooling system for the on-column injector (pressure regulator, P.N. 23748, Supelco, Inc., Bellefonte, PA and on/off valve, P.N. B-41S2, Whitey Co., Highlands Heights, OH) were also installed on the top of the oven.

In order to run the system in the field as well as in the laboratory, two, twin plug (20A, 125/250V), weather resistant receptacles (P.N. 5652, H. Hubbell Inc., Bridgeport, CN) were mounted on the side of the GC. The GC main, FID power supply, and ECD power supply plug into these. Power to these receptacles can then be supplied from a field generator or the original laboratory transformer.

MODIFICATIONS FOR FIELD USE

In order to transport and use the GC system in the field, some additional measures were taken based on the following criteria. The system must fit into and be usable from a small van or wagon. The instrument package must be easily maneuverable by one person. The electrical and gas supply connections must be quickly and easily accomplished. And, the system must be packaged so as to survive travel to the field. With these restrictions/requirements in mind, we have adopted the following GC/field configuration

Three compressed gas cylinders are needed to operate the GC. Transporting full sized cylinders (size 1A, approx. 250 cu. ft. gas capacity) is not only cumbersome, but possibly dangerous. Thus the smallest sized cylinders possible, which accepted the same regulators as their full sized counterparts, were used. This turned out to be size 2 cylinders (sometimes referred to as "stubby") which hold approximately 75 cu. ft. of gas. These weigh only 40 lbs., are 30 in. tall and easily stand upright in the restricted space of the van. In order to facilitate the attachment/removal of the gas lines from the cylinders and the GC itself, we installed Swagelok quick-connect fittings (P.N. SS-QC4-D/B-200, Crawford Fitting Co., Solon OH) on the gas lines at the back of the instrument. This allows us to remove the regulators from the bottles, disconnect them from the GC, and store them separately in a matter of minutes without ever worrying about gas leaks due to connecting/reconnecting swagelok fittings.

We were very concerned with the durability of our instrument during transportation to and from the field. An enclosure was constructed using 1/2 and 3/4 inch weatherproofed plywood (see Figure 4). The 3/4 inch base is

