Gas Chromatography (GC)

MODULE AT A GLANCE

Overview

SLIDE GC-1 – Gas Chromatography
SLIDE GC-2 – Compatibility with the Triad Approach
SLIDE GC-3 – Environmental Applications of GC and GC/MS
SLIDE GC-4 – Module Overview

Types of Available Tools

SLIDE GC-5 – Major Organic Contaminant Classes Characterized by GC and GC/MS
SLIDE GC-6 – Common Platforms
SLIDE GC-7 – Perkin Elmer Photovac, Voyager
SLIDE GC-8 – HAPSITE by INFICON
SLIDE GC-9 – HAPSITE by INFICON (continued)
SLIDE GC-10 – Other GCs
SLIDE GC-11 – Transportable Quadrupole MS
SLIDE GC-12 – GC and Data System in Mobile Laboratory

Operating Principles

SLIDE GC-13 – Basic Operating Principles of a Gas Chromatograph
SLIDE GC-14 – Principles of Compound Separation
SLIDE GC-15 – Principles of Compound Separation (continued)
SLIDE GC-16 – Chromatograms
SLIDE GC-17 – Common GC Detectors
SLIDE GC-18 – GC Injection Processes for VOCs
SLIDE GC-19 – Ambient Air Gas
SLIDE GC-20 – Soil Gas Analysis
SLIDE GC-21 – Static Headspace Extraction
SLIDE GC-22 – Principles of Operation Sequence: Headspace Sampling
SLIDE GC-23 – Tekmar™ 7000 Headspace Unit
SLIDE GC-24 – Purge-and-Trap: Theory of Operation and Advantages
SLIDE GC-25 – Purge-and-Trap Autosampler and Concentrator
SLIDE GC-26 – Comparison of Attributes of Headspace Versus Purge-and-Trap Analysis
SLIDE GC-27 – Plot of Headspace Versus Purge-and-Trap Data for Soil Analysis
SLIDE GC-28 – Sample Extraction Processes for SVOCs Analysis
SLIDE GC-29 – Sample Extraction Processes for SVOCs Analysis (continued)
SLIDE GC-30 – Summary of Extraction Techniques
Advantages

SLIDE GC-31 – Advantages of Field-Based GC Systems

Limitations

SLIDE GC-32 – Limitations

Costing and Procurement Considerations

SLIDE GC-33 – Costing and Procurement Considerations

Application of PBMS

SLIDE GC-34 – Application of Performance-Based Measurement Systems (PBMS)
SLIDE GC-35 – Demonstration of Method Applicability (DMA)
SLIDE GC-36 – Other Aspects of PBMS and QC

Case Study

SLIDE GC-37 – Monterey Peninsula Airport
SLIDE GC-38 – Monterey Peninsula Airport – Results of Real-Time Analysis
Gas Chromatography
Overview

Compatibility with the Triad Approach

- Proven, commonly-used technique
- Can meet a broad range of data quality needs (from fast screening data to in-depth characterization)
- Can produce real-time or near real-time data
- Can produce data comparable to fixed laboratory methods

Notes:

- Because gas chromatography/mass spectrometry (GC/MS) methods constitute an important subset of gas chromatography (GC) methods in general, both GC and GC/MS are discussed in this module. These two techniques form the foundation of many of EPA’s most widely-used methods for organic contaminants (for example, Method 8260 for volatile organic compounds from “Test Methods for Evaluating Solid Waste” [EPA SW-846]).

- Unlike some field based measurement technologies, field ready GC and GC/MS can offer virtually identical capabilities to fixed laboratory analysis. This makes GC and GC/MS unique and powerful tools for application in the Triad Approach.

- You truly have, in many cases, the ability to generate data in the field to provide direction to your dynamic work plan with the same quality of equipment available from a fixed off-site laboratory. Highly-equipped GC or GC/MS units can generate quantitative data for a broad range of specific compounds in a variety of environmental media. Alternatively, smaller or simplified GC systems can quickly generate screening data for selected parameters or classes of parameters to help formulate and guide more detailed data collection strategies.

- This capability does not come for free. Initial purchase price for portable or transportable GCs is very high (from around $15,000 for the more portable GCs to $150,000 for bench-top GC/MSs) and very skilled operators are required. Often, it is more feasible to rent both the equipment and the operator together.

- Many trade-offs will be considered in the following slides that will help you balance the cost/benefit for real-time data with the cost/benefit of fixed lab analysis.

Module: Gas Chromatography
Environmental Applications of GC and GC/MS

- Site characterization
- Remedial design and optimization
- Verification of remedial or removal actions
- Operation and monitoring

Notes:

- GC and GC/MS are applicable to all aspects of site restoration. In addition, there are numerous other real-time applications (for example, fence line monitoring, process monitoring, and emergency response).

- GC can be configured with a number of different detectors to meet specific project goals. Detectors include mass spectrometry (MS), flame ionization detectors (FID), photoionization detector (PID) in electron capture device (ECD), nitrogen phosphorus detectors (NPD), electrolytic conductivity detectors (ELCD), and thermal conductivity detectors (TCD).
Notes:

- The use of GC plays a key role in the Triad Approach, not only by supplying effective data of known quality, but also providing these data in real-time or near real-time. This data can then be used to refocus site activities to save time and money while meeting the project’s data quality objectives.

- This module discusses the operating principles and applications of GC methods for the characterization of a wide array of organic constituents in air/vapor, soil, and water. In particular, field portable and transportable systems will be explored, as they make the greatest contribution to Triad-based activities in effectively characterizing the nature and extent of the organic contaminants.
### Major Organic Contaminant Classes Characterized by GC and GC/MS

- Halogenated and non-halogenated VOCs
- SVOCs
- Pesticides and herbicides
- PCBs
- Dioxins and furans
- Petroleum hydrocarbons

#### Notes:

- The following list of organic contaminant classes can be characterized by GC and GC/MS:
  - Halogenated and non-halogenated volatile organic compounds (VOC), including solvents; benzene, toluene, ethylbenzene, and xylenes (BTEX); and oxygenates
  - Semivolatile organic compounds (SVOC), such as dichlorobenzenes, phenols, and polyaromatic hydrocarbons (PAH)
  - Polychlorinated byphenyls (PCB)
  - Dioxins and furans
  - Petroleum hydrocarbons
- GC is a widely used technique for field-based analysis. This technique can be used to generate data of known quality in a variety of settings including: (1) site characterization; (2) stationary source testing or monitoring; (3) determining appropriate level of personal protective equipment; (4) determine potential off-site migration of contaminants; and (5) emergency response testing.
Types of Available Tools

- Furthermore, the GC can be applied to a variety of sample media including: (1) soil; (2) soil gas; (3) water; (4) waste; (5) air; and (6) wipe samples.

- VOC analysis requires a purge step where an inert carrier gas is sparged into the sample matrix to release volatile components. Other analytes require extractions and addition preparation steps depending on the class of compounds being evaluated and the matrix of the sample.

- Some matrices can be directly injected into the GC for analysis such as soil gas and air while others require extractions such as water, soil, wastes, and wipe samples.
Common Platforms

- Portable units (handheld/suitcase)
- Transportable units (tabletop/tailgate)
- Mobile laboratory (van/trailer)

Notes:

- The following slides depict the use of GCs in several settings. Note that the degree of portability of GCs varies by manufacturer and intended use.

- In addition, most applications involve VOCs, vapor analysis (headspace, soil gas), and aqueous analysis.
Notes:

- The photograph above is a Perkin Elmer Photovac, Voyager. In this photo, the unit is being used to analyze soil gas.

- This unit is lightweight (-15 pounds), self-contained and easy to transport to a site. The unit has been designed for the analysis of VOCs in soil gas and can be configured to analyze water and soil samples.

