1.0 Introduction

This chapter is written from the perspective of an environmental professional. It focuses on those aspects of Gas Chromatography that aid in the selection of instrumentation and columns for both field and laboratory methods. In addition, it should be a useful resource for anyone who is responsible for interpreting data collected in the field.

We start by describing the theory of gas chromatography (GC), then we discuss the selection of columns, gas solid and gas liquid chromatography, phases, packed and capillary columns. This material is intended to provide the reader with sufficient information to select a proper column for analysis of a particular site or a difficult sample. In the next section, we describe the hardware required for GC. The fourth section describes the need for good temperature control even for field GC’s.

The GC detectors that are described include the photoionization detector (PID), the flame ionization detector (FID), the thermal conductivity detector (TCD), the electron capture detector (ECD), the far UV absorbance detector (FUV) and the flame photometric detector (FPD). For each detector, the theory of operation, the range, detection limits and characteristics are described. Individual species can be measured from ppt to % levels with either a specific or universal type detector.

Finally, we discuss the analysis of volatile organic (VOC) and semivolatile (SVOC) compounds, dual detectors (PID/FID), headspace, as well as concentrators for GC’s that can be used for monitoring low or sub ppb levels of toxic species at the fenceline.

2.0 Gas Chromatography Theory

Gas chromatography (GC) is a method of continuous chemical separation of one or more individual compounds between two phases. One phase remains fixed (stationary phase); the other, the mobile phase (carrier gas), flows over the stationary phase. The components enter the stationary phase simultaneously at the injector but move along at different rates. The lower the vapor pressure of the compound (higher boiling point), the longer the compound will remain in the stationary phase. The time that each compound remains in the stationary phase depends on two factors: the vapor pressure of the compound and its solubility in the stationary phase. These compounds are then detected at the end of the column. A plot of the output of the detector response versus time is termed a chromatogram.

Elution times may be reduced by increasing the temperature of the GC oven. GC’s can be run isothermally (constant temperature) to separate a narrow boiling range of solutes. If the separation of low and high boiling compounds is necessary, temperature programming (linear increase of column temperature) is used.

The Retention time is defined as the time measured from the start of injection to the peak maximum and can be used to identify resolved components in mixtures. The times measured as RT1, RT2, RT3 shown in Fig. 1 would be the retention times for components A1-A3. The retention time is characteristic for a compound and the stationary phase at a given temperature and is used for identification when the mixture of compounds is completely resolved. To confirm that a particular component is present requires the identification on two columns with different polarities of stationary phases. Some environmental methods allow confirmation of compound identity by comparing both retention times and detector response factors with known standards. Instruments that are configured for either dual columns with a single detector, or a single column with dual detectors (PID/FID) can combine analysis and confirmation in a single run.
There are a large number of GC packings available. Each of these exhibit specific retention characteristics for specific compounds. Many times, a better separation is obtained more easily by changing the liquid phase than by increasing the length of the column. A properly made capillary column of 5m in length will have about 12,000-15,000 plates effective plates, more than 100 times the resolving power of a short packed column. Interesting enough, with all of the developments in capillary column technology, at a recent symposium (1), one researcher was still talking about the utility of short, packed columns at ambient temperature. With the minimum of separating power (efficiency), many peaks could still be unresolved under a single peak. A comparison of packed and capillary columns is shown in Table I.

Table I
Comparison of Packed and Capillary Columns

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Packed</th>
<th>Capillary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (meters)</td>
<td>1.5-6</td>
<td>5-100</td>
</tr>
<tr>
<td>ID (mm)</td>
<td>2-4</td>
<td>0.15-0.53</td>
</tr>
<tr>
<td>Flowrate (ml/min)</td>
<td>10-60</td>
<td>0.5-30</td>
</tr>
<tr>
<td>Total plates (length M)</td>
<td>5000 (2 M)</td>
<td>75,000 (25M)</td>
</tr>
<tr>
<td>Film thickness (µ)</td>
<td>1-10</td>
<td>0.1-5</td>
</tr>
</tbody>
</table>

Methyl silicone stationary phase is considered non-polar generally eluting compounds in boiling point order. When polar functional groups are added in stationary phase. The Number of theoretical plates is a term taken from chemical engineering originally used to describe the efficiency of a distillation apparatus. This theory was applied to columns in gas chromatography to describe the efficiency (separation ability) of a column. Separation occurs as a result of continuous movement between the stationary phase and the mobile phase. Clearly, the larger the number of plates, the greater the resolving power of the column.

Number of theoretical plates (n) is given by: \( n = 5.545 \left( \frac{t}{w} \right)^2 \)

Where \( t \) = retention time; \( w \) = peak half height

Number of effective theoretical plates \( (N_{eff}) \) is given by: \( N_{eff} = 5.545 \left( \frac{t'}{w} \right)^2 \)

\( t' \) = adjusted retention time = \( t - t_m \);
\( t_m \) = retention time for inert peak like methane

Height equivalent to a theoretical plate (h) is given by:

\[ h = \frac{L}{n} \]

Where \( L \) = length of column

2.1.1 Gas Solid chromatography-GSC

Solid packings are generally used to separate gases and compounds with boiling points below propane. Polymers which are derivatives of styrene divinyl benzene, cross linked acrylic ester, cross linked polystyrene etc. are small particles with pores and variable surface areas. These porous polymers are available in a variety of polarities for specific separations of low molecular weight compounds (methane, ethane, ethylene, H2S). It would be difficult to analyze ethylene (gas) and benzene (very long retention time) on these porous polymers and similarly, it is difficult to analyze ethylene on a short (5M) capillary column since it would be an unretained (would elute very quickly) compound.

Zeolites or molecular sieves that employ size exclusion for separation. Certain molecules that are small enough to enter the pores exist the stationary phase exit the stationary phase later than larger molecules that cannot enter the pores.
readily. These phases are commonly used for the separation of permanent gases (including O₂ and N₂).