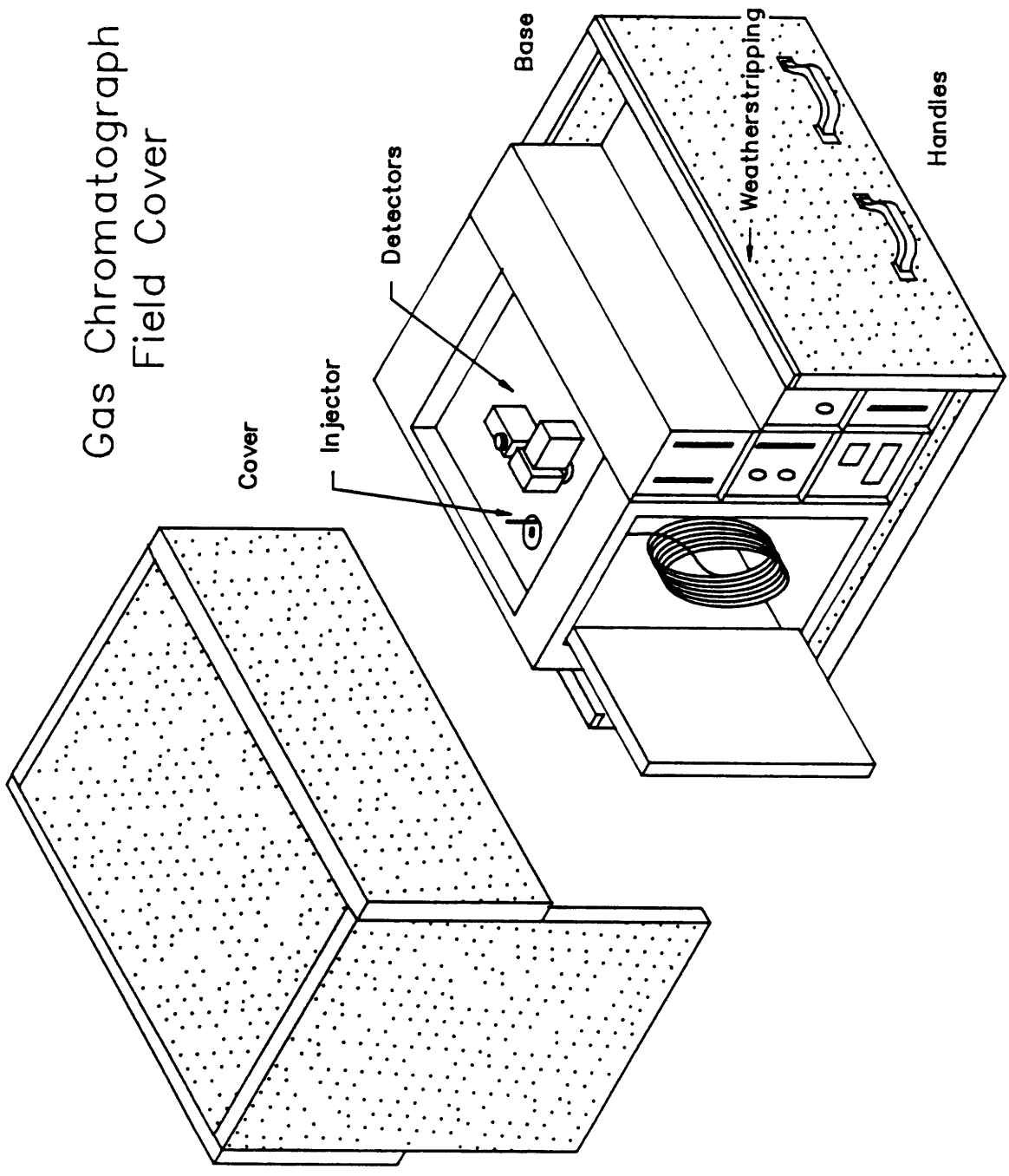

Gas Chromatograph
Field Cover
Cover
Injector
Detectors
Base
Weatherstripping
Handles

Figure 4

equipped with double handles, snap clasps, and weatherstripping with the sides and back half the height of the instrument. The top of the enclosure is 1/2 inch plywood and simply snaps down in place. This supplies the necessary support for travel as well as providing protection essential for the electronic components.

The final component of the field unit consists of a gasoline-powered portable generator. Since our system requires a 220V supply, we are forced to use a rather bulky generator (rated for 3000W total output) which supplies both regulated 110 and 220V output (Model #GA3200A-S, Kawasaki Motors Co., Santa Ana, CA).

All in all, the goals we set above are fairly readily achieved. The entire process of packing up the unit from a running state in the laboratory to loaded into the van can be accomplished in 15 minutes. The only assistance necessary is in moving the GC itself, but smaller basic units such as that sold by Tracor or Hitachi would avoid this difficulty. After being loaded into the van, the system is totally manageable by a single operator and can be warming up in a matter of minutes once on site.

INSTRUMENT OPTIMIZATION

The following sections describe the steps necessary to obtain maximum performance from this gas chromatograph once all the hardware is in place. The flow rates of the gases to the column and detectors will be discussed first. It is important to note however, that all the gas line fittings should be leak free before valid flow rates can be set. A carrier gas flow rate (2 mL^{-1} min hydrogen) was chosen to optimize the peak shape and retention time separations of the compounds which we expected to investigate. This capillary column/flow combination also compared favorably against the standardized quality test for flow rates in capillary columns as determined by Grob et al. (1978) using methane elution at room temperature.

$$\text{i.e., establish hold-up time of methane} = \left[\frac{\text{column length (m)}}{0.5 \text{ m/sec}} \right]$$

In order for the FID to operate, air and hydrogen have to be supplied to the detector base in about a 10:1 ratios. The mixture we have chosen to work with is 300 mL min^{-1} air and 30 mL min^{-1} H_2 (acceptable ranges for these gases are from 300-600 mL min^{-1} air and 25-50 mL min^{-1} H_2, McNair and Bonelli, 1968). The ECD only requires one additional gas input to the detector base. A mixture of argon-methane (95-5%) is supplied to the detector at 30 mL min^{-1} (20-40 mL min^{-1} range). These flow rates have allowed us to obtain sensitivities which are comparable to the published detection limits established for these detectors.

In the case of the ECD however, there are also electronic controls which can be manipulated to establish the ultimate detector response. The nature of

the electron capture detector (in the constant current mode) is that a constant current is maintained across an ionization chamber and a signal is manifested if the voltage across the chamber must be adjusted to maintain that current as a sample component passes. There are two adjustments that influence the detector sensitivity and linear range: the constant current and the pulse voltage necessary to maintain that current. The higher preset current settings (0-5 nA range) result in higher sensitivities and concommitent background noise levels. The lower pulse voltage settings (5-50V range) allow larger linear ranges and improved signal:noise ratios. The settings which give us the best overall results are: 1 nA preset current and 50 V pulse voltage. This gives us a linear range spanning 4 orders of magnitude and a minimum detection limit of 1 $\mu g\ L^{-1}$ for aqueous injections.

