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Review of Chemical Sensors for In-Situ Monitoring of Volatile Contaminants

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Review of Chemical Sensors for In-Situ Monitoring of Volatile Contaminants

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Abstract

This report presents a review of sensors and technologies that are capable of detecting and monitoring volatile organic compounds. The scope of this review was limited to those sensors that have the potential to be used in geologic environments for long-term monitoring applications. Four general categories of sensor technologies were reviewed: (1) chromatography and spectrometry; (2) electrochemical sensors; (3) mass sensors; and (4) optical sensors. Based on the review criteria set forth in this report, the most viable sensors for in-situ chemical sensing appear to be electrochemical sensors (specifically conductometric sensors), fiber-optic sensors, and surface-acoustic-wave sensors. However, very few chemical sensors have been successfully demonstrated in real-time, continuous, in-situ applications.

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1. Introduction

Sandia National Laboratories has sponsored an LDRD (Laboratory Directed Research and Development) project to investigate and develop micro-chemical sensors for in-situ monitoring of subsurface contaminants. As part of this project, a literature search has been conducted to survey available technologies and identify the most promising methods for sensing and monitoring subsurface contaminants of interest. Specific sensor technologies are categorized into several broad groups, and these groups are then evaluated for use in subsurface, long-term applications. This report introduces the background and specific scope of the problem being addressed by this LDRD project, and it provides a summary of the advantages and disadvantages of each sensor technology identified from the literature search.

1.1 *Background and Scope*

Tens of thousands of sites containing toxic chemical spills, leaking underground storage tanks, and chemical waste dumps require accurate characterization and long-term monitoring to reduce health risks and ensure public safety (<http://www.epa.gov/superfund>). In addition, over two million underground storage tanks containing hazardous (and often volatile) contaminants are being regulated by the EPA (U.S. EPA, 1992), and the tanks require some form of monitoring to detect leaks from the tanks and pipe network. However, current methods are costly and time-intensive, and limitations in sampling and analytical techniques exist. Looney and Falta (2000, Ch. 4) report that the Department of Energy (DOE) Savannah River Site requires manual collection of nearly 40,000 groundwater samples per year, which can cost between \$100 to \$1,000 per sample for off-site analysis. Wilson et al. (1995, Ch. 36) report that as much as 80% of the costs associated with site characterization and cleanup of a Superfund site can be attributed to laboratory analyses. In addition, the integrity of the analyses can be compromised during sample collection, transport, and storage. Clearly, a need exists for accurate, inexpensive, real-time, in-situ analyses using robust sensors that can be remotely operated.

Although a number of chemical sensors are commercially available for field measurements of chemical species (e.g., portable gas chromatographs, surface-wave acoustic sensors, optical instruments, etc.), few have been adapted for use in geologic environments for long-term monitoring or remediation applications. The purpose of this project is to identify and develop sensor technologies that can be used in these long-term geologic applications. As a result, technologies such as electrical-resistivity monitoring and ground-penetrating radar are not considered here because they require significant amounts of manual labor and supervision to operate. Instead, we seek low-cost sensors that can be emplaced and operated with minimal supervision, which yield continuous real-time monitoring capabilities.

The particular focus of this project is limited to the detection and monitoring of volatile organic compounds (VOCs). These include compounds such as aromatic hydrocarbons (e.g., benzene, toluene, xylenes), halogenated hydrocarbons (e.g., trichloroethylene (TCE), carbon tetrachloride), and aliphatic hydrocarbons (e.g., hexane, octane). As a result, sensors and technologies that detect gas-phase constituents in the vadose zone are emphasized because VOCs are most conveniently and economically monitored in the gas phase (Looney and Falta, 2000,

Ch. 4). However, the ability to detect VOCs in groundwater and saturated environments is also an important objective of the LDRD project.

1.2 Categories of Sensors

The sensors reviewed in this report have been categorized into four general groups: (1) chromatography and spectrometry; (2) electrochemical sensors; (3) mass sensors; and (4) optical sensors. The categorization of these sensors is based primarily on the principal physics and operating mechanisms of the sensor. For example, chromatography relies on separation of complex mixtures by percolation through a selectively adsorbing medium, with subsequent detection of compounds of interest. Electro-chemical sensors, for the purposes of this report, include sensors that detect signal changes (e.g., resistance) caused by an electrical current being passed through electrodes that interact with chemicals. Mass sensors rely on disturbances and changes to the mass of the surface of the sensor during interaction with chemicals. Optical sensors detect changes in visible light or other electromagnetic waves during interactions with chemicals. Within each of these categories, some sensors may exhibit characteristics that overlap with other categories. For example, some mass sensors may rely on electrical excitation or optical settings. Nevertheless, these four broad categories of sensors are sufficiently distinct for the purposes of this review. The next section provides a summary and assessment of the sensors reviewed in each of the four categories.

2. Review of Sensors

In the following sections, the four general categories of sensors are reviewed: (1) chromatography and spectrometry; (2) electrochemical sensors; (3) mass sensors; and (4) optical sensors. For each sensor, the following topics are addressed (as applicable):

- Application
 - *what does it sense?*
 - *what environment (media/phase) is it used in?*
 - *how is it used?*
- Physics
 - *how does it work?*
- Developer/Vendor
- Price (if available)
- Advantages and Disadvantages
 - *Ease of use (training required?)*
 - *Relevance to in-situ, real-time, potentially long-term detection of VOCs*
 - *Robustness and reliability*
 - *Level of development/demonstration/acceptance*

The following sections are not intended to include exhaustive reviews of all available sensors and technologies. Instead, the following sections provide a brief overview of the relevant features and applications of the different categories of sensors. The intent is to provide guidance for determining the best options for subsurface long-term monitoring applications.

A number of web sites are included in the following sections for more detailed descriptions of individual technologies. In addition, a particularly useful web site for identifying state-of-the-art technologies is www.delphion.com. This web site contains patents of technologies that can be searched by key words. For example, a search on “hydrocarbon gas sensor” yielded 7 patents containing those key words. References included in the patent descriptions yield additional relevant technologies. We found that while a large number of patents exist under the topic of chemical sensors, most of the patents and technologies of interest in this study still belong to one of the general categories in the following sections.

2.1 Chromatography and Spectrometry (Separation and Detection)

Application/Physics

Chromatography is a method for the separation and analysis of complex mixtures of volatile organic and inorganic compounds. A chromatograph is essentially a highly efficient apparatus for separating a complex mixture into individual components. When a mixture of components is injected into a chromatograph equipped with an appropriate column, the components travel down the column at different rates and therefore reach the end of the column at different times. A detector is positioned at the end of the column to quantify the concentrations of individual components of the mixture being eluted from the column. Several different types of detectors can be used with chromatographic separation and will be discussed below.

Gas chromatography may be classified into two major divisions:

- Gas-liquid chromatography, where the sorbent (material which separates the mixture into individual components) is a nonvolatile liquid called the stationary-liquid phase, coated as a thin layer on an inert, granular solid support, and
- Gas-solid chromatography, where the sorbent is a granular solid of large surface area.

The moving-gas phase, called the carrier gas, is an inert gas such as nitrogen or helium which flows through the chromatographic column packed with the sorbent. The mixture partitions itself between the moving-gas phase and the sorbent and individual components of the mixture move through the column at a rate dependent upon its partition coefficient in the liquid phase (gas-liquid chromatography) or upon its adsorption coefficient on the packing (gas-solid chromatography) and the carrier-gas flow rate. Open tubular glass or stainless steel capillary tubes of 0.005-0.02 in. (0.1-0.5 mm) inside diameter and length often as great as 300 ft (90 m), coated on the inside walls with a nonvolatile stationary-liquid phase, are also widely used in the separation of complex mixtures.