- The voyager has been verified under EPA’s environmental technology verification (ETV) program for analysis of chlorinated VOCs in groundwater. Information can be found at http://clu-in.org/download/CHAR/verstate/wellhead/pep_vr.pdf.
Notes:

- This GC is a GC/MS – it uses a mass spectrometer (MS) as its detector. The MS allows the instrument to identify more compounds and allows external calibration to aid in quantitation. This GC/MS is field-portable and used primarily for ambient air analysis. Headspace accessories (pictured on the left above) allow for the analysis of VOCs in the headspace of soil and water samples. The instrument can perform ambient air analysis while being carried in the field, but must have a surface to rest on for headspace analysis of soil and water samples.

- Headspace analysis is accomplished by heating the sample of water or soil and then analyzing the headspace gas via the GC/MS. Samples are not purged with an inert gas as is the case in conventional SW-846 8260 VOC analysis.

- The HAPSITE is battery operated (using rechargeable nickel metal hydride batteries).
Types of Available Tools

HAPSITE by INFICON

HAPSITE Field-Portable GC/MS

Notes:

- This slide shows the HAPSITE in action, checking for vapor leaks in an industrial facility.
Notes:

- The SRI GCs in this picture come preconfigured to meet the most common needs for analysis. The GCs can also be configured for the specific needs of a site. For example, one model, the 6810C GC manufactured by SRI instruments, measures 19" wide, 13.5" high and 14.5" deep. While it is very compact compared to comparable laboratory GCs from other manufacturers, it is large enough and flexible enough to perform an amazing variety of applications. Up to 4 detectors, from a choice of 14, can be mounted simultaneously. Up to 5 injector types, from a choice of 15, can be installed at the same time. Another model, the 8610C, can control up to 16 heated zones, 3 gas sampling valves, and 7 EPC gas pressures. Virtually any EPA or ASTM method can be implemented on the 8610C chassis, while still remaining small enough to ship as airline baggage or FedEx. The 8610C column oven is temperature programmable from ambient to 400°C with unlimited ramps and holds and fast cool-down. While smaller than full-sized lab GCs, the column oven still holds a standard 7 inch diameter megabore column cage, or multiple columns with smaller coil sizes. All gases, carrier and detector, are controlled by electronic pressure regulators (EPC) for maximum precision, and the carrier gas pressure is programmable. The PeakSimple data system is built in for easy serial port connection to your notebook or desktop PC. This GC is available for under $5,000 to $6,200 depending on the required configuration.
Notes:

- The slide depicts a transportable quadrupole mass spectrometer. This mass spectrometer is fully integrated and is easily transported in a van for on-site field analysis. In this case, the sample must be collected and taken to the instrument for analysis. The instrument can provide data of known quality for both identification and quantitation of compounds.

- Quadrupole MS systems are available from manufacturers such as SYAGEN (www.syagen.com) and Broker Daltronics (www.bdal.com)

- These systems employ a quadrupole ion trap that collects ion after sample ionization. The ions can then be analyzed via mass spectrometry.
Notes:

- This is an example of a GC and data system set up in a mobile laboratory. For semivolatile analyses where extraction is required, more space and controlled conditions of a trailer or office may be needed.

- Extraction techniques for samples analyzed in a mobile laboratory are generally less vigorous than off-site analyses. Mobile laboratories often employ micro-extraction techniques where a small amount of sample (water or sol) is added to a test tube and an extraction solvent such as methanol or methylene chloride is added. The sample is agitated via a vortex or by vigorous shaking, then centrifuged and the extraction solvent with target analytes directly injected into the GC. This is in contrast to extraction techniques employed by commercial laboratories where sonication, separatory funnels, soxhlets, or liquid extractions are used. Commercial laboratories also include extract clean-up techniques such as gel permeation chromatography (GPC), fluorisil clean-ups, and mercury clean-up to remove sulfur compounds.
Notes:

- The primary components of a GC include:
  
  (1) Injection port – where the sample is introduced to the system for compound separation
  (2) Column (usually within a temperature-controlled chamber or oven)
  (3) Detectors – various detectors are discussed later in this module
  (4) Integrator or data acquisition system

- Other parts include:
  
  (1) Auto-sampler(s) – introducing multiple field samples and QC samples for a run sequence
  (2) Control panel, electronic pressure control (EPC)
  (3) Injection port liners
  (4) Septa
  (5) Ferrules
  (6) Flow controllers
• The carrier gas is introduced in the injection port where the sample is volatilized and swept through the column. The compounds are separated as they travel through the capillary column with smaller and lighter compounds existing first and larger and heavier compounds exiting later. The carrier gas/sample mixture then enters the detector where the compounds are identified. The signal from the detector then is amplified and displayed by the data system.

• Various detectors can be used alone or in series, however, destructive detectors such as FID or MS must be used last because target compounds are destroyed during ionization.
Notes:

• The graphic depicts target analytes on the column.

• In the first step in the separation process molecules evaporate from the column wall into the gas phase. The molecule then hits a particle of the carrier gas and either loses or gains energy. Molecules then hit sites in the stationary phase and remain until overcoming the intermolecular forces. The interaction between gaseous molecules and the stationary phase produces separation of compounds.

• The mobile phase is comprised of the carrier gas, which usually is nitrogen, helium, or hydrogen. The compounds are transformed into the gaseous phase either by headspace or purge and trap (for VOCs) or during injection by heat transformation through the injection port liner and heat through the column (for SVOCs). Compounds are carried through the column using the carrier gas (nitrogen, helium, or hydrogen).

What modification would you make to a capillary column to decrease analysis time?
Notes:

- In figure (a), the compounds are introduced to the column.
- In figure (b), the triangular-shaped compound resides on the stationary phase (column coating) and the circular compound resides in the mobile phase (carrier gas).
- In figure (c), compound separation continues with time.
- In figure (d), the compounds finally are separated.
- Again, the general principal here is that smaller and lighter compounds require less energy to overcome intermolecular forces and move from the stationary phase of the column coating to the mobile carrier gas phase. Larger and heavier compounds require more energy (heat) to move from the stationary phase to the mobile phase so as the GC temperature ramps up during the run the capillary column effectively separates compounds. At specific energy levels known as retention times compounds enter the mobile phase and reach the detector.
Notes:

- This slide depicts the differences in compound separation with the use of two columns. The stationary phase of each column type is slightly different. Dual column analysis is a valuable QC tool for confirming the identification of a compound.

- The identity of compounds can be configured by noting the mass spectrometry response for the retention time specific to each column.

- The types and ratios of ions detected by the MS also provide a spectra that can be evaluated versus spectral libraries to assist in compound identification.
### Common GC Detectors

<table>
<thead>
<tr>
<th>Detector</th>
<th>Operating Principle</th>
<th>BND</th>
<th>Sensitivity</th>
<th>Selectivity</th>
<th>Aromatic HCs</th>
<th>Petroleum HCs</th>
<th>Chlorinated Compounds</th>
<th>Nit./Phos. Compounds</th>
<th>Bath</th>
<th>Glass</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>FID</td>
<td>Ionization in a flame</td>
<td>D</td>
<td>Low/medium</td>
<td>High</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>(X)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECD</td>
<td>Electron capture</td>
<td>B</td>
<td>High</td>
<td>Low</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>(X)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELCD</td>
<td>Modified ECD</td>
<td>D</td>
<td>Low/medium</td>
<td>High</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity</td>
<td>B</td>
<td>Low</td>
<td>Low</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ND</td>
<td>Nondestructive</td>
<td>D</td>
<td>Low/medium</td>
<td>High</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPD</td>
<td>Nitrogen/phosphorus</td>
<td>D</td>
<td>Low/medium</td>
<td>High</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Notes:

- The table above identifies a number of common detectors used to detect classes of compounds that are typically of environmental concern.