2.1.2 Gas Liquid chromatography—GLC

Columns with liquid stationary phase are generally used to separate compounds with boiling points above propane (C₃H₈). More than 70% of all separations in gas chromatography can be accomplished with a methyl silicone liquid phase (OV1, OV101, SE30). However, there are more than 1000 packed column liquid phases available attesting to their versatility for specific separations.

2.1.3 Types of column phases

The stationary phase is most influential column parameter since it determines the final resolution and has an influence on the sample capacity and the analysis time. The most important thing to remember is that “likes dissolve likes”. Separate non polar compounds on a non polar column and polar compounds on a polar column. In Fig. 2, the range of polarity of a group of organic compounds is compared with the polarity of different phases.

<table>
<thead>
<tr>
<th>Applications</th>
<th>Column Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>Carbowax 20M, OV1701</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Carbowax 20M, OV1, SE30</td>
</tr>
<tr>
<td>Amines</td>
<td>OV54</td>
</tr>
<tr>
<td>Aromatic HC</td>
<td>Carbowax 20M</td>
</tr>
<tr>
<td>Dioxins</td>
<td>OV54</td>
</tr>
<tr>
<td>Glycols</td>
<td>Carbowax 20M, OV1701</td>
</tr>
<tr>
<td>Halogenated HC</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>Ketones</td>
<td>OV1, OV54</td>
</tr>
<tr>
<td>PAH's</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>PCB's</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>Pesticides</td>
<td>OV351, OV225</td>
</tr>
<tr>
<td>Triazine herbicides</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>EPA 608</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>Phenols</td>
<td>OV1, OV225</td>
</tr>
<tr>
<td>Free</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>Acetylated</td>
<td>OV54, OV1701</td>
</tr>
<tr>
<td>Solvents</td>
<td>OV54, OV1701</td>
</tr>
</tbody>
</table>

Many of the phases used in packed columns are also used in capillary columns with much greater effect on the latter. In Fig. 3 is a schematic representation of packed and capillary columns. A comparison of the separation of packed and capillary columns is given in Fig. 4. Note that a significantly larger number of peaks are detected with the capillary column.

Fig. 2 Polarity of Compounds and Phases

In other words, if one has non polar hydrocarbons to separate, use a non polar phase like (SE30, NBW30); with more polar compounds like alcohols, esters use a polar phase like carbowax, etc. The data in Table II lists the optimum liquid phases on a packed or capillary column for a variety of analytes. The terminology in Table II is the of Ohio Valley Specialities (OV). These silicone phases in order of polarity are least polar (OV1, OV101), medium polarity (OV1701), and most polar (OV275). Their composition is as follows:
was a problem but these columns were more inert than stainless steel. Fused silica was also used as column material but it was more difficult to work with a flame than glass and was easily broken. The coatings (stationary phase) on the columns were adsorbed but not bonded.

In 1979, Dandeneau (2) described a new type of fused silica capillary column that had a coating of polyimide on the outside which made the column relatively flexible. At the same time, the use of bonded (to the fused silica) stationary phases increased dramatically because of the longer lifetime, inertness, and reduced bleed. This created a surge in the use of capillary columns, particularly in the US. Some years ago, glass lined stainless steel columns were introduced. These again improved the utility of capillary columns, particularly in the field.

Capillary columns have a high resolution (3000 plates/meter) and vary from 5-100 meters in length. The liquid phases (polar or non-polar) are bonded to the fused silica. The columns can be made of fused silica (coated with polyimide so that they are flexible or stainless steel (lined with fused silica). Column diameters can be 0.53, 0.32, 0.20 or 0.15 mm. Capillary columns can also be packed with porous polymers (bonded to the fused silica) to form highly efficient PLOT columns for separation of low molecular weight compounds or fixed gases. A comparison of columns and their characteristics is given in Fig. 5.

Fig. 5 Comparison of column types

<table>
<thead>
<tr>
<th>COLUMN TYPE</th>
<th>LENGTH (M)</th>
<th>I.B. (PV)</th>
<th>Retention Power</th>
<th>Sample Capacity</th>
<th>Inertness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wide</td>
<td>5-100</td>
<td>6.0-0.05</td>
<td>Good</td>
<td>Low</td>
<td>Excellent</td>
</tr>
<tr>
<td>Narrow</td>
<td>1-50</td>
<td>6.0-0.75</td>
<td>Good</td>
<td>Low</td>
<td>Good</td>
</tr>
<tr>
<td>Micro-packer</td>
<td>0.5-10</td>
<td>6.5-1.0</td>
<td>Acceptable</td>
<td>Moderate</td>
<td>Acceptable</td>
</tr>
<tr>
<td>Packed</td>
<td>0.5-5</td>
<td>6.5-1.0</td>
<td>Good</td>
<td>High</td>
<td>Good</td>
</tr>
</tbody>
</table>

Packed columns have a relatively high sample capacity (difficult to overload column) because the liquid (stationary) phase coating is quite high compared to capillary columns. With bonded capillary columns, the film thickness of the stationary

---

Driscoll, John N.,
Environmental Instrumentation
Wiley (2004) Ch 8
Gas Chromatography Chapter

phase can be controlled. A thin layer of stationary phase will provide a faster column that is better for high molecular weight compounds. Here, one has to consider the capacity factor, \( k \), which is ratio of the time the solute spends in the stationary and mobile phases.

\[ k = \frac{t - t_m}{t_m} = \frac{t'}{t_m} \]

There are a number of factors that effect the column performance these include:

**Inner diameter (ID)** - the smaller the ID, the higher the efficiency and the shorter the analysis time

**Film thickness** - The higher the FT, the greater the capacity; the higher the film thickness, the longer the analysis time; thickness ranges from 0.1-5um

**Length** - Increasing the length will increase resolution, the analysis time and the capacity

The effect of these parameters is shown in Fig. 6.

![Fig. 6 Effect of Film thickness and Other Parameters on column Performance](image)

In summary, the selection of a column involves a number of tradeoffs and specific knowledge of the compounds to be analyzed,

3.0 GC hardware

A schematic of the typical GC hardware is shown in Figure 7. The GC consists of the following components:

**Fig. 7 Schematic of a Gas Chromatograph**

3.1 Injector-

A sample is introduced into the heated injector, where it is vaporized and carried on to the column via a liquid or gas syringe, liquid or gas valve, concentrator, purge & trap, etc.