With direct aqueous injections, both detectors function extremely well with injections up to 2 μL. If larger injections are used, then the FID flame is extinguished and must be relit and the ECD water peak becomes inordinately large, interfering with some of the early-eluting, low-boiling-point compounds.

Once the flow rates and electronics have been optimized, some consideration should be given to the matter of temperature conditions. Too cold an initial oven temperature, and the sample condenses on the column front; too hot and the analytes pass through the column without ever being separated. Once the initial temperature is set (typically at a few degrees Centigrade above the boiling point of the solvent being used), then either an isothermal or ramped temperature program should be developed which separates the compounds of interest in the shortest possible time. Since we are analyzing samples by direct aqueous injection and are interested in analyzing for compounds targeted on the EPA priority pollutant list (anything from dichloromethane to

naphthalene), we have decided on the following temperature program:

INITIAL TEMPERATURE.....	100°C	INITIAL TIME.....	1 min.
RAMP RATE.....	10^{o} min^{-1}		
FINAL TEMPERATURE.....	250°C	FINAL TIME.....	5 min.

The initial temperature of 100°C insures that the water vaporizes and is carried quickly through the column to the detectors. This is critical to the performance of the ECD since any residual water vapor severely hampers performance. The final temperature of 250°C is necessary when high boiling point compounds are to be determined (such as naphthalene). This is also a convenient temperature for baking out the column between runs, but can be lowered if the compounds present in the samples are all of high volatility. The ramp rate chosen minimizes run time while, still providing the separation needed for the chemicals of interest.

In regards to the need for column bakeouts between runs, experience has shown that this is necessary when injecting contaminated field samples. Background noise generated by column bleed can become a factor in as few as ten field groundwater samplings, depending on the nature of the site. With bakeouts programmed in between, however, this problem can be delayed to allow a full day of field injections. In order to eliminate the noise generated after a full day of injecting field samples, the following column washing procedure can be employed. The capillary column must be disconnected from the detector. This can be accomplished by removing the column from the effluent splitter. Then, the injector end of the column can be disconnected and a few milliliters of acetone injected into the column using a syringe. At this point, the column can

be connected back up to the injector and the acetone pushed through by the carrier gas. After repeating this washing procedure three times, distilled water should be substituted for the acetone and the wash repeated once or twice to ensure the removal of all the acetone and any water soluble contaminants left in the column. The column can then be heated at 100°C for 1 hour to remove excess water vapors and then be reinstalled into the splitter.

STANDARD COMPOUNDS

We have set up an instrument which is capable of analyzing typical groundwater contaminents. These include a suite of chlorinated solvents, as well as both straight chain and aromatic hydrocarbons (generally, but not exclusively, fossil fuel associated hydrocarbons). Due to the use of direct aqueous injections, the lowest boiling point compound which we can confidently analyze is dichloromethane (CH_2Cl_2 bp: 40°C) and the lightest hydrocarbon is pentane (C_5H_{12} bp: 37°C). Table 1 lists the compounds for which we have already standardized our instrument using the 5.0 μm film thickness cross-linked SE 54 column. The film thickness of this column limits the compounds we can identify to those eluting up to and including naphthalene. This is acceptable when dealing with sites having problems with gasoline or solvent contaminations. However, there are growing concerns regarding sites which have higher molecular weight contaminants (i.e., coal tar sites). When dealing with this type of sample it becomes necessary to install a capillary column with a thinner film. Table 2 outlines the compounds which we have resolved to date on a 0.25 μm cross-linked SE 54 column. This column gives us the ability to identify and quantify the higher boiling point hydrocarbons including polycyclic aromatic hydrocarbons (PAHs) up to phenanthrene.

As can be seen in Table 1 our instrument, in its present configuration, allows us to detect chlorinated and brominated compounds in the low $\mu g\ L^{-1}$ (1-10 ppb) range (utilizing the ECD). The linear working range for this detector spans more than four orders of magnitude to include 10-100 ppm. Our ability to quantify aliphatic and aromatic hydrocarbons is limited to between 25 $\mu g\ L^{-1}$ and $\leq 100\ mg\ L^{-1}$ by the FID detector.

Table 1

COMPOUND	Retention Time (cm)*	Detection Limit ($\mu g\ L^{-1}$)
Pentane	3.55	25
Hexane	4.75	25
Chloroform	5.25	1
1,1,1-trichloroethane	5.85	1
Benzene	6.17	25
Carbon tetrachloride	6.18	1
Bromodichloromethane	6.35	1
Heptane	6.50	25
Trichloroethylene	6.75	1
Chlorodibromomethane	8.15	1
Toluene	8.20	50
Octane	8.45	50
Tetrachloroethylene	9.15	1
Chlorobenzene	9.95	50
Ethylbenzene	10.20	50
m,p-Xylene (unresolved)	10.35	50
Bromoform	10.35	1
o-Xylene	10.90	50
Dichlorobenzene	13.40	75
1,2,4-trimethylbenzene	13.90	75
Naphthalene	16.90	75

*Recorder speed 1 cm min^{-1}.