### Table Definitions:

- **Aromatic HCs**: Aromatic hydrocarbons (BTEX, PAHs)
- **D**: Destructive (destroys sample)
- **ECD**: Electron capture detector
- **ELCD**: Electrolytic conductivity detector
- **FID**: Flame ionization detector
- **MS**: Mass spectrometer
- **ND**: Nondestructive (does not destroy sample)
- **NPD**: Nitrogen phosphorus detector
- **Nit./Phos.**: Nitrogen/phosphorus compounds (such as nitrosamines, organophosphorus pesticides)
- **Petroleum HCs**: Fuels, lubricants, and other hydrocarbon mixtures
- **ppb**: parts per billion
- **ppm**: parts per million
- **ppt**: parts per trillion
- **TCD**: Thermal conductivity detector
Note that the MS detector is the most versatile. It is also the most specific. Therefore, GC/MS is widely used in preference to other GC detectors. However, the versatility of the MS detector comes at a sacrifice in terms of higher detection limits, greater instrument complexity, and higher costs.
## Operating Principles

<table>
<thead>
<tr>
<th>Detector</th>
<th>Operating Principle</th>
<th>D/ND</th>
<th>Sensitivity</th>
<th>Selectivity</th>
<th>Aromatic HCs</th>
<th>Petroleum HCs</th>
<th>Chlorinated Compounds</th>
<th>Nit./Phos. Compounds</th>
<th>Bulk Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>PID</td>
<td>Ionization w/UV lamp</td>
<td>ND</td>
<td>Low ppb/High ppt</td>
<td>Moderate</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FID</td>
<td>Ionization w/H₂ flame</td>
<td>D</td>
<td>Low ppb/High ppt</td>
<td>Low</td>
<td>X</td>
<td>X</td>
<td>(X)</td>
<td>(X)</td>
<td></td>
</tr>
<tr>
<td>ECD</td>
<td>Ionization w/Ni-63 source</td>
<td>ND</td>
<td>High ppt</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>ELCD</td>
<td>Modified FID w/conductivity cell</td>
<td>D</td>
<td>Low ppb/High ppt</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>TCD</td>
<td>Interaction w/hot filament</td>
<td>ND</td>
<td>Low ppm</td>
<td>Low</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>NDP</td>
<td>Modified FID w/thermionic bead</td>
<td>D</td>
<td>Low ppb/High ppt</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>MS</td>
<td>Ionization followed by magnetic field</td>
<td>D</td>
<td>Low to mid ppb</td>
<td>High</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>
GC Injection Processes for VOCs

- Direct injection – ambient air and soil gas analysis
- Static headspace extraction – soil and water analysis
- Purge and trap extraction – soil and water analysis

Notes:

- Methods of analysis for VOCs include direct injection for ambient air and soil gas, and static headspace extraction or purge and trap extraction for soil and water. These techniques will be discussed in the following slides.

- Analytes of interest include: (1) halogenated VOC’s, including vinyl chloride, methylene chloride, trichloroethene (TCE), tetrachloroethene (PCE), trichloroethane (TCA), chloroform, carbon tetrachloride, and ethylene dibromide; (2) Non-halogenated VOCs (solvents), including methyl iso-butyl ketone (MIBK), methyl ethyl ketone (MEK), and acetone; (3) aromatic compounds, including BTEX and chlorobenzenes; and (4) fuels, including gasoline, diesel fuel, jet fuel, and kerosene.
Notes:

- On site air analysis can be used to test for VOCs in stationary source testing (emission inventory), hazardous waste site testing to determine appropriate levels of PPE, fenceline monitoring during remediation activities, and emergency response testing.

- The preferred mode of sample collection for quick analysis is to directly draw a sample of ambient air into the on site GC or GC/MS using an internal pump. Air samples also may be collected in Tedlar bags, Summa® canisters, or Tenax tubes, or using solid phase microextraction (SPME) devices. The use of these other sampling containers will require that an air sample (1 to 5 mL) be withdrawn from the sample container or desorbed from the sorbent and injected into the GC system. (Only applies to Tedlar bags and Summa® canisters. Tenax and SPME will need an additional desorption component.)

- On site analysis of air generally is conducted using a portable GC system or GC/MS configuration. Transportable GCs (larger, laboratory-grade instruments) can also be used but provide far more logistical problems. The detection limits for air analysis will range considerably depending on the method of sample collection and GC system. Typical detection limits will range from 5 to 200 parts per billion by volume (ppbv). Detection limits will be considerably lower if the analytes are concentrated on some type of absorbent material and desorbed versus being directly drawn into the analytical system via a sampling pump. Analytical times for VOCs should be less than 10 minutes per sample. A GC/MS system can either be used to provide qualitative to semiquantitative data in a survey mode or quantitative data in an analytical or selective ion monitoring (SIM) mode.
Operating Principles

- The advantages of on-site air monitoring is the quick data which allows flexibility for on-site personnel and the project manager.

- If conducting emissions testing, samples high in moisture content or acid content will have to be pretreated prior to analysis. If a MS is not used, exact analyte identification (coelution problems) may not be possible in complex mixtures. Coelution refers to multiple compounds overlapping within the same retention time windows so compounds identification is difficult.
Soil Gas Analysis

- Applications
- Direct injection/detection limits
- Sample containers
- Injection volume
- Holding time
- Advantages
- Limitations

Notes:

- Soil gas analysis commonly is used to identify “hot spots” or source areas of VOCs in the subsurface. It also can be used to approximate the extent of a subsurface plume.

- Active soil gas analysis involves actively pumping subsurface gases to the GC while passive soil gas involves collection of target compounds onto sorbent materials through passive diffusion followed by extraction and analysis.

- The detection limit for most VOCs is 10 nanograms per liter (0g/l). Calibrations consist of direct injection using an air standard mix or methanol-based standards. The concentration is reported in 0g/l. One liter of air weighs approximately 1 gram. Therefore on a weight basis, 0g/l is approximately equivalent to ppb.

- Typical sample containers include glass bulbs, Tedlar bags, Summa® canisters, syringes or 22 or 40-mL vials. Teflon®-coated syringes, plungers, or stop-cocks should be avoided, because some VOCs (for example, 1,1,1-TCA) are strongly sorbed to Teflon® surfaces.

- Usually inject approximately 1 to 5 mL of the sample into the GC column. However, this action may result in more rapid deterioration of the column stationary phase and oxidation of the ECD foil.
Operating Principles

- Holding time for soil gas is 12 hours. Longer hold times can be achieved by employing sorbent materials and a desorption phase prior to injection.

- The advantages of soil gas analysis are that it is rapid, inexpensive, provides real-time results, and causes minimal disturbance to the site.

- One limitation of soil gas analysis is that it does not always reflect a true soil concentration. The technique is limited to high volatility and low solubility compounds. Coelution problems can occur in complex mixtures if a MS is not used. Sample carryover or cross contamination may be a problem in highly concentrated samples. Decontamination of syringes is crucial, especially for chlorinated VOCs.
Static Headspace Extraction

- Soil and water analysis
- Theory of operation
- Analysis times
- Detection limits
- Sample collection and preparation
- SW-846 Method 5021 "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis"

Notes:

- Static headspace extraction is widely used in determining VOCs in waste water, soil, and drinking water. This extraction method is highly productive and cost effective, requiring minimal sample preparation.

- Efficiency of headspace extraction is based on soil and water partition coefficients of the analytes.

- Based on Henry’s Law.
  \[ H = \frac{P}{X} \]
  where
  - \( H \) = Henry’s Law constant (atm-m³/mole)
  - \( P \) = pressure of gas above liquid (atm)
  - \( X \) = equilibrium mole fraction of dissolved gas at 1 atm (mole/m³)

- Two stages:  (1) Diffusion of analyte into the headspace
  (2) Diffusion of analyte back into the matrix

A steady state equilibrium is reached when the concentration in the headspace is equal to the concentration in the matrix.