3.2 Packed Columns-

1/4", 1/8" or 1/16" (micropack) 2-3 meters in length- 300-500 plates per meter-packing material: porous polymer, liquid phase (1-3%) on diatomite

3.3 Capillary columns-

0.53, 0.32, 0.20 , 0.15 mm column with liquid phase bonded to the fused silica; available in fused silica lined stainless steel with the liquid phase bonded to the silica; efficiency≈ 1000-3000 plates/M with typical length 15-30 M

3.4 Carrier gas-

mobile phase that is used to move the components through the column to the detector; note that the high sensitivity detectors (PID, FID, ECD, FUV, FPD) require high purity carrier; the ECD requires that oxygen and water be eliminated (trap is usually required) from the carrier since these species can absorb electrons and effect sensitivity

3.5 Oven-

Isothermal or temperature programmed heated device; the higher the temp. the shorter the retention time; good temperature stability \(+/- \ 0.1-0.2^\circ C\) is required (see section 4)

3.6 Detector-

Produces a response proportional to component that is separated by column. Detectors may include a photoionization detector (PID), flame ionization detector (FID), thermal conductivity detector (TCD), electron capture detector (ECD), flame photometric detector (FPD) or far UV absorbance detector (FUV)

3.7 Amplifier-

Receives an output from a detector (typically picoamps for an ionization detector) and
amplifies it so that the signal can be detected by a recorder or integrator

3.8 Integrator- takes signal from amplifier and produces an output (chromatogram) and peak height or area (used for quantitation). If we note Fig. 1, The height of the peak measured from the baseline to the peak maximum and the area which is determined by integrating the area underneath the peak are proportional to concentration. Generally integrators will provide both area and height values. At low concentrations with packed columns, peak height may provide a better value.

4.0 Temperature Control

Many of the portable gas chromatographs of the nineteen eighties were typically ambient temperature instruments with no temperature control and short chromatographic columns. Even today, some of these portable instruments do not have very good temperature control. The problem with these instruments was that a change of just a few degrees centigrade in the temperature of the column can result in a significant change in the retention time of the species of interest. The chromatographic separation depends upon solute’s (material being analyzed) partitioning between the stationary and mobile phase. This controls the efficiency or separating power of the column. Temperature control is very important, therefore we have added this section.

Giddings (3) has developed an expression for the efficiency or plate height (H) as follows:

\[ H = \frac{2D}{v} + d_P + 2R (1-R) \nu t_d \]

where:  
- \( D \) is the ordinary diffusion coefficient;  
- \( R \) is the ratio of zone velocity to mobile phase velocity;  
- \( t_d \) is the lifetime in the stationary phase;  
- \( d_P \) is the particle diameter; and  
- \( v \) is the velocity.

The partition or distribution constant (K) has a temperature coefficient (related to R) which is given by:

\[ K = k \left( e^{-\frac{\Delta H}{RT}} \right) \]

Where: \( k \) is a constant; \( \Delta H \) is the enthalpy of sorption; \( R \) is the ideal gas constant; and \( T \) is the absolute temperature.

In addition to the temperature dependence of K, the ordinary diffusion coefficient (D) has a temperature dependency as does the term (t_d), the lifetime in the stationary phase. The latter can be approximated through the Arrhenius equation (4).

Retention time is defined as the time from injection to the peak maximum and can be used to identify resolved components in mixtures. Since the retention times are used to identify the species of interest, a shift in temperature could lead to the wrong species being identified, particularly in a complex mixture. Ambient temperatures, as anyone knows, are anything but constant.

If the separation of low and high boiling compounds is required, temperature programming (linear increase of column temperature) is needed.

The difficulty with temperature control is that it takes power to maintain the temperature and the higher the temperature the greater the power consumption. Thus, in the design of field portable GC's, much of the flexibility is lost if battery operation is the most important criteria. Alternatives to internal batteries are generators and batteries in vehicles. the GC311 has been designed to operate from generators or vehicle batteries. Using these alternative methods, for the HNU GC311, one has to make few concessions in performance of the instrument.

In the nineteen eighties, a number of portable GC's were introduced that employed temperature control and, for the first employed capillary columns. Since resolution is proportional to column length considerably better performance can be obtained with a 5 meter column than a 0.3 meter column. The longer the column the better the separation. Some of the portable GC's maintain temperatures of only 50°C (to minimize power consumption) and are limited in the variety of species that can be analyzed.

5.0 GC Detectors

The detectors selected for this section include the most popular detectors for field work. We have not included the mass selective detector (MSD) in this section.
5.1 PID
In 1976, the first commercial PID was described by HNU Systems, Inc. (5). The process of ionization which occurs when a photon of sufficient energy is absorbed by a molecule that results in the formation of an ion plus electron:

\[ \text{R} + h\nu \rightarrow \text{R}^+ + e^- \]

where:
- \( \text{R} = \) an ionizable species
- \( h\nu = \) a photon with sufficient energy to ionize species \( \text{R} \)

In the ion chamber, the ions (\( \text{R}^+ \)) formed by absorption of the UV photons are collected by applying a positive potential to accelerating electrode and measuring the current at the collection electrode. A PID consists of an ion chamber, a UV lamp with sufficient energy to ionize organic and inorganic compounds, a voltage source for the accelerating electrode and an amplifier capable of measuring down to one picoamp full scale. A schematic of a PID is shown in Fig. 8. A list of ionization potentials is given in the Chapter on Photoionization.

The PID is a concentration sensitive detector (sample is not destroyed) where the sensitivity is increased as the flowrate is reduced. Thus, the sensitivity can be improved by operating the PID at lower flowrates, however, one must have sufficient flow to sweep the sample through the PID.

\[ C_{\text{PID}} \propto \frac{1}{F} \]

where:
- \( C = \) concentration
- \( F = \) flowrate of the carrier gas

In terms of sensitivity, the PID is from 10-100 times more sensitive than the FID making this detector ideal for environmental applications. This results from the higher ionization efficiency of the PID. The apparent ionization efficiency of the PID is approximately \( 10^{-4} \) while that of the FID is \( 10^{-5} \).