The apparatus used in gas chromatography consists of four basic components: a carrier-gas supply and flow controller, a sample inlet system providing a means for introduction of the sample, the chromatographic column and associated column oven, and the detector system.

Although the carrier gas is most commonly nitrogen or helium, other gases such as carbon dioxide, argon, xenon, and hydrogen are occasionally used. Use of a carrier gas of higher molecular weight will improve column efficiency. Therefore nitrogen or perhaps a gas of even higher molecular weight is preferred to helium if a detector other than thermal conductivity is being used.

A rotometer may be used in the carrier-gas system to give an approximate indication of flow rate. A rotometer consists of a graduated tube with slowly increasing inside diameter and a glass or metal ball that is suspended in the gas flow within the tube at a height dependent upon the flow rate. Since the position of the ball is a function of both the flow rate and the column back pressure when positioned at the column inlet, a rotometer can be used only for rough approximations of flow rate. A soap-bubble flowmeter is used for more accurate measurements.

Sample inlets are of two general types depending upon whether the sample is gaseous, liquid, or solid. Liquid samples are generally injected by means of a calibrated hypodermic syringe through a silicon rubber septum into a metal or glass-lined metal injection port, while gaseous samples are introduced by means of a valve and sample loop system. Injection techniques somewhat similar to those used for liquid samples are used for solids. In order to produce sharp chromatographic peaks with minimum peak overlap, solid and liquid samples must be vaporized rapidly upon injection by maintaining the injection port at a temperature greater than the boiling point of the sample.

Solid-phase microextraction (SPME) is a relatively new method that allows trace analytes to be introduced into the chromatographic system without the need for solvents. The method, which was developed in the early 1990's at the University of Waterloo in Ontario, Canada, involves exposing a small segment of fused silica fiber coated with a non-volatile polymeric material. The coated fiber is mounted in a syringe-like device that can expose the fiber to the desired environment and also withdraw it for protection during transfer to the GC. The analyte of interest adsorbs on the fiber coating and is thermally desorbed when introduced into the chromatographic injection port. SPME has been commercialized by Supelco, Inc.TM and Varian.TM

The column is the heart of the gas chromatograph, and separation of components on packed columns depends more on the choice of liquid phase than on any other factor. Typically the column is a glass or metal tube of 0.125 or 0.25 in. (6 or 13 mm) in diameter and 4-6 ft (1-2 m) in length, packed with an inert diatomaceous earth support coated with a nonvolatile liquid to 3-20% by weight. In open tubular or capillary column technology, the support for the thin film of liquid phase is the wall of the capillary itself. Support-coated open tubular columns are also sometimes used, the sample capacity of the columns being increased by the presence of very loosely packed support or by a roughening of the capillary walls.

The detector produces a response that is proportional to component that is separated by column and is located at the end of the column. Different detectors may be utilized dependant upon the

analyte of interest and 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). Some of these detectors, such as the PID, have been commercialized as hand-held units. RAE Systems (<http://www.raesystems.com>) has developed a hand-held PID device that has high sensitivity to VOCs (several ppm). The unit uses a small pump to suck vapor through the ionization chamber. Water vapor is completely ignored, but this unit cannot provide discrimination among different chemicals. The unit costs about \$2000.

An amplifier, which could be considered part of the detector "package" receives an output from a detector and amplifies it so that the signal can be detected by a recorder or integrator. Subsequently, an integrator takes the signal from the amplifier and produces an output (chromatogram) and peak height or area (used for quantification). 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.

2.1.1 Bench-Top Gas Chromatographs

The Agilent 6890 plus Gas Chromatograph (Figure 1) is a laboratory bench-top GC which provides flexibility and performance required for research and method development in industry applications (<http://www.chem.agilent.com/Scripts/PDS.asp?lPage=161>). It is rugged and reliable, so it can be used for routine methods that require multiple columns or valves, specialty inlets or detectors, or a broad temperature range. This unit can be configured with a variety of columns or detectors and can be tailored to individual needs. Approximate dimensions are 50 x 58 x 54 cm and it weighs approximately 49 kilograms. It should be operated in temperatures ranging from 15° C to 35° C in 5 to 95% humidity. The price for the bench-top model varies depending upon specifications but is typically in the range of \$20,000 to \$50,000.

Pros: The bench-top GC can provide superior discrimination capabilities (relative to other devices and sensors) with excellent precision, sensitivity, and reproducibility.

Cons: Not portable. Expensive. Requires training to operate.



Figure 1. Agilent 6890 Gas Chromatograph.

2.1.2 Portable Gas Chromatographs

Femtoscan (<http://www.femtoscan.com/evm.htm>) has developed a new, hand portable Gas Chromatograph/Ion Mobility Spectrometer (GC/IMS) instrument (see Section 2.1.4 for information on IMS devices). The instrument is called the Environmental Vapor Monitor II (EMV II) (Figure 2) and is based on Ion Mobility Spectrometry (IMS) technology for sensitive detection of gas phase analytes with high speed. Automated Vapor Sampling Transfer Line Gas Chromatography sampling and separation capabilities developed by FemtoScan and the University of Utah are also included. The EVM II is a sensitive and selective near-real-time vapor detector. A wide range of volatile and semi-volatile contaminants can be detected with EVM II which can be operated from a 24 volt battery pack or from an external power supply. Price information not provided.

Pros: Portable. Reliable with good reproducibility. Real-time measurement (in seconds). Parts per billion (ppb) level sensitivity to vapors. Remote monitoring capability. No carrier gas required for operation. Wide range of volatile and semi-volatile components.

Cons: Cannot use in situ. No price information given, but most likely fairly expensive per unit.



Figure 2. Femtoscan portable GC/IMS instrument.

HAPSITE (<http://www.hapsite.com>) is a field-portable gas chromatograph/mass spectrometer (GC/MS) for on-site analysis of volatile organic compounds (VOCs). The device is battery-powered, lightweight, and weatherproof, and it can discriminate and quantify VOCs in short time periods (minutes). HAPSITE is advertised as “easy to use in the field.” A technician selects a

method, and HAPSITE sets and monitors all the operating conditions, signaling when to start sampling. Results are displayed on the instrument's front panel. The unit weighs approximately 35 pounds and can be carried into the field with a shoulder strap or a backpack-type rigging (Figure 3).

Pros: Provides verifiable test results on-site with direct-sampling system. Works for all VOCs. Weatherproof. Battery-powered.

Cons: Fairly large packaging and size (35 lbs). Most likely fairly expensive. Cannot be used in-situ.



Figure 3. HAPSITE portable GC/MS device.

Bruker-Daltronics, Inc. (<http://www.bruker-daltonik.de>) have developed the EM 640 and EM 640S, which are GC/MS systems (Figure 4), equipped with sampling and sample transfer modules for the analysis of air, water and soil. Both types have been advertised as mobile systems, being extremely lightweight, rugged, and operating on a 24V DC power supply. The EM 640S has better specifications for trace analysis, and the analysis takes approximately 30 minutes after arrival on-site. These units run off of a 24 volt battery and are fairly portable at approximately 62 kilograms (without computer system).

Pros: Automated analysis for continuous air monitoring. Operate under harsh conditions. Wide range of chemicals (VOC, Explosives, chemical warfare agents, etc.)