- Low viscosity liquids reach equilibrium faster. Solids take longer.
Operating Principles

• A constant heat time is recommended for samples that do not reach equilibrium within a reasonable time.

• Analysis time ranges from 10 to 30 minutes depending on number and boiling point of analytes of interest.

• Detection limits for BTEX compounds and most chlorinated VOCs using headspace analyses are in the range of 1 to 10 ppb; detection limits for TPH-purgeable compounds are 1 to 10 ppm in water and 10 to 50 ppm in soil.

• Water samples can be collected in 40 mL volatile organic analysis (VOA) vials or directly in a 22-mL headspace vial. Soil samples can be collected in a 4-ounce glass jar or directly into a 22-mL headspace vial. Mass or volume is measured into a headspace vial (generally 5 mL or 5 grams). No sample preparation is required for water samples. Sample preparation for soil samples may vary depending on the initial analyte concentration and soil type. For high concentration soil samples (ppm levels), studies have shown that methanol-flood achieves the greatest extraction efficiency. An aliquot of the methanol can then be analyzed using the static headspace technique. Methanol-flood techniques, however, are not appropriate for soil samples that contain less than 200 mg/kg of an analyte due to the dilution effect. For these low concentration soil samples, Method 5021 recommends the addition of an aqueous matrix modifying solution. For field analysis, the addition of a matrix modifier may not be necessary due to the quick analysis times.

How can detection limits be lowered for headspace extraction?
Notes:

Listed below are the steps in the operational sequence of an automated headspace sampler.

- The sample is introduced to the platen heated zone and allowed to equilibrate at a fixed temperature for a fixed time period. Typical heating temperatures range from 40 to 80°C. Heating times vary from 10 to 30 minutes. After the sample is heated, it is then mixed to help volatilization into the headspace.

- Next, the vial is raised onto a needle which pierces the teflon septum and pressurizes the vial with nitrogen to a pressure of 3 to 27 pounds per square inch (psi).

- The pressure in the vial is then allowed to equilibrate for 0.5 to 2.5 minutes.

- The vent valve is then opened and the pressure in the vial displaces the headspace through the needle into the sample loop, filling the loop at the proper loop fill time. Pressure in the vial will equal atmospheric pressure. Loop volumes can range from 0.1 to 5 mL. Typical loop volumes used are 1 or 2 mL.

- After the loop fill, the vent valve and pressure valve are closed, allowing the sample vapor to equilibrate and pressure and flows to stabilize.
Operating Principles

- When the GC-ready signal is received by the headspace unit, the 6-port valve rotates and the sample loop contents are transferred to a heated line with column carrier gas. Carrier gas then back flushes the loop, sweeping through the heated transfer line into the GC injection port (0.3 to 6 minutes).
Notes:

- This figure shows the Tekmar™ 7000 headspace unit with the 7050 sample carousel. The 7050 sample carousel is an autosampler that allows the analyst to set up a run sequence of field samples and QC samples. Other manufacturers of headspace autosamplers include Hewlett-Packard and Perkin Elmer.
**Purge-and-Trap: Theory of Operation and Advantages**

- Theory of operation
- Dynamic process
- SW-846 methods 5030A and 5035

**Notes:**

- Helium is bubbled through the solution at ambient temperature and volatile compounds are transferred from the matrix to the vapor phase. The volatiles are then swept through the sorbent column where they are trapped. Then, the sorbent column is heated and backflushed with helium gas to desorb the components. The components are then transferred to a GC via a heated line, where they are separated using the appropriate column and detected using a MS or other detector. Typically, a 5 mL sample is used for water analysis and a 5 gram sample is used for soil and sediment analysis.

- The primary advantage of purge and trap over static headspace is that it is a dynamic process. It is a more efficient extraction technique for those VOCs which have a higher octanol/water partition coefficient, especially in soils with high organic matter content.

- Purge and trap is the recommended VOC extraction technique used for GC analysis. The recommended extraction methods are 5030A and 5035.
Notes:

- This slide depicts a purge-and-trap autosampler and concentrator.

- Obviously, the purge-and-trap extraction techniques require additional equipment over headspace analyses including a purge system and a sorbent trap system.

- Purge-and-trap methods require slightly longer analyses times to properly purge VOCs then sorb and desorb compounds for GC injection, however, this can usually be accomplished in the time it takes the GC to cool down to the initial run temperature from the end temperature of the previous run.
Comparison of Attributes of Headspace Versus Purge-and-Trap Analysis

<table>
<thead>
<tr>
<th>Variable</th>
<th>Headspace</th>
<th>Purge and Trap</th>
</tr>
</thead>
<tbody>
<tr>
<td>System process</td>
<td>Static</td>
<td>Dynamic</td>
</tr>
<tr>
<td>Solvent use</td>
<td>Minimal solvent use</td>
<td>Minimal solvent use</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>Weigh sample in headspace vial</td>
<td>Weigh sample; transfer to separate purge vessel</td>
</tr>
<tr>
<td>Sample decontamination</td>
<td>No transferring vessels to decontaminate</td>
<td>Reusable purge vessels must be decontaminated</td>
</tr>
<tr>
<td>Upper dynamic range</td>
<td>Limited due to saturation of headspace before equilibrium reached</td>
<td>Not limited by headspace saturation because the compounds are purged in a dynamic system</td>
</tr>
<tr>
<td>Detection limit</td>
<td>No mechanism for concentration of compounds</td>
<td>Ability to purge for long periods of time and concentrate compounds onto trap before analysis</td>
</tr>
<tr>
<td>Loss of contaminants</td>
<td>If headspace vial is not properly crimped, compounds may be lost during pressurization</td>
<td>Less loss of compounds because purge vial is not pressurized; outlet goes directly to trap; however, loss of compounds during sample transfer may occur</td>
</tr>
<tr>
<td>Cost</td>
<td>Less than purge and trap system</td>
<td>More than headspace system</td>
</tr>
<tr>
<td>Space requirements</td>
<td>Less space than purge and trap system</td>
<td>More space than headspace system and requires more plumbing</td>
</tr>
<tr>
<td>Throughput</td>
<td>50 samples per day</td>
<td>20 samples per day</td>
</tr>
</tbody>
</table>

Notes:

- The headspace technique is a static process, while purge-and-trap is a dynamic process. Some of the differences between the two processes are listed in the table above.

- Use of organic solvents is comparable for the two techniques; however, for purge-and-trap analysis, water is used as a solvent for soil purging, increasing the amount of liquid waste produced in the field laboratory.

- For headspace analysis, samples can be collected directly into preweighed headspace vials; no transferring of sample is required. For purge-and-trap analysis, a measured amount of sample must be weighed and then transferred into a specially designed purge vessel. The purge vessels are reusable glassware and must be decontaminated. Use of such vessels increases the potential for carryover contamination.

- Because the headspace process is static, the headspace can become saturated before equilibrium is reached between the medium (soil or water) and the headspace concentration. Therefore, high concentrations of compounds may not be transferred efficiently to the headspace and subsequently detected. Results for high-concentration samples may be biased low. In purge-and-trap analysis, compounds can be purged continuously from the medium and collected onto the trap, allowing higher concentrations to be transferred and detected effectively.
Operating Principles

• Because the headspace system does not allow for concentration of compounds onto a trap over a period of time (like the purge-and-trap system), trace amounts of compounds that are not mobilized effectively at equilibrium may not be detected. Thus lower detection and reporting limits are achieved through purge-and-trap.

• Both systems have the potential for loss of compounds. During pressurization of the headspace vial, compounds can be lost if the cap is not properly sealed. In the purge-and-trap system, loss of compounds will occur as a result of volatilization during the weighing of the sample and its transfer to the purge vessel.