Some characteristics of the PID are given in Table III. The sensitivity of the PID response with the structure of organic compounds (6) is given in Table IV.

![Fig. 8 Schematic Representation of the PID](image)

### Table III
**PID Characteristics**

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity increases as the carbon number increases (carbon counter)</td>
<td></td>
</tr>
<tr>
<td>For 10.2 eV lamp, responds to carbon aliphatic compounds &gt; C₆, all olefins and all aromatics</td>
<td></td>
</tr>
<tr>
<td>The PID also responds to inorganic compounds such as H₂S, NH₃, Br₂, I₂, PH₃, AsH₃, e.g. any compound with an ionization potential of &lt; 10.6 eV</td>
<td></td>
</tr>
<tr>
<td>The PID is more sensitive than the FID; 40 x more sensitive for aromatics, 20 times for olefins, &amp; 10 times for alkanes &gt; C₆</td>
<td></td>
</tr>
<tr>
<td>Non destructive detector; other detectors can be run downstream</td>
<td></td>
</tr>
<tr>
<td>Only carrier gas (prepurified nitrogen or helium) is required for operation</td>
<td></td>
</tr>
<tr>
<td>Concentration sensitive detector</td>
<td></td>
</tr>
</tbody>
</table>

### Table IV
**PID Sensitivity for Organic Compounds**

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity increases as carbon number increases</td>
<td></td>
</tr>
<tr>
<td>For n-alkanes, SM = 0.715n-0.457 where SM = molar sensitivity relative to benzene (benzene = 1.0) and n = carbon number</td>
<td></td>
</tr>
<tr>
<td>Sensitivity for alkanes &lt; alkenes &lt; aromatics</td>
<td></td>
</tr>
<tr>
<td>Sensitivity for alkanes &lt; alcohols &lt; esters &lt; aldehydes &lt; ketones</td>
<td></td>
</tr>
<tr>
<td>Sensitivity for cyclic compounds &gt; non cyclic compounds</td>
<td></td>
</tr>
<tr>
<td>Sensitivity for branched compounds &gt; non branched compounds</td>
<td></td>
</tr>
<tr>
<td>Sensitivity for fluorine substituted &lt; chlorine substituted &lt; bromine substituted &lt; iodine substituted</td>
<td></td>
</tr>
</tbody>
</table>

Driscoll, John N.,
*Environmental Instrumentation*
Wiley (2004) Ch 8
For substituted benzenes, ring activators (electron releasing groups) increase sensitivity. For substituted benzenes, ring deactivators (electron withdrawing groups) decrease sensitivity (exception: halogenated benzenes).

For soil and water samples that involve solvent extraction, there are a number of solvents that can be used to produce a small or negative response with the PID. These are shown in Table V. The advantage of these solvents is that many of the volatile hydrocarbons can still be detected since the solvent peak is like an unretained compound and elutes very quickly. The FID, for example, does not respond to carbon disulfide. This can be used for a similar purpose but a hood will be needed to minimize odor problems.

Table V
PID Response with Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ionization Potential (eV)</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>12.35</td>
<td>Negative peak</td>
</tr>
<tr>
<td>Methanol</td>
<td>10.85</td>
<td>Negative peak</td>
</tr>
<tr>
<td>Chloroform</td>
<td>11.42</td>
<td>Negative peak</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>11.47</td>
<td>Negative peak</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>12.22</td>
<td>Negative peak</td>
</tr>
<tr>
<td>Pentane</td>
<td>10.35</td>
<td>Small positive peak</td>
</tr>
</tbody>
</table>

5.2 FID
The process of ionization which occurs in organic compounds when the carbon-carbon bond is broken via a thermal process in the flame that results in the formation of carbon ions. These ions are collected in the flame by applying a positive potential to the FID jet and the ions are pushed to the collection electrode where the current is measured. The response (current) is proportional to the concentration and is measured with an electrometer/amplifier. An FID consists of a combustion/ion chamber, a flame, a voltage source for the accelerating electrode (usually applied to the jet) and an amplifier capable of measuring down to one to five picoamperes full scale.

Table VI
FID Characteristics

<table>
<thead>
<tr>
<th>Sensitivity increases as the carbon number increases (carbon counter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity to substituted species depends on the mass of carbon present and the ability to break the carbon bonds</td>
</tr>
<tr>
<td>The FID is most sensitive to hydrocarbons</td>
</tr>
<tr>
<td>Detector is destructive since sample is burned</td>
</tr>
<tr>
<td>Requires the use of zero grade (high purity) hydrogen and air to produce the flame</td>
</tr>
</tbody>
</table>

The FID is a mass sensitive detector, the output of which is directly proportional to the ratio of the compound’s carbon mass to the total compound mass. Thus, the sample is destroyed in the flame. Some characteristics of the FID are as listed in Table VI.

5.3 ECD
The ECD consists of an accelerating and collection electrode as well as a radioactive source. The source, $^{63}$Ni, is a beta (electron) emitter and produces a high background level of free electrons in the carrier gas. Any compounds that enter the detector which are electron absorbing reduce the background level of free electrons and there is a resultant drop in the current which is measured by an electrometer. The newer type of electronics (pulsed constant current) have improved the performance dramatically increasing the linear response from $10^2$ to $>10^5$. With no sample, the pulse frequency is low. When electron absorbing compound passes through the detector, the frequency increases to compensate the current loss to the sample. The concentration is then proportional to the pulse frequency.

Earlier ECD’s (with DC electronics) had problems with saturation of the current and subsequent reduction of the linear range of the detector to just over 100. The most sensitive compounds for this are chlorinated hydrocarbons which have sensitivities as low as 0.1 ppb of lindane.