Cons: Cannot be used in-situ. Fairly large packaging (vehicle portable). No price information provided.



Figure 4. Bruker-Daltronics GC/MS system.

Process Analyzers (http://processanalyzers.net/fpi/311_hp.html) produces a field portable instrument which is able to analyze liquids, solids, and gasses with the same instrument. The microprocessor controlled Model 311-D Portable Gas Chromatograph (Figure 5) has a dual detector capability, chosen from six interchangeable detectors: Photoionization (PID), Flame Ionization (FID), Electron Capture (ECD), Flame photometric detector (FPD), Thermal conductivity detector (TCD), or Far-UltraViolet Absorbance (FUVAD). Peakworks™ for Windows® software (runs on a portable PC) and temperature programming allow for the simultaneous measurement of volatile and semi-volatile organic compounds. This unit can be used for dedicated applications as it has 10 port valve that can be programmed for automatic operation at ppb levels.

Pros: Can run in-series with non-destructive such as PID, FUV, or can run in parallel mode. Different detectors available for specific, selective, or general chemical discrimination. Built-in pre-concentrator available for ppb to ppt measurement levels. Fairly small packaging.

Cons: Cannot be used in-situ. No pricing information.



Figure 5. Process Analyzers portable gas chromatograph.

2.1.3 Micro-Chem-Lab (μ ChemLab) on a Chip

The μ ChemLab has been developed at Sandia National Laboratories, Albuquerque, New Mexico (<http://gaas6.mdl.sandia.gov/1315.docs/chem.html>). This sensor is not commercially available at this time.

Microfabrication has been utilized to provide a miniaturized GC-type device that provides a fast response with an ability to utilize multiple analysis channels for enhanced versatility and chemical discrimination. The μ ChemLab is an autonomous chemical analyzer the size of a palm-top computer that incorporates a gas phase analysis system for detecting chemical warfare agents (e.g., sarin, soman, mustard gas) and a liquid phase analysis system for detecting explosives.

The μ ChemLab improves the sensitivity and selectivity to individual chemicals by using a cascaded approach where each channel includes a sample collector/concentrator, a GC separator, and a chemically selective surface acoustic wave (SAW) array detector (see Section 2.3.1 for more information on SAW detectors). All three components have been developed and demonstrated and can be fit in an area less than that of a U.S. dime. These small components allow miniature systems incorporating multiple analysis channels to be produced. Discrimination of analytes is improved by allowing simultaneous use of more than one channel at a time. Versatility of the μ ChemLab can increase by allowing different channels to be tailored to detect different chemical analytes.

The collector/concentrator includes a thin film porous adsorbent to selectively collect chemical analytes to be detected and a heater for thermal desorption of the collected analyte into a concentrated pulse. The GC column separator is a long flow channel coated with a stationary phase material. As analytes pass through the column, the analytes are separated in time based on differences in partitioning into the stationary phase. Detection of the analyte is achieved using an array of SAW sensors acting as sensitive mass detectors. By coating the SAW devices with chemically distinct thin film materials, a unique pattern of responses for different chemical analytes can be used to provide chemically selective detection.

Pros: Batch microfabrication provides several advantages for the μ ChemLab. The low heat capacity of the thermal desorption stage allows it to be heated rapidly with low power. The rapid heating provides sharp chemical pulses that provide improved temporal separation in the GC column. Additionally, components for the μ ChemLab can be manufactured at low cost which can open a variety of new markets where current chemical analysis systems are cost prohibitive. Finally, the extreme miniaturization of this device may open new markets where traditional GCs and portable GCs were too large or where other microsensors cannot adequately discriminate the analytes of interest.

Cons: The μ ChemLab is still under development and requires additional research and testing before being deployed to in-situ settings.

2.1.4 Ion Mobility Spectrometry

Application/Physics

The ion mobility spectrometer (IMS) can be considered a sub-class of chromatographic separators. The principle of every IMS is a time-of-flight measurement. After a gaseous sample has entered the spectrometer it will be ionized by a radioactive source, the resulting positive and negative charged species will be accelerated over a short distance and the time-of-flight will be determined. The IMS is different than the mass spectrometer in that it operates under atmospheric conditions and does not need large and expensive vacuum pumps. Because of this, IMSs can be easily miniaturized.

Developer/Vendor

Bruker-Daltronics, Inc. (<http://www.bruker-daltonik.de/>) has developed a hand-held chemical agent detector, designed for automatic chemical agent detection referred to as Rapid Alarm and Identification Device (RAID) (Figure 6). It is suited for the screening of traces in gas and for the detection of toxic industrial compounds and chemical warfare agents down to the ppb-range. Equipped with automatic polarity switching, the instrument enables continuous monitoring. The built-in microprocessor evaluates the recorded ion mobility spectra. The results, identified substances and their concentrations, are shown on the display. An integrated alarm function responds according to programmed threshold values. The substance library can be updated at any time, as a special Teach-in function allows the integration of new substance data. Main application fields are on-site investigations and personnel protection, especially for fire brigades, rescue services and military use.

RAID features a rugged IMS tube with excellent analytical reproducibility and performance and high-speed reversible voltage source for automatic polarity switching. The RAID device can be controlled using the WIN-IMS control and data system and works on personal computers under the Microsoft Windows user interface. Dimensions of the unit are 75 x 165 x 180 mm with the total packaging bringing the unit weight to 2.6 kg. This hand-held device operates under a wide temperature range (-10° C to 50° C) and is completely battery powered.

Pros: Small packaging. Can be used to detect toxic industrial compounds and chemical warfare agents in ppb-range. Integrated alarm for threshold detection. Radioactive ionizing source.

Cons: Cannot be used in situ. No price information.



Figure 6. Bruker-Daltronics portable IMS device.

DLK spectro (<http://www.spectro.org/gasanalysis.htm>) has produced an ion mobility spectrometer with gas-chromatographic cell (GC-IMS) which is capable of gas analysis in air down to the parts per billion (ppb) level. The advantage of the GC-IMS is that it provides a direct measurement, display, and control of aromatics, hydrocarbons, halogens, halogen hydrocarbons and other substances in air without time-consuming sample preparation. When run on a battery pack, it can continuously monitor for up to 4 hours. Operating conditions range from 0° C to 40° C with a range of 0 to 90% relative humidity. The packaging occupies a space of 20 x 30 x 40 cm and weighs around 6 kilograms. No price information was provided.

Pros: Very portable. Detects wide range of chemicals. Continuous measurement with a short response time. Sensitive to ppb levels.

Cons: Cannot be used in situ. Short battery life. No price information provided.

2.1.5 Mass Spectrometry

Application/Physics

The principle of the mass spectrometer is similar to the ion mobility spectrometer, except a vacuum is required. Sampled gas mixtures are ionized, and charged molecular fragments are produced. These fragments are sorted in a mass filter according to their mass to charge ratio. The ions are detected as electrical signals with an electron multiplier or a Faraday plate.

Low mass ions are displayed as a vertical line at the left end of a scale while heavy ions are displayed towards the right. The length of a line represents the quantity of that ion in the gas mixture.

Developer/Vendor

A large number of commercialized vendors exist that sell mass spectrometers. A few of the vendors that sell portable units are listed below:

- <http://www.geo.vuw.ac.nz/analytical/dycor.htm>
- <http://www.kore.co.uk/tcat.htm>
- <http://www.moorfield.co.uk/newprodqms2.htm>

Pros: The mass spectrometers have good discrimination capabilities and can detect a wide range of chemicals. Some of the mass spectrometers are portable enough to carry into the field.