50 m SE 54 capillary column; 2 mL min^{-1} H_2.

98°C initial temperature, 1 minute hold
to 250°C at 10°C min^{-1},
5 minute final hold.

Table 2

COMPOUND	Retention Time (cm)*	Detection Limit ($\mu g\ L^{-1}$)
Benzene	1.70	25
Toluene	1.78	50
Ethylbenzene	1.85	50
m,p-Xylene (unresolved)	1.90	50
o-Xylene	1.99	50
1,2,4-trimethylbenzene	2.45	75
Naphthalene	2.95	75
2-methylnaphthalene	3.50	75
1-methylnaphthalene	3.60	75
Phenanthrene	6.40	100

*Recorder speed 1 cm min^{-1}.

24 m SE 54 capillary column; 2 mL min^{-1} H_2.

98°C initial temperature

to 250°C at 20°C min^{-1}

5 minute final hold.

PREPARATION OF STANDARDS AND BLANKS

At this point, it is worth mentioning the methodology used in the preparation of standards for direct aqueous injections. We begin by creating a saturated water solution of the compound of interest (See Table 3). This is done by adding pure compound to water in either a separatory funnel or a volumetric flask. Less dense compounds are added on top of water in separatory funnels and gently rocked back and forth (enough to aid in mixing, but not so much as to emulsify the immiscible layers). After equilibration (a minimum of 24 hours), the saturated aqueous solution can be drawn off carefully from the bottom without including any of the pure compound. Compounds denser than water are added below the water level in volumetric flasks so that they sink to the bottom without forming a miniscus at the water surface. Then, after equilibration occurs, the saturated water is withdrawn using pipettes, again, to ensure that there is no contamination from the pure compound at the bottom of the flask. Once a saturated solution is obtained, then a dilution series can be prepared. It should be remembered that most of these compounds are volatile and care must be taken to ensure that losses to headspace gases are minimized. The method we have found satisfactory is as follows. After weighing empty volumetric flasks and stoppers, which have 8-10 glass beads added to them (mixing aids), clean water is added to the flasks until filled to overflowing. The flasks are then stoppered, dried and weighed full which allows for the calculation of the total weight (therefore volume) of water in the flask without headspace. Next, a volumetric pipette is used to withdraw a known amount of clean water. This is then replaced by the same amount of a solution which has

Table 3

COMPOUND	$-Log_{10}$ Solubility (M)	Density (g mL^{-1})
Pentane	3.25	0.63
Hexane	3.83	0.66
Chloroform	1.19	1.48
1,1,1-trichloroethane	2.07	1.34
Benzene	1.64	0.88
Carbon tetrachloride	2.20	1.59
Bromodichloromethane	1.52	1.98
Heptane	4.51	0.68
Trichloroethylene	2.04	1.46
Chlorodibromomethane	1.65	2.45
Toluene	2.25	0.87
Octane	5.20	0.70
Tetrachloroethylene	3.04	1.62
Chlorobenzene	2.35	1.11
Ethylbenzene	2.80	0.87
m,p-Xylene (unresolved)	2.77	0.86
Bromoform	1.91	2.89
o-Xylene	2.76	0.88
1,4-Dichlorobenzene	3.39	1.25
Naphthalene	3.61	1.03
Phenanthrene	5.20	0.98

the compound of interest, either saturated or of a known previous dilution. After mixing 5 minutes, an aliquot can be removed for the next dilution. At this point some amount of freshly mixed solution is also transferred to a smaller flask with no headspace and saved for GC analysis. This ensures that the standards are not handled or stored with any headspace gas during preparation or before analysis, where exchange to air would occur. After all the dilutions have been made, the standards can then be analyzed on the GC, beginning with the lowest concentration first. This helps to minimize artifacts in the analysis by limiting the effects of carry-over contamination in the syringe (especially important when the standards span orders of magnitude concentrations).

One of the advantages of direct aqueous chromatography is the injection precision that is obtainable. Over the course of 15 compound calibration determinations, encompassing 30 sets of replicate injections, the average error for 1 μL injections was only 2.6% (calculated using the difference in peak heights divided by the average peak height). We have also looked at the response factors generated by injections of various volumes and found that in the linear range of detector response it does not matter if the injection volume is 1 μL or 4 μL, the response factor is identical.