5.4 TCD
Measures difference between the thermal transfer characteristics of the gas and a reference gas, generally helium but hydrogen or nitrogen can be used depending on the application. The sample and reference filaments are two legs of a Wheatstone Bridge. A constant current is applied with a resultant in a rise in filament temperature. As the sample passes through the detector, the resistance changes as the reference gas is replaced by the sample which has a lower thermal conductivity. The thermal conductivities for a number of compounds are given in Table VII. This difference in resistance is proportional to the concentration. The response is universal since the detector responds to any compound that conducts heat. The minimum detection limit is in the 100-200 ppm. The maximum concentration is 100%.

### Table VII
Thermal Conductivities for Selected Compounds

<table>
<thead>
<tr>
<th>Component</th>
<th>Thermal Conductivity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.78</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.90</td>
</tr>
<tr>
<td>Butane</td>
<td>0.68</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.55</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.32</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.75</td>
</tr>
<tr>
<td>Helium</td>
<td>5.97</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.15</td>
</tr>
<tr>
<td>Methane</td>
<td>1.25</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>0.35</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.21</td>
</tr>
</tbody>
</table>

* relative to air 0°C

5.5 FPD

The sample is burned in a hydrogen rich flame which excites sulfur or phosphorus to a low lying electronic level. This is followed by a resultant relaxation to the ground state with a corresponding emission of a blue (S) or green (P) photon. This type of emission is termed chemiluminescence. The emission is at 394 nm for Sulfur and 525 nm for phosphorus. The S:C selectivity ratio is > 10,000:1. This detector uses rare earth filters instead of interference filters for S & P to improve detection limits and eliminate some of the deficiencies of interference filters (7). Detection limits in the 5 pg and 20 pg range for P and S respectively.

5.6 FUV

Most organic and inorganic species absorb strongly in the far UV. Notable exceptions are the inert gases, helium and nitrogen which absorb very weakly in this region. Certain diatomic species such as O₂ which have low absorption in the region of the lamp energy (124 nm) will have a poor response but low ppm levels can still be detected.

The far UV detector is relatively new to gas chromatography (compared to other GC detectors) since it was introduced by HNU Systems in 1984. It is frequently compared with the thermal conductivity detector since it will respond to any compound that absorbs in the far or vacuum UV. The latter name is a misnomer since with a carrier gas flowing through the cell, a vacuum is not needed. Thus, the detector has a response that is nearly universal, a low dead volume (40 µl), and a fast electrometer time constant. The primary emission from this lamp is the 124 nm line. Although there are visible lines from this lamp, the photodiode is unresponsive to any long wavelength UV or visible emissions and only the absorption at 124 nm needs to be considered (8) for the absorption process.

The minimum detection limits for organic compounds, oxygen, water, and inorganic compounds are in the range from 0.1 to 10 ppm. A summary of the detection limits for organic and inorganic compounds is given in Table VIII.

### Table VIII
Detection Limits for the FUV Detector

<table>
<thead>
<tr>
<th>Compound</th>
<th>Detection Limit (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>0.7</td>
</tr>
<tr>
<td>Methane</td>
<td>0.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>14</td>
</tr>
<tr>
<td>Water</td>
<td>3</td>
</tr>
<tr>
<td>Propane</td>
<td>1</td>
</tr>
<tr>
<td>Chloroform</td>
<td>5</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1</td>
</tr>
</tbody>
</table>
A summary of the response and range of the various detectors is shown in Table IX. Note that the response ranges from universal (TCD) to selective (FPD for S & P) while the detectors span a concentration range of a billion.

Table IX
Summary of Detector Characteristics

<table>
<thead>
<tr>
<th>Type</th>
<th>Response</th>
<th>Carrier Gas</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>PID</td>
<td>organic, inorganic</td>
<td>Nitrogen*, helium*, hydrogen*</td>
<td>2 ppb to low %</td>
</tr>
<tr>
<td>FID</td>
<td>Organic</td>
<td>Nitrogen*, helium*, hydrogen*</td>
<td>100 ppb to %</td>
</tr>
<tr>
<td>FUV</td>
<td>Organic, inorganic, fixed</td>
<td>Nitrogen*, helium*, hydrogen</td>
<td>0.1 ppm to low %</td>
</tr>
<tr>
<td>ECD</td>
<td>Halogenate d, nitro cpds.</td>
<td>Argon-methane*, helium, nitrogen*</td>
<td>0.1 ppb to 1 ppm</td>
</tr>
<tr>
<td>TCD</td>
<td>Organic, inorganic, fixed</td>
<td>Helium, hydrogen</td>
<td>200 ppm to 100%</td>
</tr>
<tr>
<td>FPD</td>
<td>sulfur, phosphorus</td>
<td>Nitrogen*, helium*, hydrogen</td>
<td>25 ppb-100 ppm</td>
</tr>
</tbody>
</table>

* high purity

6.0 Discussion
The framework of the EPA methodology involves five levels of investigative screening or analyses. The first level (Level I) involves field screening of VOC's with hand held analyzers (EPA protocol specifies a photoionization detector like HNU Model PI or DL101) and other site characterization equipment such as an oxygen meter, explosimeter, radiation survey equipment and chemical testing tubes (9). This type of measurement is described in the Chapter on Photoionization not here.

Level II screening can establish the identity of the compound(s) and relative concentrations. In the early to mid nineteen eighties, this was done predominantly by sending samples to a laboratory for detailed analysis. It is interesting to note that > 50% of the samples returned to the lab during the 1980's for the EPA CLP program were no detects. This demonstrates just how important field methods actually are. The intermediate Level II analysis was introduced by EPA in order to reduce both the time required to start remedial actions and the high costs associated with laboratory analysis. An additional factor was the cost of keeping trained personnel in the field waiting for results (9). Level II measurements involve field analysis with more sophisticated instrumentation (i.e., portable GC or a GC in a laboratory GC in a trailer) to provide identification (as far as possible) of specific components present.

The final three levels (Levels III-V) use laboratories located "off site" and frequently involve CLP analysis (9). We will not be concerned with these latter techniques. Of course, a certain percentage of field samples should be returned and analyzed by laboratory results with standard EPA methods. Semivolatile hydrocarbons do not migrate but may have to be removed as a result of their proximity to a source of drinking water. The two most serious threats from the volatiles involve evaporation into the air and migration away from the original source of contamination through the soil and into a source of groundwater. Remediation of the groundwater to EPA levels may take years.