Cons: The units appear to be quite expensive (the ecoSys-P device is in excess of \$40,000). Spectral overlaps can be a problem in detecting mixtures of unknown composition. Cannot be placed in situ.

2.2 *Electrochemical Sensors*

Electrochemical sensors have been categorized by Wilson et al. (1995, Ch. 36) and Janata (1992) into three groups: (1) potentiometric (measurement of voltage); (2) amperometric (measurement of current); and (3) conductometric (measurement of conductivity). A summary of gas and vapor phase analytes that can be detected by these groups of sensors is summarized in Table 36.3 of Wilson et al. (1995).

In this report, we first review the conductometric class of sensors. These types of sensors appear to be most relevant for detecting and monitoring VOCs. Then, a brief overview of potentiometric and amperometric sensors is provided.

2.2.1 Conductometric Sensors

Three different types of conductometric sensors are presented in this section. The first is a polymer-absorption sensor that indicates a change in resistance in the conductive polymer electrode when exposed to chemicals. The second is the catalytic bead sensor, which requires elevated temperatures to burn combustible hydrocarbon vapors and change the resistance of an active element. The third sensor is the metal-oxide semiconductor sensor, which responds to changes in the partial pressure of oxygen and requires elevated temperatures to induce combustion of chemical vapors that change the resistance of the semiconductor.

2.2.1.1 *Polymer-Absorption Chemiresistors*

Application/Physis

The concept of using polymeric absorption to detect the presence of chemicals in the vapor phase has existed for several decades. These polymer-absorption sensors (chemiresistors) consist of a chemically sensitive absorbent that is deposited onto a solid phase that acts as an electrode. When chemical vapors come into contact with the absorbent, the chemicals absorb into the polymers, causing them to swell. The swelling changes the resistance of the electrode, which can be measured and recorded. The amount of swelling corresponds to the concentration of the chemical vapor in contact with the absorbent. The process is reversible, but some hysteresis can occur when exposed to high concentrations. Several companies and organizations have developed chemiresistors, but the specific attributes and types of absorbents, which are generally proprietary, vary among the different applications.

Developer/Vendor

Cyran Sciences™ (<http://cyranosciences.com/technology>) developed a hand-held “electronic nose” device that employs an array of chemiresistors. They use an array of 32 chemiresistors that consist of polymer films as the adsorbent. The large number of chemiresistors in the hand-held unit is used to increase analytic discrimination. However, the unit must be “trained” for each analyte of interest. The cost of this hand-held device is ~\$7000, but it is not currently amenable for in-situ sensing

Adsistor Technology™ (www.adsistor.com; 206-368-9110) developed and patented a chemiresistor for the particular application of vapor detection of gasoline spills and leaks in the subsurface. This simple sensor consists of a metal leads connected by a conductive polymer (Figure 7). This company manufactures only the sensor itself, and they desire to team with vendors or customers to implement the sensors. Their focus appears to be on the passive detection of hydrocarbons like gasoline, and they do not appear to have developed integrated software packages for data acquisition and interpretation. Additional details on their vapor sensors can be found in Attachment D of U.S. DOE (1994) and in U.S. EPA (1992, 1995). They have been selling sensors of this type for more than 15 years under some patents which may have expired by now. They seem to be very small and not aggressive in going after these markets, for example they have never published any performance data or come to the chemical sensor meetings, they haven't made an instrument or tried to do pattern recognition to identify species. We purchased one of their sensors some 10 years ago and found that it was a cheap tube carbon tube resistor coated with their "ink". Such a configuration is hard to temperature control or integrate into an array. The price of each sensor is quoted to be ~\$50-\$60.

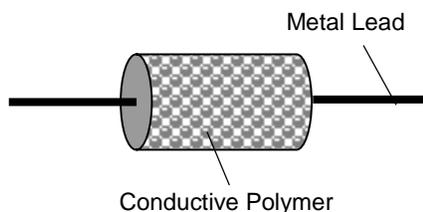


Figure 7. Polymer-absorption sensor developed by Adsistor Technology.™

Several companies have incorporated the Adsistor™ sensor into their own vapor sensing devices for use in subsurface sensing:

- SiteSentinel™ Hydrocarbon Vapor Sensor used by PetroVend™ (www.petrovend.com)
- Veeder-Root™ Vapor Sensor (www.veeder.com)
- VadoScan™ Hydrocarbon Vapor Sensor (<http://www.biorenewal.com/vadohydro.htm>).
\$200-\$300

The first two companies provide services to petroleum stations ranging from automated fueling systems to monitoring systems. The third company focuses on applications in soil remediation and long-term monitoring. None of the companies exhibited information regarding quantification of the sensor data (e.g., discrimination of analytes, characterization of the contaminant plume, etc.). The engineer who developed the SiteSentinel™ Hydrocarbon Vapor Sensor indicated that they would be interested in augmenting their system with models or software that could aid in the quantification of the sensor data (personal communication, Ian Jarvey, 01/11/2001).

Sandia National Laboratories (<http://gaas6.mdl.sandia.gov/1315.docs/chemir.html>) has developed chemiresistors using polymer films deposited on microelectrodes. Rather than using a single electrode and conductive polymer, the chips used at Sandia can house an array of chemiresistors (see Figure 8). The Sandia sensor-array chip has several advantages over the Adsistor™: 1) an array of differing sensors can be used to identify different VOCs; a single Adsistor cannot; 2) the footprint of a cylinder is not conducive to temperature control and measurement like the Sandia chip, which is also much smaller; 3) the fact that we control our own formulations is important for understanding how to improve performance through better processing; and 4) our chip geometry and preconcentrator design allows us to look for improvements in sensitivity in an integrated MEMs produced package. See Hughes et al. (2000) for more details of the Sandia chemiresistor array.

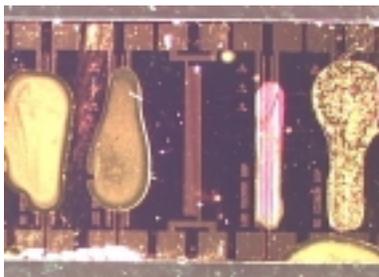


Figure 8. Chemiresistor array developed at Sandia National Laboratories with four different conductive polymer films deposited on different electrodes.

Advantages and Disadvantages

Pros: Chemiresistors are small, low power devices that have no moving parts and have good sensitivity to various chemicals. As a result, they are amenable to being placed in situ in monitoring wells. Another big advantage for chemiresistors in comparison to the standard electrochemical sensors is that they don't require liquid water to work properly. This will be seen more clearly in the section on electrochemical sensors below, but in brief, standard electrochemistry requires a well controlled liquid environment for the electrodes to work predictably in detecting analytes. That liquid (usually water with controlled ionic strength and pH buffers) must be supplied by the sensing medium (like a well) or a reservoir in the sensor package, which can dry out.

Cons: May not be able to discriminate among unknown mixtures of chemicals. Some polymers react strongly to water vapor. Uncertain durability of polymers in subsurface environments; need to develop robust packaging. May need pre-concentrator to detect very low limits (for regulatory standards). Although reversible, signal may experience hysteresis and a shift in the baseline when exposed to chemicals.