• The cost of the purge-and-trap system is typically more than that of a comparable headspace system.

• The headspace system is an attachment to the GC that requires little additional bench space; however, the purge-and-trap system is a separate stand-alone system that may require twice as much bench space as the GC alone.

• The throughput of the headspace system is significantly larger than that of the purge-and-trap system, primarily because the purge-and-trap system requires more handling, transfer, purging, and decontamination of samples than the headspace system.

• Comparative studies have been performed and are presented in the additional information section of this module.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Headspace</th>
<th>Purge and Trap</th>
</tr>
</thead>
<tbody>
<tr>
<td>System process</td>
<td>Static</td>
<td>Dynamic</td>
</tr>
<tr>
<td>Solvent use</td>
<td>Minimal use of solvent</td>
<td>Minimal use of solvent</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>Weigh sample in headspace vial</td>
<td>Weigh sample; transfer to separate purge vessel</td>
</tr>
<tr>
<td>Sample decontamination</td>
<td>No transfer vessels to decontaminate</td>
<td>Reusable purge vessels must be decontaminated</td>
</tr>
<tr>
<td>Upper dynamic range</td>
<td>Limited because of saturation of headspace before equilibrium is reached</td>
<td>Not limited by headspace saturation because the compounds are purged in a dynamic system</td>
</tr>
<tr>
<td>Detection limit</td>
<td>No mechanism for concentration of compounds</td>
<td>Ability to purge for long periods of time and concentrate compounds onto trap before analysis</td>
</tr>
<tr>
<td>Loss of contaminants</td>
<td>If headspace vial is not properly crimped, compounds may be lost during pressurization</td>
<td>Less loss of compounds because purge vial is not pressurized; outlet goes directly to trap; however, loss of compounds may occur during transfer of a sample</td>
</tr>
<tr>
<td>Cost</td>
<td>Less than that of purge-and-trap system</td>
<td>More than headspace system</td>
</tr>
<tr>
<td>Space requirements</td>
<td>Less space than purge-and-trap system</td>
<td>More space than headspace system and requires more plumbing</td>
</tr>
<tr>
<td>Throughput</td>
<td>50 samples per day</td>
<td>20 samples per day</td>
</tr>
</tbody>
</table>
**Operating Principles**

**Module: Gas Chromatography**

---

**Plot of Headspace Versus Purge-and-Trap Data for Soil Analysis**

![Graph](image)

Figure 3. log-log plot of mean concentrations (µg/g) of all high-level VOC determinations in the fortified Point Barrow soil.

**Notes:**

- This slide depicts a log-log plot of mean concentrations (µg/g) of high-level VOCs in a spiked sample of soil, analyzed by headspace analysis and purge-and-trap analysis.

- Note how the concentrations identified by headspace are significantly lower than the concentrations identified by the purge-and-trap method.
Plots of Headspace Versus Purge-and-Trap Data for Soil Analysis

Figure 2. log–log plot of mean concentrations (µg/g) of all high-level VOC determinations in the fortified USA THAMA soil. Slope and correlation coefficient for all points, 0.956 and 0.954; single highest point omitted, 0.946 and 0.937.

Figure 3. log–log plot of mean concentrations (µg/g) of all high-level VOC determinations in the fortified Point Barrow soil.

Figure 4. Linear plot of mean (µg/g) trans-1,2-dichloroethylene and benzene (Ben) concentrations in fortified soils. Slope and correlation coefficient, 0.944 and 0.993.

Figure 5. log–log plot of mean (µg/g) trichloroethylene (TCE) and toluene (Tol) concentrations in fortified soils.
Sample Extraction Processes for SVOCs Analysis

- Solvent extraction
  - Liquid-liquid or sonication
  - Accelerated solvent extraction (ASE)
  - Microwave-assisted extraction (MAE)

Notes:

- Semivolatile compounds that are analyzed in soil and water and corresponding methods are listed below.

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>SW-846 Analysis Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>8041 (GC-FID or ECD)</td>
</tr>
<tr>
<td>Phthalates</td>
<td>8061A (GC-ECD)</td>
</tr>
<tr>
<td>Amines</td>
<td>8070A (GC-NPD)</td>
</tr>
<tr>
<td>Chlorinated pesticides</td>
<td>8081A (GC-ECD)</td>
</tr>
<tr>
<td>PCBs</td>
<td>8082 (GC-ECD)</td>
</tr>
<tr>
<td>PAHs</td>
<td>8100 (GC-FID)</td>
</tr>
<tr>
<td>Chlorinated hydrocarbons</td>
<td>8121 (GC-ECD)</td>
</tr>
<tr>
<td>Organophosphorus compounds</td>
<td>8141A (GC-NPD or FPD)</td>
</tr>
<tr>
<td>Chlorinated herbicides</td>
<td>8151A (GC-ECD)</td>
</tr>
<tr>
<td>SVOCs/base neutral acids (BNA)</td>
<td>8270C (GC/MS)</td>
</tr>
<tr>
<td>Dioxin</td>
<td>8280 (GC/MS)</td>
</tr>
<tr>
<td></td>
<td>8290 (GC/High-Res MS)</td>
</tr>
</tbody>
</table>
• In the past, typical “formal lab” extraction methods included soxhlet, liquid-liquid, and sonication. More recently, accelerated solvent extraction (ASE) has become the extraction method of choice because it is more rapid and uses less solvent. Microwave-assisted extraction (MAE) is another extraction method that is promising for fixed laboratory analysis because it too is more rapid and uses less solvent compared to the “older” solvent extraction methods.

• The key in the field is to simplify the solvent extraction methods to minimize solvent waste, save time, and reduce cost. Typical solvents used in the field include hexane, methanol, methylene chloride, and methyl tert-butyl ether (MTBE). Simplified field, solvent extraction methods normally do not include a cleanup step. A concentration step may also be eliminated if elevated detection limits are acceptable. ASE and MAE are not as commonly used in the field (especially on small projects) because of the initial expense of the equipment and other logistical constraints such as power and space requirements.
Sample Extraction Processes for SVOCs Analysis

◆ Minimal solvent or solvent free extraction
  » Supercritical fluid extraction (SFE)
  » Solid phase extraction (SPE)
  » Solid phase microextraction (SPME)
  » Thermal desorption

Notes:

• Extraction techniques that use a minimal amount of solvent are preferred for field applications. The techniques listed above fit into this category.

• Although supercritical fluid extraction (SFE) is an EPA-approved technique for fixed-laboratory applications, it has not gained wide use in the field because of the expense of the apparatus and limited portability.

• Solid-phase extraction (SPE) and solid-phase microextraction (SPME) are ideal techniques for field use because they are rapid, simple, inexpensive, and use little or no solvent. SPE is primarily limited to water samples, although it can be used as a cleanup technique for liquid extracts of solid samples. SW-846 method references for these extraction techniques are provided on the next slide.

• SPME has gained much more popularity in the last 2 to 3 years. Its advantage over SPE is that it can be used for both VOCs and SVOCs and no solvent is required.

• Thermal desorption for SVOCs is analogous to a more rigorous static headspace extraction for VOCs. It also is convenient for field use because it is simple, rapid, and requires no solvent.
Summary of Extraction Techniques

<table>
<thead>
<tr>
<th>Extraction Type</th>
<th>Matrix</th>
<th>SW-846 Method Number</th>
<th>Advantages for Field Use</th>
<th>Limitations for Field Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-Liquid</td>
<td>Aqueous</td>
<td>3510C, 3520C</td>
<td>Easy to use and simple</td>
<td>High solvent use</td>
</tr>
<tr>
<td></td>
<td>Solids</td>
<td>3540C, 3541</td>
<td>Easy to use and simple</td>
<td>High solvent use</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3550B</td>
<td>Easy to use and simple</td>
<td>High solvent use</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Can be used for VOCs</td>
<td>Equipment is rented or purchased</td>
</tr>
</tbody>
</table>

- **Advantages for Field Use**: Simple, Rapid, No solvent use, Less solvent use, Simple and rapid, Efficient, Can be used for VOCs, Uses disposable cartridges, No solvent use.
- **Limitations for Field Use**: High-moisture samples, Analyte breakthrough, High solvent use, Glassware use/cleaning, Long extraction times, Interferences, normally no cleanup steps, Choosing the correct sorbent, Logistical constraints (power and space).