FIELD SITE CONSIDERATIONS

The system, as it is configured now, is limited in its field applications only by where the lab van is able to go. We have found no degradation in performance of the instrument when it is running in the field. One of the concerns we had initially, was how long the instrument would need to warm up once it had arrived on site. The ECD is noted for being particularly sensitive to shutdown/startups while the FID, due to its nature, has virtually no warm up time associated with it. From our initial experiences it has become apparent that the warm up time needed by the ECD is partially controlled by the conditions utilized when the system is shutdown. If the heaters are turned off and the system allowed to return to ambient temperatures before the gases are shutdown and the instrument moved, then the ECD appears to need only a 30-45 minutes of an hour to stabilize in the field. If the gases are discontinued before the ECD returns to ambient temperatures, the system will need in excess of 1 hour to stabilize and even then will behave somewhat erratically (this is probably due to airborne contaminants plating onto the hot detector surfaces).

By the time the instrument is warmed up on site, water can have been collected from the first well and an analysis begun. Every 20 minutes after that a new sample can be analyzed and interpreted. An example of an on site analysis is shown in Figure 5. At a coal tar site somewhere in New England, after the GC was suitably calibrated, a groundwater sample was analyzed by FID/ECD. Only 1.0 μL of the sample was needed and in 7 minutes most of the chemical composition and concentration of that sample was known. In addition, some interesting 'ECD active' compounds were discovered which probably would go unnoticed in more conventional analyses. By providing almost instantaneous