2.2.1.2 Catalytic Bead Sensors

Application/Physics

Catalytic bead sensors are low-power devices (50-300 mW) that have been used for many years in the detection of combustible gases, particularly methane in air (U.S. EPA 1995). They are used widely in portable gas detection instruments. The catalytic bead sensor is comprised of a passive and active element, both made from an embedded coiled platinum wire in a porous ceramic (Figure 9). The active element is coated with a catalyst such as platinum, and the passive element is coated with an inert glass to act as a reference element to compensate for environmental conditions. Both elements are heated to a prescribed operating temperature ranging from 300°C to 800°C. When a combustible gas such as methane contacts the elements, the vapor combusts on the active element and the active element increases in temperature. As a result, the resistance of the platinum coil changes. The two elements are connected to a wheatstone bridge circuit, so the changes in resistance are measured as a change in voltage.

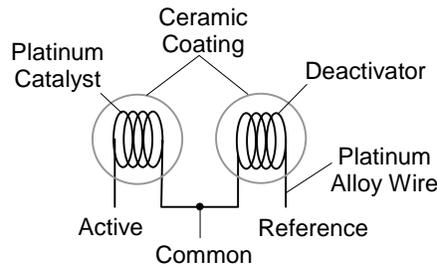


Figure 9. Diagram of catalytic bead sensor.

Developer/Vendor

GasTech™ (<http://www.gastech-inc.com/>) has a portable soil vapor monitor (\$1775) that uses the catalytic bead sensor for detecting combustible hydrocarbon gases. The benefits of this monitor are that it has the ability to eliminate methane from the readings. Methane occurs naturally in the subsurface, so it can provide false readings. This is a hand-held device that provides discrete readings of real-time gas concentrations. Sampling occurs through a probe, and an internal pump draws the sample. It is lightweight (~5 pounds) and has a built-in data logger. User-defined alarm points (visual and audible) can be programmed. The battery can last up to 20 hours. Cost ~\$2000.



Figure 10. GasTech™ Portable Soil Vapor Monitor.

Advantages and Disadvantages

Pros: This unit is very portable and can allow the operator to distinguish between methane and other volatile hydrocarbon vapors.

Cons: This unit is not amenable for long-term in-situ operation. The catalytic bead sensor requires elevated temperatures for operation. Internal pump is required to sample gas. Sensitivity to aromatic and halogenated hydrocarbons is questionable.

2.2.1.3 Metal-Oxide Semiconductor Sensors

Application/Physics

The metal-oxide semiconductor (MOS) sensor is comprised of a tin oxide that is sintered on a small ceramic tube. A coiled wire is placed through the center of the ceramic tube to act as the sensor heater. Metal wires provide electrical contact between the tin oxide and the rest of the electronics. The MOS sensor requires between 300 mW and 600 mW of power to operate the sensor at elevated temperatures between 200°C and 450°C. The combination of the sensor operating temperature and the composition of the metal oxide yields different responses to various combustible gases.

When the metal oxide is heated, oxygen is adsorbed on the surface with a negative charge. Donor electrons are transferred to the adsorbed oxygen, leaving a positive charge in the layer. Inside the sensor, electrical current flows through the grain boundary of metal oxide micro crystals. Resistance to this electrical current is caused by negatively charged oxygen at grain boundaries. In the presence of a reducing gas, a surface catalyzed combustion occurs and the surface density of negatively charged oxygen decreases, thereby decreasing the resistance of the sensor. The relationship between the amount of change in resistance to the concentration of a combustible gas can be expressed by a power-law equation.

Developer/Vendor

Figaro (<http://www.figarosensor.com/>) has developed MOS sensors for detection of solvent vapors (Figure 11). The TGS 2620 is sensitive to alcohol and organic solvent vapors (e.g., methane, carbon monoxide, iso-butane, hydrogen, ethanol), and it shows some sensitivity to

humidity. It requires a heater current of 42mA, and it has a quick response time when exposed to solvents (seconds). The sensor shows a stable baseline for periods over a year.

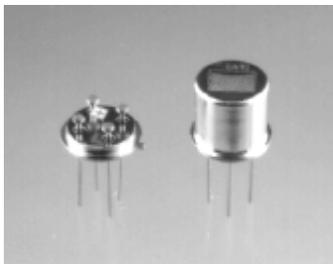


Figure 11. Figaro TGS 2620 Solvent Vapor Sensor.

Advantages and Disadvantages

Pros: The MOS sensors have high sensitivity to combustible gases (e.g., hydrogen, carbon monoxide, methane, ethane, propane, alcohols, etc.). They are compact and durable. The cost is also relatively inexpensive.

Cons: U.S. EPA (1995) performed tests on some Figaro MOS sensors and found that they had more drift during exposure to xylene than the polymer-absorption sensors. The MOS sensor has a fair amount of sensitivity to water humidity, which may be problematic in subsurface environments. Sensitivity to aromatic and halogenated hydrocarbons is questionable.

2.2.2 Potentiometric and Amperometric Sensors

Application/Physics

Potentiometric and amperometric sensors employ an electrochemical cell consisting of a casing that contains a collection of chemical reactants (electrolytes or gels) in contact with the surroundings through two terminals (an anode and a cathode) of identical composition. For gas sensors, the top of the casing has a membrane which can be permeated by the gas sample. Oxidization takes place at the anode and reduction occurs at the cathode. A current is created as the positive ions flow to the cathode and the negative ions flow to the anode. Gases such as oxygen, nitrogen oxides, and chlorine, which are electrochemically reducible, are sensed at the cathode while electrochemically oxidizable gases such as carbon monoxide, nitrogen dioxide, and hydrogen sulfide are sensed at the anode. Potentiometric measurements are performed under conditions of near-zero current. Amperometric sensors are usually operated by imposing an external cell voltage sufficiently high to maintain a zero oxygen concentration at the cathodic surface; therefore, the sensor current response is diffusion controlled (Tan and Tan, 1996). According to Tan and Tan (1996), sensitivity of amperometric sensors is better than potentiometric sensors. In addition, U.S. DOE (1994, p. A-1) reports that amperometric methods

are used in high-performance liquid chromatography because of its enhanced sensitivity. Additional details of potentiometric and amperometric sensors can be found in Janata (1990).

A common application for potentiometric and amperometric sensors is for water analysis. The most common is the pH sensor system. The basic principal of these devices is that they require two separated, carefully controlled liquid reservoirs with two different chemically unstable electrodes (called reference electrodes), for example a silver wire with a coating of silver chloride. The pH is measured by the voltage difference between the two reference electrodes, so the unknown sample must be in electrochemical connection with both solutions through a glass membrane. However, these thin porous membranes can break, the solutions can leach out or dry out, or the chemistry of the reference electrode itself can change giving a slightly different voltage. Small changes in the chemistry can result in large changes in output voltage. Consequently these systems require constant attention and calibration against known pH solutions.

Many so-called ion selective electrodes for particular ions are sold using basically the same system described above but with special membranes taking the place of the pH-sensitive glass that give potential differences for different ions. The same maintenance and calibration problems exist, as well as interference problems from other ions. Some gases that can be detected using potentiometric methods include carbon dioxide, oxygen, carbon monoxide, hydrogen, chlorine, arsenic oxides, and oxidizable pollutants.

We could not find a commercial supplier potentiometric cells for VOCs; most are used for toxic gases and oxygen. There are several research papers describing how to measure different VOCs in liquid electrochemical cells (Sawyer et al., 1995). The same corrosion and drift problems exist for these experiments as described above. In addition, a membrane or porous plug must be used to provide the diffusion of the vapor phase VOC molecules from the gas phase into the electrolyte and electrode surface. To speed up the process, the working electrode is placed virtually on top of the gas-permeable membrane. A recent research example of trace detection of explosive molecules is given in Berger (2000) with some discussion of the difficulties (interference of electroactive O₂ is a big one) and virtues (under controlled conditions, very low vapor-phase concentrations (ppb) of TNT can be detected). Currently, at Sandia we have no fieldable electrochemical systems for VOC detection to compare with the polymer-absorption and surface-acoustic wave devices (see Sections 2.2.1.1 and 2.3.1).