**Module: Gas Chromatography**
## SUMMARY OF EXTRACTION TECHNIQUES

<table>
<thead>
<tr>
<th>Extraction Type</th>
<th>Matrix</th>
<th>Analytes</th>
<th>SW-846 Method Number</th>
<th>Advantages for Field Use</th>
<th>Limitations for Field Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-Liquid</td>
<td>Aqueous</td>
<td>SVOCs</td>
<td>3510C, 3520C</td>
<td>C Rigorous method C Proven method</td>
<td>C High solvent use C Labor intensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Accepted method</td>
<td>C Long extraction times C Glassware use/cleaning</td>
</tr>
<tr>
<td>Soxhlet</td>
<td>Solids</td>
<td>SVOCs</td>
<td>3540C, 3541</td>
<td>C Rigorous method C Proven method</td>
<td>C High solvent use C Long extraction times</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Accepted method</td>
<td>C Glassware use/cleaning</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Solids</td>
<td>SVOCs</td>
<td>3550B</td>
<td>C Rigorous method C Proven method</td>
<td>C High solvent use</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Shorter extraction times than soxhlet</td>
<td>C Potential breakdown of some analytes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Expensive equipment C Less efficient for nonpolar analytes</td>
</tr>
<tr>
<td>Abbreviated Solvent</td>
<td>Aqueous and Solids</td>
<td>SVOCs</td>
<td>None</td>
<td>C Rapid C Less solvent use</td>
<td>C Method development time C Interferences, normally no cleanup steps</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Little equipment needed C Uses disposable glassware</td>
<td>C Not as rigorous C Can be labor intensive</td>
</tr>
<tr>
<td>ASE</td>
<td>Solids</td>
<td>PAHs, PCBs, Pesticides</td>
<td>3545</td>
<td>C Rapid C Less solvent use</td>
<td>C Expensive extraction apparatus C Logistical constraints (power and space)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Efficient C Accepted, proven method</td>
<td>C Safety concerns C Not accepted yet for organics</td>
</tr>
<tr>
<td>MAE</td>
<td>Solids</td>
<td>TPH, PAHs, PCBs, Pesticides</td>
<td>None</td>
<td>C Rapid C Less solvent use</td>
<td>C Expensive equipment C Logistical constraints (power and space)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Efficient</td>
<td>C Safety concerns</td>
</tr>
<tr>
<td>SFE</td>
<td>Solids</td>
<td>SVOCs</td>
<td>3560, 3561</td>
<td>C Rapid and efficient C No solvent waste</td>
<td>C Expensive equipment C Logistical constraints (not portable)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Proven method for some analytes</td>
<td>C Sample size is limited C Optimization for different analytes</td>
</tr>
<tr>
<td>SPE</td>
<td>Aqueous</td>
<td>SVOCs and VOCs</td>
<td>3535</td>
<td>C Simple C Rapid</td>
<td>C Dirty samples may plug disks or cartridges C Analyte breakthrough C Can be labor-intensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Uses small volumes of solvent C Inexpensive</td>
<td>C Choosing the correct sorbent</td>
</tr>
<tr>
<td>SPME</td>
<td>Aqueous, Soil</td>
<td>SVOCs and VOCs</td>
<td>None</td>
<td>C Simple and rapid C No solvent use</td>
<td>C Not yet an EPA-accepted method C Can be labor-intensive unless expensive automated equipment is rented or purchased</td>
</tr>
<tr>
<td></td>
<td>Headspace, Air</td>
<td></td>
<td></td>
<td>C Can be used for VOCs and SVOCs C Inexpensive</td>
<td>C Not yet an EPA-accepted method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C Can be labor-intensive</td>
</tr>
<tr>
<td>Thermal Desorption</td>
<td>Solids</td>
<td>TPH, PAHs, PCBs</td>
<td>8275</td>
<td>C Rapid C Simple</td>
<td>C Expensive apparatus C Power requirements</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C No solvent use</td>
<td>C High-moisture samples C Not suited for thermally unstable compounds</td>
</tr>
</tbody>
</table>

**Module:** Gas Chromatography

**GC-42**
Advantages of Field-Based GC Systems

- Real-time or near real-time results
- High correlation with laboratory data
- Detection limits below regulatory levels
- Established QA/QC protocols
- Highly reliable identification and quantitation for many applications
- Compound specific for direct comparison to action levels

Notes:

- Real-time results (within 30 minutes of arriving on-site) support dynamic work plans by allowing decisions to be made about the direction of site activities in real or near real-time, reducing down time and preventing the needless collection of samples in areas determined to be outside the contamination boundary. Furthermore, these refocused efforts can save time and money by preventing the need to return to the site at a later time to gather more data. With GC/MS results, contaminants may be detected that were initially not suspected and modifications made to the dynamic work plan in the field without having to remobilize after receiving results from a fixed laboratory. Real-time results are equally important to health and safety as they are to work plan modifications. Real-time results can be used for exposure monitoring for site workers, determining personal protective equipment (PPE) level, and to evaluate potential off-site exposures.

- Environmental Technology Verification reports (www.epa.gov/etv/verifrpt.htm#02) are available on-line and downloadable on a variety of field portable/transportable GCs. Data comparisons between fixed laboratories and the field have achieved correlations nearing 1.000 for the Inficon, Inc. HAPSITE GC/MS at two sites: 0.983 at the Department of Energy’s (DOE) Savannah River Site, near Aiken, South Carolina and 0.978 at McClellan Air Force Base near Sacramento, California (see attached case studies at the end of this section).
Advantages

• Even with instruments having less strong correlations to off-site laboratories, the data can be used to evaluate areas for further sampling or to choose which samples to send for confirmation (define plume extent).

• Detection levels are comparable to laboratory instruments and, in some cases, lower (EPA Innovations in Site Characterization, Technology Evaluation: Real-time VOC Analysis Using Field Portable GC/MS, EPA, August 2001).
Notes:

• These limitations could be said to apply to fixed laboratories as well, the point here is that the project teams must “worry” about these limitations not the laboratory where samples would otherwise be sent to for analysis.

• Instrument cost range from $170,000 to $9,000. At the high end are the transportable GC/MS systems with the middle cost range occupied by the transportable GC and the lower cost range are the portable GC systems. Most systems can be rented or leased.

• Operator training costs tend to follow the system costs with the full fledged GC/MS systems requiring the most training and the lower end GC systems generally requiring less training. Operator training times run from one day for an experienced technician to three days on the simpler systems for a novice (training costs, approximately $500 per day per person, typically not included in the instrument costs). Some systems can be rented along with an operator to run the system.

• Instrument maintenance is an additional cost if it is decided to purchase the GC or GC/MS. In addition to parts, having sufficiently trained personnel or paying an outside company to service the equipment will cost extra. Servicing instruments will also include down-time where samples cannot be analyzed and additional QC samples such as generation of a new initial calibration.
**Limitations**

- If a site has more than two families of chemicals or wide concentration ranges more than one instrument may need to be set up to accommodate the complexity.

- Ideally, field based GCs and GC/MS work best in dynamic investigations where target constituents of interest are restricted to one or two classes of compounds, such as halogenated VOCs or pesticides.