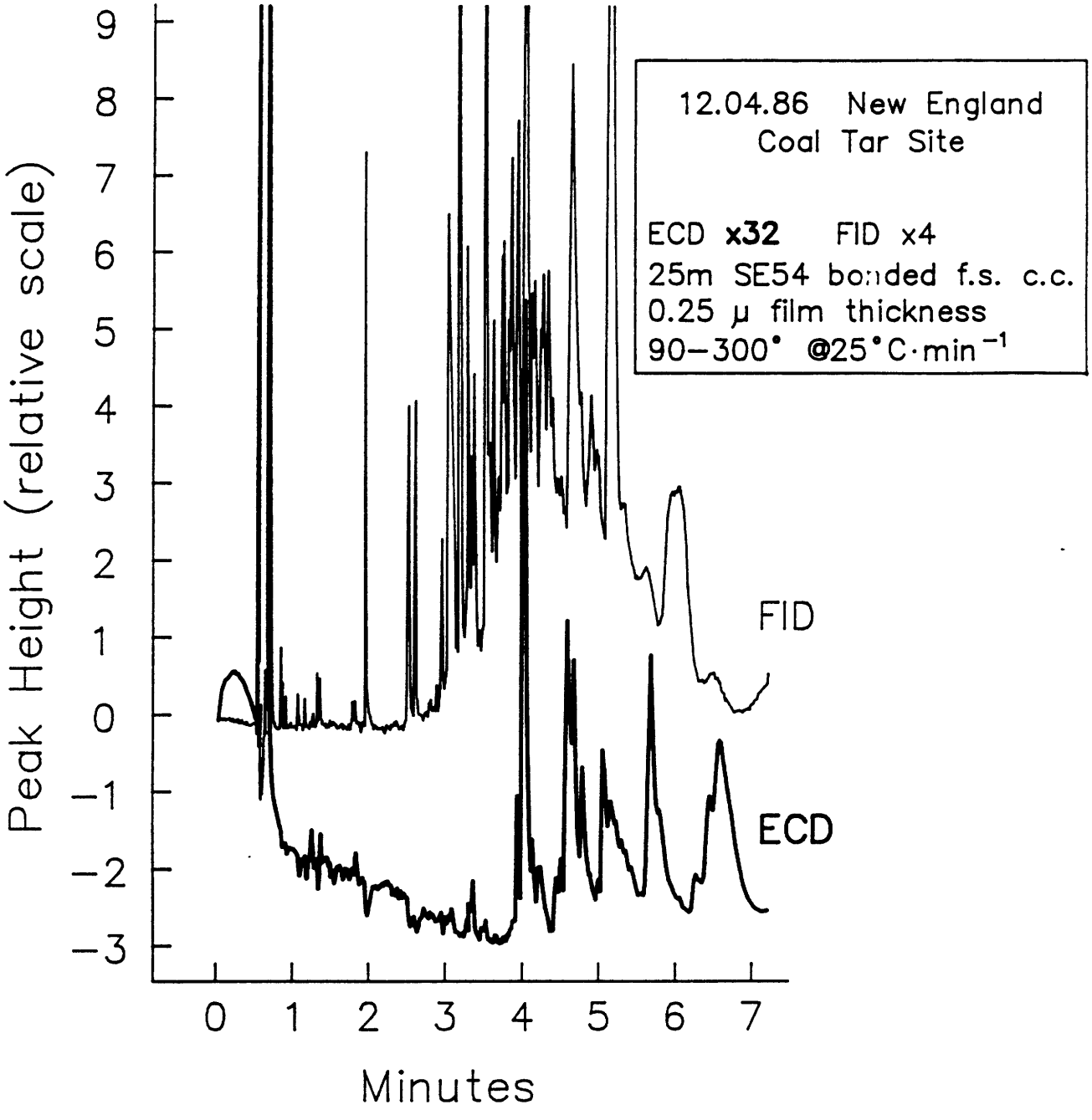

12.04.86 New England
Coal Tar Site
ECD x32 FID x4
25m SE54 bonded f.s. c.c.
0.25 μ film thickness
90–300° @25°C·min⁻¹
FID
ECD
Peak Height (relative scale)
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
0 1 2 3 4 5 6 7
Minutes

Figure 5

feedback to workers in the field, the need for placement of subsequent wells or the collection of more samples from the same well for more rigorous GCMS analysis can be determined at substantial savings.

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APPENDIX I

BACKGROUND INFORMATION ON CAPILLARY GAS CHROMATOGRAPHY WITH FLAME IONIZATION OR ELECTRON CAPTURE DETECTION

Gas chromatography is a physical method of separation in which volatile chemicals are distributed between two phases (mobile and stationary) while travelling through a column. The mobile phase, as the name suggests, is a gas (known as the carrier gas). The stationary phase is a thin, liquid film which coats a support material of high surface area. There are two major categories of support materials available which have led to the development of two distinct GC methodologies: packed column and capillary column chromatography. Packed column chromatography utilizes porous micro-sized particles which are coated with thin films of stationary phase liquid. Because these particles have large surface:volume ratios, they are generally packed in short ($\lesssim$ 2.4 m) glass or metal columns with relatively large interior diameters (2-4 mm). Capillary chromatography, on the other hand, uses an open tubular approach. The stationary phase is applied directly to the insides of long, narrow columns of either borosilicate glass or fused silica (lengths run upwards of 100+ m with I.D.s from 0.25-0.75 mm). The long length is necessary in order to supply the high surface area needed for enhanced column efficiency. Columns with interior diameters of 0.25-0.32 mm are known as narrow bore capillary columns while columns with I.D.s of 0.75 mm are called megabore columns.

The film thickness of stationary phases is varied in capillary columns depending on the results desired. Thin films (0.2-0.5 μm) are generally used in

columns that separate sample mixtures of high boiling point compounds. Thick films (0.5-5.0 μm) are used for separating low boiling point, complex mixtures. Thick film columns also have the added attractiveness of having resolving capacities equal to a thin film column of roughly twice the length (Supelco, 1986).

In gas chromatography, the sample is either introduced into a heated injector, vaporized and carried onto the front of the column by the carrier gas or deposited directly into the column and vaporized by the heat of the column. The latter method of on-column injection insures that no fractionation occurs during sample introduction. Either way, once the sample is vaporized the individual components are separated, as they are carried through the column, by continuous partitioning between the stationary phase liquid and the moving gas stream. Compounds having a high affinity for the stationary phase are retarded to a greater extent than compounds with low affinities. Phases are generally categorized into three types: nonpolar, low/intermediate polarity, and polar. A general rule of thumb in selecting phase types is 'like dissolves into like'. This means, for example, that nonpolar compounds such as gasoline hydocarbons and chlorinated solvents will dissolve into a nonpolar phase and have a better chance of being separated effectively while polar compounds will not generally be chromatographed efficiently. Obviously, the choice of the stationary phase liquid becomes critically important in determining classes of compounds for which a column will be useful.

If the proper column/liquid phase coating has been chosen, the volatilized sample emerges from the column end with it's components separated in time. The chromatographic column may be held at a constant temperature for the duration of the sample elution (isothermal). However, by using variable temperatures

(temperature programming) during chromatographic processing, the ability of a given column to separate compound mixtures may be enhanced. This technique becomes increasingly more important as the complexity of the samples increases.

Detection of the eluting compounds occurs by continuously monitoring some physical or chemical property of the column effluent. For this project, only two types of detectors are presently considered: Flame Ionization Detectors (FID) and Electron Capture Detectors (ECD). Flame ionization involves combusting the sample components in a hydrogen flame and producing ions which are detected as they pass between two electrodes (see Figure 6). The resultant current is converted to a voltage and passed on to a strip chart recorder. This type of detector destroys the sample components while processing it. Electron capture is a non-destructive type of detection. It takes advantage of the ability of some molecules (or parts of molecules) to capture, momentarily, the free electrons emitted from a radioactive beta source (^{63}Ni or ^{3}H). Electrons emitted by the β source collide with molecules of the carrier gas and initiate an ionization process which produces secondary electrons. The secondary electrons migrate between two electrodes and generate a constant current (see Figure 7). When a sample component passes which can capture electrons, the current between the electrodes is reduced resulting in a decreased signal being passed to the recorder.