Developer/Vendor

Delphian Corporation (<http://www.delphian.com/>) manufactures several potentiometric devices for sensing toxic gases (e.g., carbon monoxide, chlorine, hydrogen sulfide) and oxygen.

GasTech (<http://www.gastech-inc.com/>) also manufactures devices that use potentiometric sensors for toxic gases and oxygen.

Advantages and Disadvantages

Pros: These devices can be specific for a particular gas or vapor and are typically very accurate. They do not get poisoned and can monitor at ppm levels.

Cons: Primary sensitivity is for toxic gases and oxygen, not VOCs. Not amenable for in-situ applications. Membranes are sensitive and may degrade with time. Devices are not very durable and have short shelf lives. Subject to interfering gases such as hydrogen.

2.3 Mass Sensors

2.3.1 Surface Acoustic Wave Sensors/Portable Acoustic Wave Sensors

Application/Physics

Surface Acoustic Wave Sensors (SAWS) are small miniature sensors used to detect VOCs. A SAW device consists of an input transducer, a chemical adsorbent film, and an output transducer on a piezoelectric substrate (see Figure 12). The piezoelectric substrate is typically quartz. The input transducer launches an acoustic wave which travels through the chemical film and is detected by the output transducer. The device runs at a very high frequency 100MHz. The velocity and attenuation of the signal are sensitive to the viscoelasticity as well as the mass of the thin film which can allow for the identification of the contaminant. Heating elements under the chemical film can also be used to desorb chemicals from the device. A signal pattern recognition system that uses a clustering technique is needed to identify various chemicals.

SAWS have been able to distinguish organophosphates, chlorinated hydrocarbons, ketones, alcohols, aromatic hydrocarbons, saturated hydrocarbons, and water.

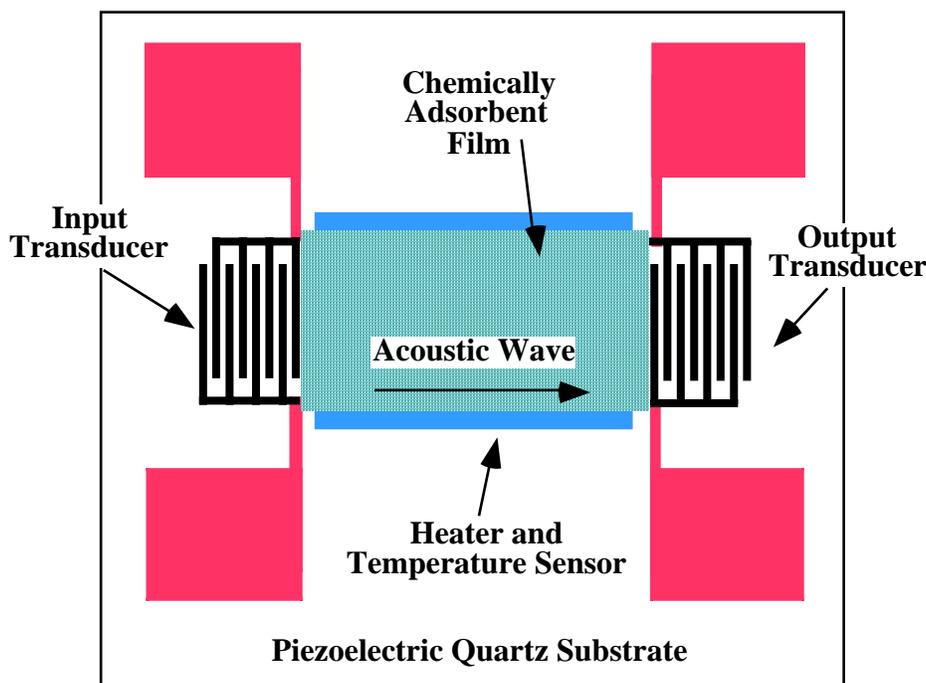


Figure 12. Schematic of SAW device.

Developer/Vendor

Sandia National Laboratories has developed and tested a six-SAW device array and have been able to identify 14 different individual organic compounds over a wide range of concentrations with 98% accuracy (<http://gaas6.mdl.sandia.gov/1315.docs/sawarray.html>). They have also been able to identify 21 different binary mixtures of 7 of the compounds with 96% accuracy. They also claim that with random calibration errors of 25%, they were still able to identify individual chemicals with 92% accuracy. They were able to isolate chemicals in the following classes: organophosphates, chlorinated hydrocarbons, ketones, alcohols, aromatic hydrocarbons, saturated hydrocarbons, and water. Contact: Richard Cernosek (wcerno@sandia.gov).

Sandia National Laboratories has developed an integrated GaAs SAW sensor (<http://gaas6.mdl.sandia.gov/1315.docs/sawgaas.html>). This micro-sensor is a SAW device that has been integrated with a microprocessor on a single 5mmx5mm chip. GaAs is used as the piezoelectric material instead of quartz. This device has the advantages of being small, having reduced power consumption, and having simple packaging. Contact: Steve Casalnuovo (sacasal@sandia.gov).

Sandia National Laboratories has developed a hand held PAWS system (<http://gaas6.mdl.sandia.gov/1315.docs/paws.html>). This system is 5.5"x3.3"x1.5" (27 in³) which includes batteries for portable or field operation. This device contains a single SAW sensor. The system uses a pump to pull air samples into the test cavity and data is fed into a computer for control, real-time display, data storage, and pattern recognition. A down-hole monitor has also been developed. Also developed with Texas A&M, New Mexico Institute of Mining and Technology, and industrial partners. Contact: Greg Frye-Mason (gcfrye@sandia.gov).

PNL (<http://www.technet.pnl.gov/sensors/chemical/projects/es4cwsen.html>) has developed a portable sensor to detect real-time CW dispersal in the field. They have developed a portable SAW chemical sensor. Contact: Brion Burghard (brion.burghard@pnl.gov)

ORNL (<http://htm29.ms.ornl.gov/diffgroup/zeol.html>) is developing SAWS devices using a zeolites as the chemical capture material.

Sandia National Laboratories has developed high temperature SAW devices (<http://gaas6.mdl.sandia.gov/1315.docs/hightempacoustic.html>). These SAW sensors can be fabricated using different materials so that the device can be used at temperatures as high as 525 °C. Lithium Niobate, Lithium Tantalate, and Gallium Phosphate are used for the piezoelectric substrate. Chemical sensing materials consisting of pure or mixed noble metal catalytic thin films, binary oxide thin films (zirconia, titania, tin dioxide) with and without metal ion doping, and transition metal ion activated surfactant-templated mesoporous metal oxide films. Contact: Richard Cernosek (wcerno@sandia.gov).

Advantages and Disadvantages

Pros: Small, low power, no moving parts other than the high-frequency excitation, good sensitivity to various chemicals. Can detect chemicals in very low concentrations.

Cons: May not be able to discriminate among unknown mixtures of chemicals. Some polymers react strongly to water vapor; uncertain durability in subsurface environments.