<table>
<thead>
<tr>
<th>INSTRUMENT</th>
<th>ADVANTAGE</th>
<th>DISADVANTAGE</th>
</tr>
</thead>
</table>
| Viking Instruments Corporation Spectratrac 672 GC/MS | – Definitive identification of compounds  
– Low detection limits (ppb)  
– Rapid deployment and fast analysis time  
– Good correlation of sample results with out-side lab  
– Analysis of all sample types and media (for example, purge and trap, headspace, air, etc.) | – Cost $145,000  
– Requires trained technician  
– Requires a vehicle |
| Inficon, Inc., HAPSITE GC/MS | – Definitive identification of compounds  
– Rapid deployment and fast analysis time  
– Low detection limits  
– Portable  
– Good correlation of sample results with out-side lab | – Cost $75,000  
– Requires trained technician  
– Sample pre-concentrator and auto-sampler render the instrument transportable  
– runs only headspace water and soil VOC samples |
| Electronic Sensor Technology, Model 4100 | – Cost $25,000  
– Rapid deployment and fast analysis time  
– Less operator training  
– Portable  
– Good correlation with out-side lab results  
– Detects to ppt | – No definitive identification of compounds  
– Development of new methods may require more training  
– Sample pre-concentrator and auto-sampler render the instrument transportable  
– Vapor detection only |
| SRI Instruments, Model 8610 GC | – Cost $9,000  
– Transportable  
– Can be modified to perform other methods of analysis | – No definitive identification of compounds  
– Not portable  
– Field evaluations showed 25% false positives in one application |
Costing and Procurement Considerations

- **Equipment**: lease, rent, or purchase
- **Operator**: train or hire a technician
- **Training and set-up**: manufacturer, vendor, third party training
- **Customized systems and add-ons**
- **Operating costs**: consumables, maintenance, repair
- **Data management**

**Notes:**

- Most of the instruments can be leased, rented or purchased. The instrument can be “rented” with the operator as well. Multi-year service contracts are available which may provide some peace of mind given the large risk involved with the purchase of the more expensive systems. Equipment vendors such as Field-Portable Analytical (www.fieldportable.com) can provide both consultation regarding site specific analytical needs as well as provide equipment and technicians to meet those needs.

- Many commercial laboratories and EPA regional offices can provide on-site laboratory analyses providing high quality data in real-time. It should be noted that on-site “mobile” laboratories require additional start-up and maintenance costs.

- Training costs run around $500 per day at the provider’s location. SRI Instruments provides training with the purchase of their instrument (www.srigc.com).

- The actual price of these systems varies greatly with the application they will need to be set-up for. The GC/MS systems typically vary due to sample introduction system needs where as the GCs tend to vary by sample introduction system needs as well as detector type(s) needed. For example, the Inficon, Inc. HAPSITE GC/MS system has a base price of $75,000, and the headspace accessory is an additional $15,750.00. Furthermore, the service module is another $22,050 – a total of $112,800. The SRI 8610C GC, on the other hand, starts at $5,000 with sample inlet systems (purge and trap $8,000), columns ($100 - $500), and detectors (FID
Costing and Procurement Considerations

$2,000) added on for a total of around $16,000.00. Visit the SRI web-site above if you need more specifics or if you would like to see some pre-configured systems SRI sells.

• Operating costs vary widely depending on the need for technicians to run the equipment and the sophistication of the equipment. Some estimates for the high end GC/MS systems like the $170,000 Bruker-Franzen EM640 require $700.00 per day to operate (including cost of the technician). To have an outside firm provide the GC/MS and the operator can run in the $1,200 to $2,000 per day range.

• Unlike the high costs associated with sophisticated GC/MS systems, some of the monitoring GCs can run at approximately $1,000 per year after initial purchase costs. The decreased operation costs reflect the lower operator costs due to unnecessarily highly skilled operators and cheaper system components such as carrier gases and inlet systems.
Application of Performance-Based Measurement System (PBMS)

- Initial demonstration of method applicability (pilot test) – highly recommended for defensible data
- Address operational method performance in site media of concern
  » Method sensitivity and reporting limits
  » Precision and bias
  » Potential interferences
  » Sample concentration ranges of interested relative to method
- Comparison studies to fixed labs may be necessary or helpful

Notes:

- Demonstration of method applicability (DMA) will allow fine tuning of the method in terms of adjusting instrument settings and method parameters, and will also allow weighing of method options. For example, split injectors or duplicate sampling can send the same sample to two different columns and detectors for better identification and quantification of contaminants. Dual column analysis allows confirmation of the compound identity and concentration of a compound. This is can be important when MS is not used for confirmation. A single injection can go to a single column with one non-destructive detector (for example, PID) in tandem with a destructive detector (FID) and differences in the detector response can differentiate the compounds. By conducting the DMA, the entire system can be optimized to meet project needs with the least sample preparation, best detector configurations and QC procedures.

- For sites having only 1-2 families of compounds, properly selected detectors can ensure specificity with low detection limits.

- Some confirmation samples may bolster your confidence and field data can guide the location and number of confirmation samples collected. Unfortunately there can be poor correlation between the confirmation samples and field data. This difference can be attributed to sample aging in shipment or to sample heterogeneity (sample support) issues. New sample preparation methods (for example, methanol flood) are rapidly lowering the difference between field analysis results and fixed laboratory results and are becoming more wide-spread in their application.
Application of PBMS

- The large number of compounds characterized by the GC/MS lends itself to sites where it would be difficult to know all of the potential contaminants otherwise. Furthermore, GC set-ups are specific to the method for characterizing specific classes of compounds and several GCs with varying detectors other than MS would have to be set-up to get defensible data.
Demonstration of Method Applicability (DMA)

- Site samples that represent predicted concentration range
- Low spike replicates (in site matrices) to assess reporting limits
- Matrix spike replicates (medium to high)
- Field sample replicates
- Splits for off-site lab analysis
- Performance evaluation samples

Notes:

- An example of a DMA for GC/MS analyses of methyl t-butyl ether (MTBE) and other oxygenates in specific groundwater matrices was recently published in the January issue of LCGC Magazine (www.lcgcmag.com). This study incorporated many of the DMA elements listed on this slide.

- Attendees are referred to the EPA Methods Team homepage (www.epa.gov/epaoswer/hazwaste/test/abtteam.htm) for more information on method validation and DMA.

- Ideally, the DMA should include a range of sample concentrations expected at a site. High sample concentrations may require sample dilutions and a DMA would provide an indication of the system performance at high or low concentrations.

- Replicates of low level spiked samples will identify any matrix recovery or interference issues as well as help establish site-specific reporting limits.

- Field sample replicates in the medium to high range can be used to establish relative percent difference (RPD) goals and evaluate for precision replicate analyses.

- Finally, split samples and PE samples can be used to further assess system accuracy.
Other Aspects of PBMS and QC

- Site-specific method SOP
- Data management and documentation protocol
- Method calibration and control samples
- Method blanks
- Surrogate and/or internal standard spikes
- Field sample duplicates
- Matrix spike/matrix spike duplicates
- Other (performance evaluation samples, field blanks, fixed lab comparison)

Notes:

- External standard calibration generally consists of a three-point or five-point calibration.
- A medium-level standard (continuing calibration) is analyzed once a day to check the response of the instrument compared to the average response of the initial calibration. Continuing calibration must be within a specified percentage of the initial calibration response.
- Method blanks are analyzed to check for laboratory-induced contamination and instrument blanks are analyzed to check for contamination induced by the instrument (usually by sample carryover). Method blanks are especially critical in soil gas analysis when chlorinated VOCs are target analytes.
- Performance evaluation (PE) samples are spiked matrix samples that have certified concentrations of analytes and that can be purchased from reputable vendors (for example, Environmental Resource Associates or Absolute Standards). They are usually analyzed “blind” by the analyst (meaning the analyst does not know what analytes are present or their concentrations). The analyst must report the proper analytes and concentrations within the certified concentration ranges for the laboratory’s accuracy to be acceptable. PE samples are normally not analyzed for soil gas or ambient air analysis.
• Matrix spike/matrix spike duplicate (MS/MSD) samples are spiked field samples analyzed to check for overall bias and precision of the analytical system. Percent recoveries are calculated and must fall within an acceptable range for the degree of method bias to be acceptable. Percent recoveries are also compared to each other by calculating relative percent differences (RPD) to assess the precision of a method. MS/MSDs are not typically run for soil gas or ambient air analysis.