Samples suitable for GC analysis must be sufficiently volatile at the temperature of analysis to ensure that they remain in the vapor phase. They must also be thermally stable so that no decomposition occurs during the chromatographic or detection processes. Once these conditions are met, the instrument can be calibrated by analyzing mixtures of standards that encompass the concentration ranges expected to be found in the field. This allows

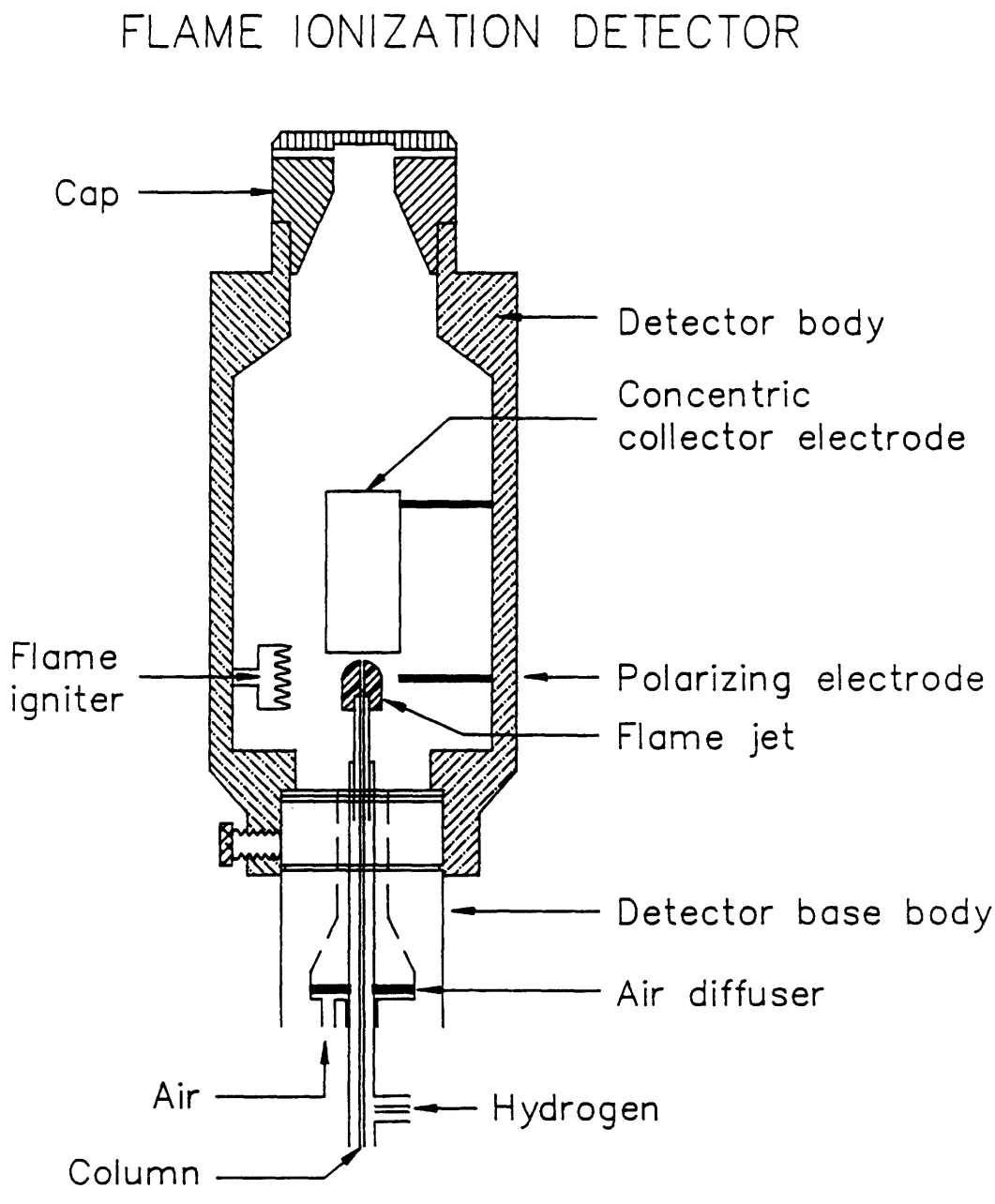
FLAME IONIZATION DETECTOR
Cap
Detector body
Concentric
collector electrode
Flame
igniter
Polarizing electrode
Flame jet
Detector base body
Air diffuser
Air
Hydrogen
Column