2.3.2 Microcantilever sensors

Application/Physics

Microelectromechanical systems can be composed of multiple micron-thick cantilevers (visualize miniature diving boards) that respond by bending due to changes in mass. Appropriate coatings are applied to the cantilevers to adsorb chemicals of interest. This particular technology has been used for developing infrared sensors to “see” images in darkness (<http://www.sarcon.com/>), but commercial devices using microcantilever sensors to detect volatile organic chemicals were not found. Active research in this area is being performed by Oak Ridge National Laboratory (<http://lsd.ornl.gov/babs/thundat/Thundat.htm>).

2.4 Optical Sensors

2.4.1 Fiber Optic Sensors

Application/Physics

Fiber optic sensors are a class of sensors that use optical fibers to detect chemical contaminants. Light is generated by a light source and is sent through an optical fiber. The light then returns through the optical fiber and is captured by a photo detector. Some optical fiber sensors use a single optical fiber while others use separate optical fibers for the light source and for the detector. There are three general classes of fiber optic sensors (see Figure 13). The first type is completely passive. A spectroscopic method can be used to detect individual types of contaminants. This method involves sending a light source directly through the optical fiber and analyzing the light that is reflected or emitted by the contaminant. The refractive index of the material at the tip of the optical fiber can be used to determine what phases (vapor, water, or NAPL) are present. A second class of fiber optic sensors consist of a fiber optic sensor with a chemically interacting thin film attached to the tip. This film is formulated to bind with certain types of chemicals. Contaminant concentration can be found by measuring the color of the thin film, the change in refractive index, or by measuring the fluorescence of the film. The third type of fiber optic sensors involves injecting a reagent near the sensor. This reagent reacts either chemically or biologically with the contaminant. The reaction products are detected to give an estimate of the contaminant concentration.

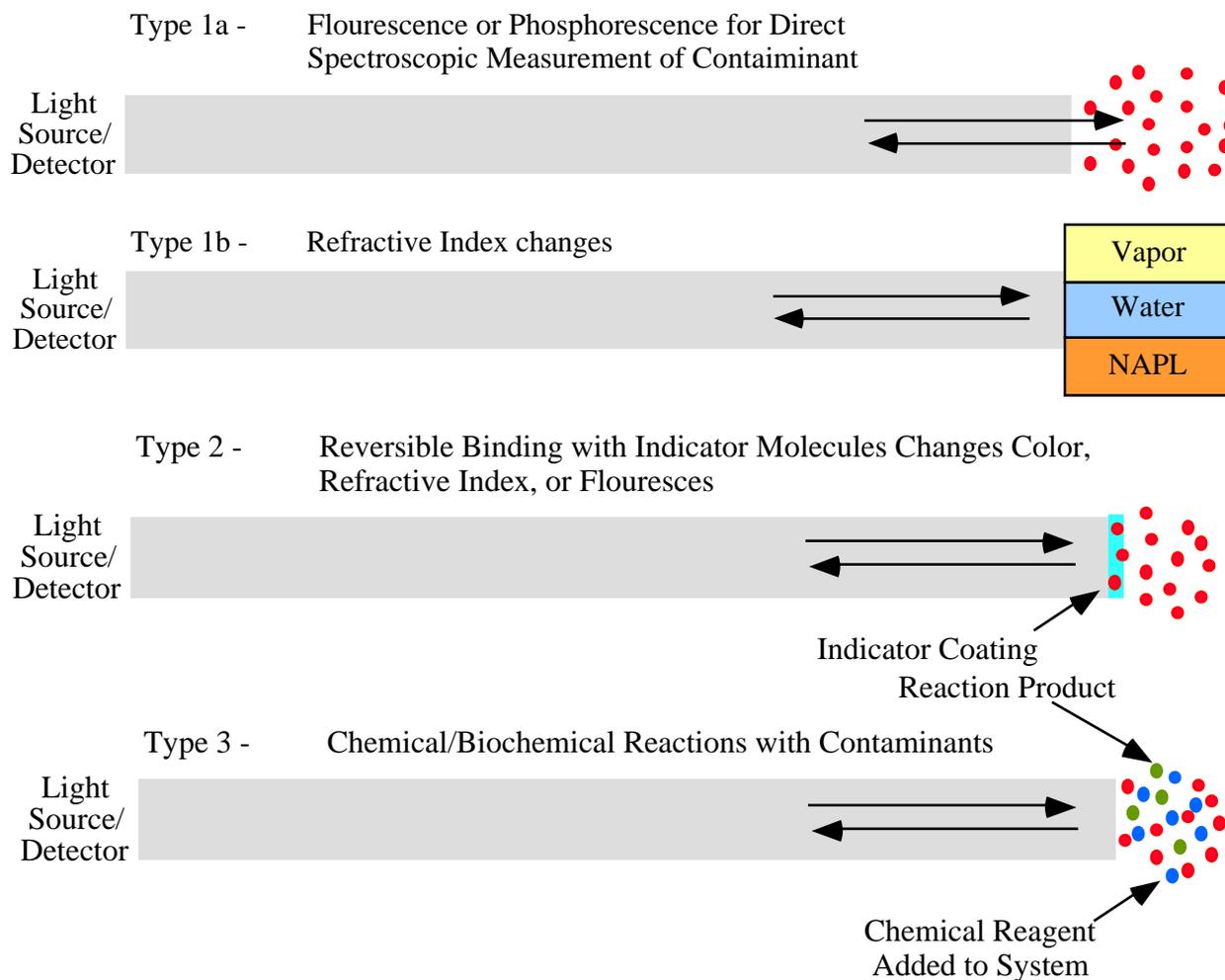


Figure 13. Three types of fiber-optic sensors.

Developer/Vendor

LLNL developed an optical fiber sensor for TCE, using pyridine as the reagent, and has performed both lab and field tests. This system uses separate light source/detector fiber optic lines. The estimated error for measurements between 25-500 ppb was 10%.

EIC Laboratories (<http://www.eiclabs.com/resspeccone1.htm>) has developed two types of optical fiber sensors that are encased inside of a cone penetrometer. One sensor detects the refraction index changes and is used to detect the presence of DNAPL contaminants. This probe has been tested in the field. The other is a Raman fiber optic probe that identifies DNAPLs by measuring the raman scattering pattern generated from chemical contaminant that have adsorbed on the surface of specially treated metals. This probe has been used in the field to detect nitrate-based aromatics (piric acid and TNT) typically found in landmines. Contact: Dr. Kevin M. Spencer (spencer@eiclabs.com).

NASA Goddard has developed sol-gel filled optical fibers. The sol-gel is doped with chemiluminescent or fluorescent indicators. Detection occurs within the doped optical fiber.

PNNL (<http://www.technet.pnl.gov/sensors/chemical/projects/es4i2fibopt.html>) has developed a hand-held sensor to detect iodine vapors for concentrations as low as 5 ppm. Coating developed that changes the optical absorption properties when in presence of iodine. Two-wavelength fiber optical probe to provide robust measurement. Other vapors can be detected using other coatings. Contact: Mary Bliss (mary.bliss@pnl.gov).

Advantages and Disadvantages

Pros: Low power; several types have no moving parts; can detect various chemicals at very low concentrations.

Cons: Limited ability to transmit light through the optical fiber over long distances. Some organic pollutants are not easily differentiated using UV-visible spectroscopy. Concentration range sensitivity may be limited. Sensors that use chemically sensitive coatings may degrade with time.