During the nineteen seventies and eighties, the passage of the Resource, Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Recovery Act (CERCLA or Superfund) expanded the list of chemicals under EPA regulation. This led to the development of field screening methods for volatile organics to augment the CLP program (10). The portable GC was one of the stars of EPA's field screening programs for the analysis of volatiles (11). In 1988, EPA published a "Field Methods Catalogue" (10) that described simplified methods for volatile and semivolatile hydrocarbons, which had been used for field screening. It is clear that a portable GC or a compact GC for an on-site trailer best meet the needs for field measurement. A portable GC, the HNU Model GC311 is shown in Fig. 9 and a compact GC, the HNU Model 321 is...
shown in Fig. 10. Both are capable of analyzing volatile and semivolatile hydrocarbons.

6.1 Sampling

6.1.1 Air, water, soil

Volatile hydrocarbons can be present in a variety of matrices in field samples including: air, water, soil, soil gas, sludge, etc. Of course, the air samples can be analyzed directly by manually injecting a 1 or 5 cc of air into the GC. Many of the portable GC’s have an automatic mode where the air is injected into the GC at a fixed interval. Water or soil samples can not be measured by directly injecting into the GC since the former would quickly overload the column and the possible the detector. Instead, methods such as headspace, purge and trap (volatiles), or solvent extraction (for VOC’s or SVOC’s) are used to change the environment of the sample for analysis by GC.

6.1.2 Headspace

In order to measure VOC’s with good precision and accuracy, the sample has to be in a dilute (ppm level or below) solution. Henry's law applies as long as solute molecules never interact significantly, because then the escaping tendency is strictly proportional to the number of solute molecules in the in the fixed amount of solvent. The measurement of low concentrations of organics in water can be accomplished through the application of Henry’s Law which states that, at equilibrium, the solubility of a gas in a liquid is proportional to the partial pressure of a gas in contact with a liquid as given below:

\[
{\text{VOC (aq)}} \leftrightarrow {K PVOC}
\]

where VOC (aq) is the concentration of benzene in the liquid phase, K is the Henry’s Law constant which governs the solubility of gases in water, and PVOC is the partial pressure of benzene in the gas phase.

As a result of the above equation, it can be seen that if the concentration of benzene in the gas phase and at equilibrium is measured, this is related to the concentration of benzene in the dilute aqueous solution by a proportionality constant \((K)\) that can be determined by calibration. Simple headspace measurements can be made by equilibrating the liquid or soil sample in a sealed container (jar, VOA vial, or plastic bag) with a small headspace. Stewart and colleagues have developed the Static Headspace Method so that it provides a useful and reproducible methodology for field measurements. This is described in a following section.

6.1.3 Soil gas

Driscoll, John N.
Environmental Instrumentation
Wiley (2004) Ch 8
Although headspace analyses (13) are common for volatile hydrocarbons, one of the most commonly used field analysis technique for site characterization is soil gas analysis (13) where the sample is collected by in-situ pumping of a well. These wells are relatively inexpensive to drill and can be surveyed rapidly (as many as 35-50 per day). This is a useful procedure to quickly evaluate the extent and source (since specific pollutants can be identified with the GC) of contamination for a site. With an HNU GC311, that has a built in sampling system, the sample stream can be sampled and analyzed directly.

6.1.4 Carbon Bed

The GC is an ideal device for monitoring the output of a carbon bed. These devices are used to remove the residual hydrocarbons from the air pumped into the soil and pulled out (pump and treat method). EPA requires a monitor on the output of these devices. To obtain a faster response, the GC column can be replaced with a piece of 1/8” or 1/16” tubing. Now the instrument will be a monitor for total VOC’s.

6.2 Extraction Methods

6.2.1 Purge & trap-

This method is for VOC’s which are not very soluble in water. This technique was adopted by EPA (1) for water analysis and is the basis for most of the water methodology. A 15 mL sample is purged (10-15 minutes) with clean nitrogen or helium to sweep the VOC’s out of the water sample. The VOC’s in the nitrogen are collected on a tenax trap which absorbs the hydrocarbons. Once the purging is complete, the tenax trap is rapidly heated and the sample is injected onto the GC column for analysis. This method can be used for water and soil samples and will detect low ppb concentrations of many hydrocarbons.

6.2.2 Solvent extraction-

In Europe and other parts of the world, the purge and trap method has not been accepted for the analysis of volatiles. Instead, solvent extraction is the method of choice. The sample can be water or soil and an organic solvent is used to extract the trace organic compounds from the sample. Then the solvent can be injected into the heated injection port of the GC.

Field methods for the extraction and analysis of volatiles and semivolatiles (pesticides, PCB’s, and PAH’s) have been described in detail previously (10). Provided that the GC has sufficient versatility, all of these samples can be analyzed with the same instrument. GC oven temperature control at temperatures between 150-200 °C and a heated injection port are required for analysis of the semivolatiles.

In Table X, we compare the detection limits for soil and water samples for extraction and headspace methods (14).

### Table X

**Detection Limits for Soil and Water Samples by GC**

<table>
<thead>
<tr>
<th>Method</th>
<th>HC conc. In soil/water extract</th>
<th>HC conc. Inj. Into GC</th>
<th>GC detection limit FID</th>
<th>GC detection limit PID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headspace</td>
<td>10 ppm</td>
<td>10 ng</td>
<td>0.1 ng</td>
<td>0.005 ng</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>1 µg/ml.</td>
<td>1 ng</td>
<td>0.1 ng</td>
<td>0.005 ng</td>
</tr>
<tr>
<td>Static headspace - soil</td>
<td>&lt; 0.5 ppm</td>
<td>&lt; 10 ppb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static headspace - water</td>
<td>&lt; 50 ppb</td>
<td>&lt; 1 ppb</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. 1 g. of soil or water in 100 cc container, heated mildly and cooled- assume aromatic HC
2. assume 1 cc gas sample injected
3. 4 g. in 25 cc DI water , 50 µL headspace injected

6.2.3 Static headspace
This field method (static headspace) will allow the analyst in the field to rapidly screen the soil or ground water samples and if a no detect is found, another sample can be taken and analyzed. One obvious advantage of this technique is that the equipment needed is minimal compared to the purge and trap technique yet Robbins and Stuart (14) have shown that comparable results can be obtained with detection limits of the order of 1 ppb.