• Laboratory duplicates are analyzed to assess the precision of the method and homogeneity of the sample. The laboratory duplicates consist of the analysis of two aliquots of the same sample. The results from the laboratory duplicates are compared to each other through RPD calculations.

• Surrogate spikes are necessary to evaluate the extraction efficiency on a per sample basis. A surrogate compound is one that is chemically similar to the target compounds but does not coelute with any of them. A percent recovery of the known spiked concentration is calculated for each sample and compared to site specific control limits. (Not typically analyzed in soil gas or ambient air samples.)

• Laboratory control samples (LCS) consist of a standard or reference matrix spiked with a known concentration of standard purchased from a separate vendor other than the one from which the calibration standards were purchased. The percent recovery for all analytes must be within an acceptable range for the accuracy of the calibration to be acceptable.
Monterey Peninsula Airport

- Triad approach applied to a site with TCE contaminated ground water
- Site investigation of the extent of ground water contamination
- 14 ground water samples collected from boreholes on-site
- HAPSITE GC/MS used to provide real-time quantification of ground water samples and determine placement of additional borings and future monitoring wells
- Two years later, real-time GC/MS results used to characterize the vertical extent of the contamination

Notes:

- As part of the Triad approach, the field portable Inficon HAPSITE GC/MS was used to provide real-time data in support of the dynamic work plan at the Monterey Peninsular Airport (MPA) Site Investigation. The HAPSITE GC/MS was used to measure VOCs (TCE) in ground water on a real-time basis. The results were effective for making decisions in the field that guided characterization of the plume and optimal placement of monitoring wells. Real-time use of the technology allowed well installation at a lower cost than if more conventional technologies (for example, conventional off-site fixed laboratory analyses) had been used.

- The MPA is located near the city of Monterey, California. Past Department of the Navy (DoN) activities released TCE contamination into soil and ground water. The U.S. Army Corps of Engineers (USACE) began conducting a series of activities to characterize the extent of the TCE contamination and migration. During 1999, the USACE collected ground water samples from soil borings and monitoring wells both inside and outside the boundaries of MPA for on-site analysis of VOCs. The HAPSITE GC/MS instrument was used as the determinative method according to the EPA’s SW-846 Method 8260. Sample preparation and introduction into the GC/MS was accomplished using an equilibrium headspace technique (SW-846 Method 5021).

- The USACE had previously used the Field-Portable Analytical, Inc. in 1998 as a contracted analytical service provider to furnish on-site analysis of MPA ground water VOC samples. During this earlier work, the USACE requested split sample VOC analyses, so that the same
ground water samples were run both on-site and by a conventional fixed laboratory. This activity established that the on-site analytical service provider could generate VOC data of known and documented quality comparable to traditional VOC data on the site-specific sample matrix. During the 1999 project, ground water samples collected from the soil borings were analyzed by the HAPSITE instrument only. It was not necessary to again split the samples for confirmatory analysis by an off-site laboratory because the reliability of the analytical service provider had already been demonstrated. The validity of the 1999 field-generated VOC data was confirmed through the use of a field QA/QC program specified in the project’s quality assurance plan.

• Upon completion of the plume definition, the HAPSITE left the site, and the installation of permanent monitoring wells in selected borings was completed. After the wells had been developed by surging, bailing, and purging, ground water samples were collected and sent to a conventional laboratory for VOC analysis using methods 5030 (purge and trap) and 8260 (GC/MS). The two sets of data (on-site versus off-site) were not expected to be directly comparable (water collected from a boring versus water collected form a fully developed well). Although a comparison between the two data sets shows expected variations, there is an excellent agreement between the two data sets when they are assessed according to their ability to support project decision making.
Monterey Peninsula Airport –
Results of Real-Time Analysis

- Model the plume
- Guide additional borings
- Select monitoring well locations
- Delineate vertical extent of plume
- Saved 26 percent of total projected costs
- Saved 4 days of field time

Notes:

- The HAPSITE was again used at the MPA in 2001 for real-time characterization of the vertical extent of TCE contamination. Although this report does not include an evaluation of the data set generated in 2001, the USACE again reported complete satisfaction with the ability of the field GC/MS to provide reliable data supporting a dynamic work plan strategy that modeled vertical stratification of the TCE plume to a degree not feasible using traditional off-site analysis. In addition to presenting the performance of the HAPSITE GC/MS in the MPA project, this report briefly reviews the HAPSITE’s performance in an EPA Environmental Technology Verification (ETV) demonstration that assessed the ability of several field portable instruments (including the HAPSITE) to detect and measure VOCs in ground water. The ETV reports for this demonstration including the HAPSITE report, are available through the website for “Well-Head Monitoring-VOCs,” which can be found on the Internet at http://www.epa.gov/etv/verifrpt.htm#monitoring.

- According to the USACE, the portion of the MPA site characterization that encompassed the summer of 1999 cost approximately $75,000. This figure included not just the HAPSITE activities, but also the drilling team and USACE personnel costs. The USACE estimates that the use of the HAPSITE instrument resulted in the savings of approximately $27,000 and at least four days of field time, when compared to projected work flow assuming the fastest possible turnaround of data from an off-site laboratory.
Case Study

• The USACE was charged a daily rate by the analytical service provider, who provided all instrumentation and supplies and personnel as part of a turnkey service. If purchased from the instrument vendor, the HAPSITE GC/MS unit costs approximately $60,000 and the headspace sampling accessory costs approximately $15,000, for a total cost of $75,000. (A vacuum pump and a service module costs an additional $20,000.) Both the instrument and the accessory may be available for lease. Depending on the type and number of analysis being performed, varying amounts of consumables items, such as syringes, vials, gloves, bottled gases and reagents may be required at costs ranging from $50 to $250 per day.

• Instrument operation requires at least one well-trained GC/MS operator. Sample throughput can vary depending on a number of factors, including the target analyte list and the number of samples submitted for analysis, which can be up to 25-30 samples per day. As with all on-site analysis, comparing the cost of analytical alternatives on a “cost per sample” basis is seldom reflective of true economic value of using field analytical technologies. The real value in field methods is the time and labor savings realized when the ability to make accurate real-time decisions minimizes (1) the down-time of costly equipment and services, and (2) repeated mobilizations back to fill in the data gaps. In addition, the opportunity to make more measurements in the field while the analytical equipment is available on-site provides a cost effective means of managing the major source of uncertainty, which is due to sampling variability in heterogenous environmental media.

• The HAPSITE GC/MS and accessories provides the versatility to generate reliable, real-time, and cost efficient data for measuring VOCs in ground water, soil media (such as soil and sediment samples), and gaseous samples (for example, ambient air, exhaust, stack emissions, and soil gas). (EPA 542-R-01-011, August 2001)

• The following links may be followed for publications and certifications regarding some or all of the technologies in this module:

  http://clu-in.org

  http://www.epa.gov

  http://www.hapsite.com

  http://www.srigc.com

  http://www.estcal.com

  http://www.daltonics.bruker.com

  http://www.instruments.perkinelmer.com
Case Study

http://innova.dk

http://www.fieldportable.com

http://www.sentex.com