Figure 6

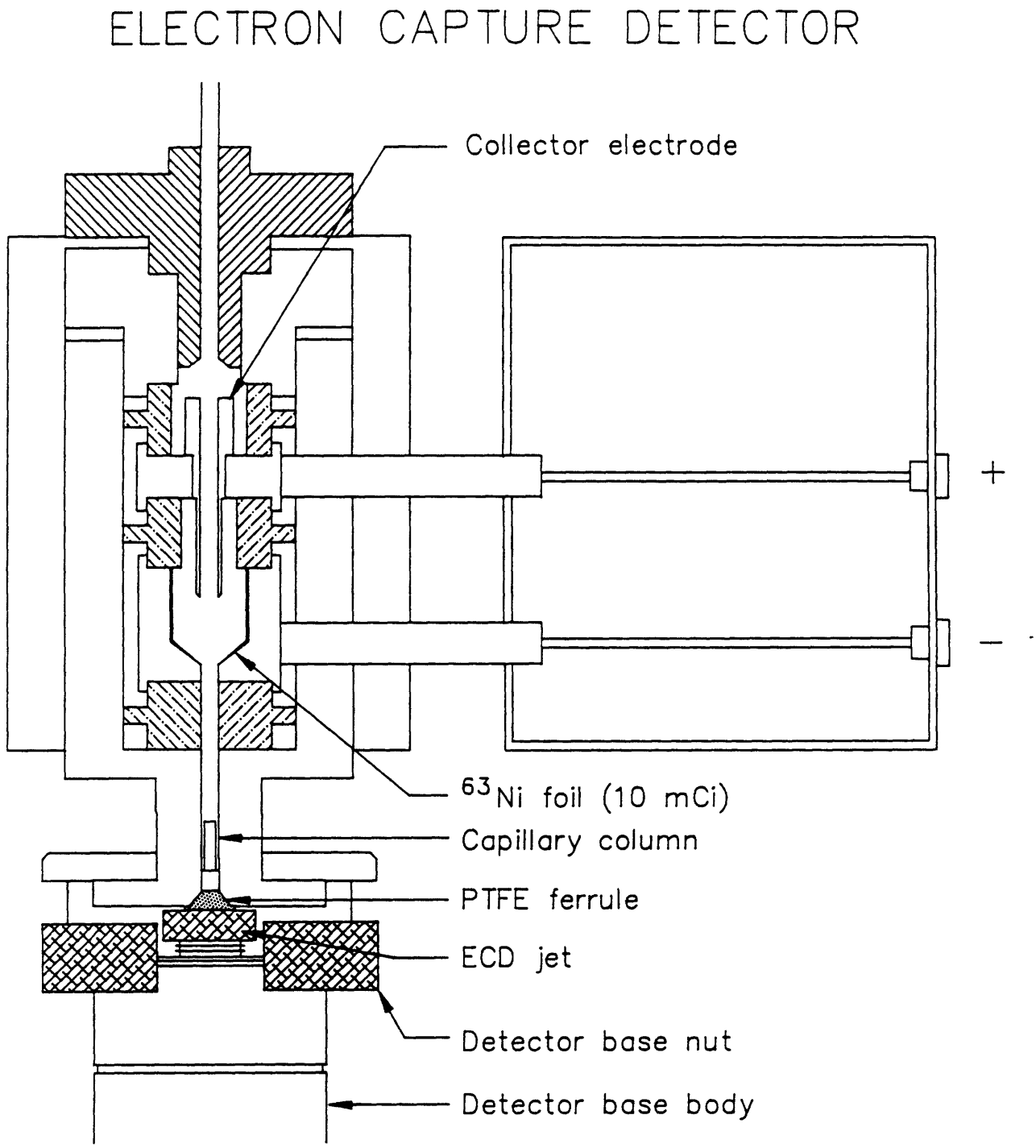
ELECTRON CAPTURE DETECTOR
Collector electrode
+
−
^{63}Ni foil (10 mCi)
Capillary column
PTFE ferrule
ECD jet
Detector base nut
Detector base body

Figure 7

response factors (peak height or peak area per amount of compound injected) and linear working ranges to be calculated for compounds of interest. Only after thorough calibration is it possible to accurately determine the concentrations of components that make up field samples. As more standards are analyzed and their retention times (time between injection and detection) documented, the GC becomes a useful tool for identifying unknown compounds included within a field sample.