This method was developed by Robbins and Stuart (15) at the University of Connecticut for the extraction of low levels of volatile organics from water. A 4 g. soil sample is added to 25 ml of water in a 40 ml VOA vial and 100 µL of mercuric chloride (2.4 g/L) was added as a preservative. Each vial was shaken for 10 seconds, inverted and placed in a water bath for thirty minutes at 25 +/- 0.3 C to reach thermal equilibrium. A 50 uL gas sample is injected into the GC. An example of the comparison between static headspace and purge and trap for benzene and toluene is shown in Table XI. The correlation coefficients (r²) for the static headspace and purge and trap data in Table XI was 0.999 for benzene and 0.89 for toluene. A chromatogram of VOC’s in water is shown in Fig. 11.

### Table XI
Comparison of Static Headspace & Purge & Trap Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static HS</td>
<td>17.3</td>
<td>61.8</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>12.7</td>
<td>40.6</td>
</tr>
<tr>
<td>Static HS</td>
<td>1144</td>
<td>4320</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>709</td>
<td>2170</td>
</tr>
<tr>
<td>Static HS</td>
<td>496</td>
<td>3180</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>330</td>
<td>2800</td>
</tr>
<tr>
<td>Static HS</td>
<td>21.2</td>
<td>ND</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>18.0</td>
<td>ND</td>
</tr>
<tr>
<td>Static HS</td>
<td>10.5</td>
<td>ND</td>
</tr>
<tr>
<td>Purge &amp; Trap</td>
<td>8.1</td>
<td>ND</td>
</tr>
</tbody>
</table>

### 6.3 VOC’s

Typically, at a site, the GC can initially be used for industrial hygiene surveys to evaluate the level of toxic VOC’s and implement a plan to protect the workers. Then it can be used for soil gas surveys, and checking contaminated soil and water. An example of a sample containing BTX by PID is shown in Fig.12.

### Fig. 12
Air Sample of BTX via PID

Several years ago, some underground gasoline tanks ruptured in Fallmouth, MA. Since the soil is sandy, the contents of the tanks spread quickly over a considerable area. Initially, the site was investigated using a portable PID (HNU Model 101) by measurements in a number of soil gas wells to determine the extent of the plume. The plume had migrated more than 300 yards from the original source. This type of Level I screening could be used to determine the extent of contamination of...
the soil ("total" but not individual hydrocarbons) and groundwater which occurred. Following this, a portable GC (GC311) was used to characterize the composition of the fuel detected and the ultimate source of the contamination. When multiple sources are present, this fingerprinting data can be used to identify the source of a leak.

6.4 SVOC's

Semivolatiles including pesticides, herbicides, polychloro biphenyl's (PCB's), and polycyclic aromatic hydrocarbons (PAH's) do account for nearly 30% of the field samples. Field methods for sample preparation and analysis have been described (10). Some chromatograms of PCB's and PAH's are given in Fig. 13 and 14.

One field method (10) involves taking an 800 mg soil sample or 10 ml water sample, add 1 cc of a 1:4 water methanol mixture, the add 1 ml of hexane, shake for 30 seconds then let stand for 30 seconds (if the mixture emulsifies, then centrifuge the sample) and inject the top layer (hexane) into the GC. This technique is useful for extraction of PAH's, polychlorobiphenyls (PCB's) and other non volatile hydrocarbons.

This method was modified (16) and used for the determination of DDT in soil. A GC311 with a PID (10.2 eV) was employed for the field analysis. This site was one if the best examples of the need for a field method of analysis. The site had been visited two times previously and samples had been sent back to a laboratory for analysis. Although this was the third time in the field, new areas of contamination were discovered that had not been encountered previously (16). Forty four samples were collected and analyzed in a three day time period and enough information was gathered to finally cleanup the site. Nearly a year had passed since the first visit to the site and if this doesn’t demonstrate the need for good field methodology for volatiles, nothing does. Excellent agreement was observed between the field (PID) and laboratory (ECD) methods even though the methodology and detectors were both different.

A useful detector combination for sample confirmation is the PID and ECD. Detector response ratios are used to provide additional confirmation of the presence or the structure of a particular compound in a peak. For example, trichlorobenzene would be expected to have a strong response on both the PID and ECD while another compound with same retention time would produce a very different response ratio. As observed above, the need of field screening is obvious even for semivolatiles. Driscoll and Atwood (17) evaluated the 8000 series of EPA methods and found that essentially all of the methods including phenols, pesticides, herbicides, nitrosamines, PAH's, nitroaromatics, PCB's, and phthalate esters can be analyzed by GC using a PID and

Fig. 13 Chromatograms of PCB's

Driscol, John N.,
Environmental Instrumentation
Wiley (2004) Ch. 8
ECD individually or in common. A typical chromatogram for some of the semivolatiles is shown in Fig. 11.

**6.5 Dual detectors**

Dual Detectors are an important consideration for field analyses because they are the minimum needed for confirmation of a particular compound. With GC, one has to run a sample on two columns of different polarity (e.g. polar and non polar) to confirm the identity of a particular compound. This is not necessarily something that should be done in the field. Instead, it is more useful to identify compounds by comparing both retention times and detector response factors with known standards. This is the basis of a number of environmental methods.

Gasoline hydrocarbons are one of the most common contaminants found in the field. PID and FID response ratios (18) can be used to identify alkanes (PID/FID ratios of 8-10), alkenes (PID/FID ratios of 18-24) and aromatics (PID/FID ratios of 40-50) in complex mixtures (18).

For groundwater applications in the vicinity of gasoline stations, it is necessary to measure levels of aromatic hydrocarbons in the presence of gasoline or fuel oil contaminated samples. EPA method 602 or 8020, does not have adequate selectivity for this particular analysis since high molecular weight alkanes can coelute with the aromatic hydrocarbons resulting in an interference. The approach we took (18) following purge and trap involved the use of a highly polar capillary column (carbowax initially but then DB5 because of the improved long term stability) which would elute the non polar alkanes quickly (and in one broad peak) while providing adequate resolution for the aromatic hydrocarbons, particularly the xylenes. An added feature of this method is that alkanes and aromatics can be quantitated, if desired. One advantage of this technique is that we can identify interferences from aliphatic hydrocarbons in the determination of aromatic hydrocarbons from the differences in their relative responses on the PID and FID (19). For example, it is possible for C14 or C15 (from fuel oil) hydrocarbons to coelute with the aromatic hydrocarbons. The PID/FID response ratio will be an order of magnitude lower if an aliphatic hydrocarbon is present in place of the aromatic hydrocarbon making the identification process relatively easy.

Dual detectors have been used in the laboratory for many years to analyze difficult "unknown" environmental samples. The PID has interchangeable lamps and the 11.7 eV lamp can detect the low molecular weight chlorinated hydrocarbons, which are so prevalent in wells and groundwater. The PID with a 10.2 eV lamp is used for hydrocarbons aromatic, olefinic, and alkanes >butane.

The FUV detector has a more general response and is very useful for landfills since it responds to CH₄, CO & CO₂. None of these compounds respond with the PID. The detector is also useful for the detection of low molecular weight chloroalkanes which are not detected by the PID (10.2 eV). These latter species are quite common on hazardous waste sites.

**6.6 Site or Fenceline Monitoring**

When working with air samples at the ppb levels, severe errors can be introduced by carryover from the teflon in the syringe. With an unskilled analyst precision as poor as 20-30% would not be unusual. The latter technique does not depend on the operator since it is automatic. This sample introduction mode can be used for air, headspace (soil, water, sludge), and soil gas. The precision at low ppm levels is +/- 1-2%; at ppb levels +/- 5-10%. The instrument can be run in a continuous mode or one sample at a time. Automatic calibration at a specified time interval can be programmed if an area is to be monitored over a period of time.

During the remediation process, pockets of pollution can be stirred up and VOC's and semivolatile hydrocarbons can be released to the atmosphere. Since many of these sites are in urban areas, it is important to continuously monitor the fenceline to minimize the exposure of surrounding neighbors to these pollutants.

A concentrator was described previously (20) which is available as an option for the GC311. This system allowed the detection of ppt levels of aromatic hydrocarbons in the atmosphere on an automatic basis. A typical chromatogram of
an ambient air sample is shown in Fig. 15. This system improves chromatography by eliminating any

Fig. 15
Ambient Air Analysis with a Concentrator

air or water peaks which would interfere with the early eluting peaks at low ppb levels. The concentrator also improves the performance of the FUVAD as shown in Fig. 6. This detector is useful down to 0.1 ppm without preconcentration but the interference from both water and oxygen is very significant since both these species absorb uv and thus produce a detector response. The material in the concentrator is hydrophillic and the water can be swept through without any loss of volatiles. Applications for this accessory include fenceline monitoring, background soil checks, following the emissions from or to a particular source, checking carrier gases for contamination, and any applications where additional sensitivity is required.

In this chapter we have described a number of basic aspects of chromatography in order to provide the reader with a reasonable understanding of both field and laboratory methods. Should the reader be interested in learning more about chromatography or detectors, the books in references 3 or 19 would be recommended.

References
17. Driscoll, J. N., and E.S. Atwood, "Use of Selective Detectors for Field Analysis of
Gas Chromatography Chapter

Semivolatiles in Soil and Water", J. Chromatog. (July 1993)

List of Figures
Fig. 1 Retention Times
Fig. 2 Polarity of Compounds and Phases
Fig. 3 Schematic Representation of Packed and Capillary Columns
Fig. 4 Chromatogram of Packed and Capillary Columns
Fig. 5 Comparison of column types
Fig. 6 Effect of Film thickness and Other Parameters on column Performance
Fig. 7 Schematic of a Gas Chromatograph
Fig. 8 Schematic Representation of the PID
Fig. 9 Photo of HNU GC311
Fig. 10 Photo of HNU GC321
Fig. 11 Chromatogram of VOC’ s in Water
Fig. 12 Air Sample of BTX via PID
Fig. 13 Chromatograms of PCB' s
Fig. 14 Chromatogram of PAH's
Fig. 15 Ambient Air Analysis with a Concentrator

List of Tables
Table I- Comparison of Packed and Capillary columns
Table II- List of GC Applications and Column Phases
Table III- PID Characteristics
Table IV- PID Sensitivity for Organic Compounds
Table V- PID Response with Various Solvents
Table VI- FID Characteristics
Table VII- Thermal Conductivities for Selected Compounds
Table VIII- Detection Limits for the FUV Detector
Table IX- Summary of Detector Characteristics
Table X- Detection Limits for Soil and Water Samples by GC
Table XI- Comparison of Static Headspace & Purge & Trap Techniques

Keywords
Gas chromatography, photoionization, PID, flame ionization, FID, thermal conductivity, TCD, electron capture, ECD, far UV absorbance, FUV, flame photometric, FPD, theoretical plates, stationary phase, solid support, packed columns, capillary columns, detector, air, soil, water, solvents, detector characteristics, accuracy, precision, environmental, sampling, sample prep, detection limit, resolution, fenceline, soil gas, groundwater, EPA, contaminated, CLP, concentrator, Level II, purge & trap, static headspace, headspace, extraction, carrier gas, chlorinated hydrocarbons, organic, inorganic, sulfur, IP, packings, liquid phase, peaks, GSC, GLC, polarity, plates, capacity, partitioning, diffusion, lab and field methods, temperature, dual detector, VOC, SVOC, phases, mobile phase, elution, retention time, peak height, peak area, resolved, confirmation