2.4.2 Colorimetry

Application/Physics

Pocket colorimeter test kits can be used to measure trace levels of contaminants. They work by analyzing the color of contaminated water that has been mixed with a particular chemical reagent. Hach sells pre-measured, unit-dose reagent that react with water samples. To test water samples, the pocket colorimeter compares a reacted sample with a sample blank and yields results in concentration units.

Developer/Vendor

Hach (www.hach.com) makes a variety of colorimetry kits. The only chemical of interest on the list of available kits is total petroleum hydrocarbons (TPH in water and in soil). TPH levels in water can be found between 20-200 ppm in soil and 2-10 ppm levels in water. Most of the test kits available are focused on metals (chromium, copper, iron, etc.) or for parameters of interest for drinking water (chlorine, fluoride, hardness, pH, etc.). Products include hand-held devices and strips that can be dipped in water.

American Gas & Chemical Co. (<http://www.amgas.com/ttpage.htm>) also makes color strips to detect a variety of toxic gases (e.g., carbon monoxide, hydrogen sulfide, chlorine). These strips are intended to be worn for visible detection of toxic gases.

CHEMetrics, Inc. sells the RemediAid kit (<http://www.chemetrics.com/TPH.html>) that will determine total petroleum hydrocarbons across a wide range of soil types and petroleum products, so it is suited use in the field. The system enables the user to run 10 tests concurrently, providing the potential to run 25 tests in one hour. RemediAid can also be calibrated to measure quantitative amounts of specific petroleum products including: BTEX, PAH, diesel fuel, leaded

and unleaded gasoline, weathered gasoline, Brent crude, and lubricating oil. The LED based colorimeter gives ppm hydrocarbons. The cost of the unit is ~\$800.

Advantages and Disadvantages

Pros: Portable, simple to use. Visual evidence of gas detection event. Not prone to interferences.

Cons: Limited chemical sensitivity to individual VOCs; needs actual water samples (cannot be used in situ); most kits do not meet U.S. EPA method requirements and may not be used for compliance monitoring. Requires visual inspection and is not amenable to long-term in-situ applications.

2.4.3 Infrared Sensors

Application/Physics

Infrared sensors can be used to detect gases, which, in general, have unique infrared absorption signatures in the 2-14 μm range. The uniqueness of the gas absorption spectra enables identification and quantification of chemicals in liquid and gas mixtures with little interference from other gases. These devices are typically comprised of a source of infrared radiation, a detector capable of seeing the infrared radiation, and a path between the detector and source that is exposed to the gas being detected. When gas in the path absorbs energy from the source, the detector receives less radiation than without the gas present, and the detector can quantify the difference.

Developer/Vendor

GasTech (<http://www.gastech-inc.com>) has developed an FX-0IR Infrared Single Gas Transmitter. This device uses a dual infrared technology to detect hydrocarbon gases (e.g., hexane (0-1000 ppm), methane (0-5000 ppm), propane (0-2000 ppm)). Cost ~\$1200.

Ion Optics (<http://www.ion-optics.com/MEMSGasSensor-Detailed.htm>) has developed an infrared sensor that uses a silicon element that acts as both the infrared emitter and detector. The emitted radiation is reflected off the far-end of the chamber and absorbed by the silicon micro-bridge. When a gas is present, the detector will absorb less radiation and a lower temperature will exist, which is detected.

Advantages and Disadvantages

Pros: These devices can be made to identify specific gases; they require less calibration than other sensors; good durability with minimal maintenance.

Cons: They can only monitor specific gases that have non-linear molecules; they can be affected by humidity and water; they can be expensive; dust and dirt can coat the optics and impair response, which is a concern in in-situ environments.

3. Summary and Discussion

Four general categories of technologies were reviewed for their potential application in real-time, in-situ chemical sensing applications. The first category reviewed was chromatography/spectrometry, which included ion-mobility spectrometry and mass spectrometry. The gas chromatographs reviewed provide excellent discrimination among various chemicals of interest. The size of gas chromatographs range from large bench-top systems to portable hand-held systems and microchips the size of a coin. Although the portable GCs can be taken to the field and used manually to sample monitoring wells, the majority of these devices are not yet amenable to real-time, in-situ downhole applications. The μ ChemLab might be a potential candidate, but it requires micro-pumps to circulate gas through the system, and these moving parts may not be able to withstand long periods in geologic environments. The ion-mobility and mass spectrometers also have excellent discrimination capabilities, but like the gas chromatographs, they are not currently amenable for in-situ applications.

The second category reviewed was electrochemical sensors, which included conductometric, amperometric, and potentiometric sensors. The amperometric and potentiometric devices traditionally are used to monitor oxygen, carbon monoxide, chlorine, and other constituents for air quality purposes. Water quality parameters such as pH can also be measured with these devices. However, the amperometric and potentiometric devices are not widely used for detection of VOCs. The conductometric sensors reviewed include polymer-absorption chemiresistors, catalytic bead sensors, and metal oxide semiconductors. These devices are sensitive to VOC exposure, resulting in large changes to resistance in the device. However, current commercial devices intended for use in situ (primarily polymer-absorption sensors) cannot discriminate different constituents in a mixture. Some hand-held polymer absorption devices *can* discriminate different species because of the use of arrays of chemiresistors, but they are not amenable to in-situ applications. Catalytic bead sensors and metal-oxide semiconductors require elevated temperatures for operation, and they may not be amenable for prolonged periods in situ. In fact, the durability of all electrochemical sensors needs to be tested in geologic environments.

The third type of technology reviewed was the mass sensor. These devices typically absorb the chemical of interest onto a surface, and the device detects the change in mass. The detection can be accomplished through changes in acoustic waves propagated along the surface (SAW devices) or by actual bending or a change in shape of the device as mass is accumulated (micro-cantilever devices). These devices are very sensitive to the presence of various volatile and semi-volatile chemicals. However, the sensitivity of the device depends on high-frequency excitation or extremely small changes in shape; these aspects have not been tested in prolonged geologic environments.

Finally, the fourth category of devices reviewed was optical sensors. These include fiber optical sensors, colorimetry, and infrared sensors. These sensors rely on changes in electromagnetic radiation (e.g., visible, infrared) to detect and identify the presence of chemicals. The sensitivity of these sensors to VOCs can be good, and a TCE fiber optical sensor integrated with a cone penetrometer already exists. Its use in long-term applications still requires testing. Colorimetry is a simple and quick method to detect changes in color in solutions mixed with the sample, but it requires manual intervention. The infrared sensor appears to be useful for detecting combustible

hydrocarbons (e.g., methane, propane), but the devices reviewed were not amenable for real-time, in-situ applications involving other lower volatility VOCs.

The most viable sensors for in-situ chemical sensing appear to be electrochemical sensors, specifically conductometric sensors, based on their simplicity and robustness. Reports from the U.S. EPA (1992, 1995) have indicated that polymer-absorption and metal-oxide-semiconductor sensors are viable candidates for use at underground storage tanks. In addition, fiber-optic sensors and mass sensors (SAW devices in particular) also appear to be viable candidates for in-situ applications. The general issue among all of these sensors is that few, if any, have been tested and demonstrated in long-term geologic environments. In addition, the data obtained from these sensors is not typically quantified (e.g., What chemical species are present? How much is present? Where is it located?).

In U.S. EPA (1992, 1995), they report that interference from water and methane are concerns for sensor technology because they can trigger false positives in geologic environments; therefore, tests on potential candidate sensors should be performed to determine if methane and water vapor significantly impact the signal from the sensors. In addition, the ability to discriminate among different chemical species needs further investigation among the polymer-absorption and SAW sensors, especially in geologic environments and applications, such as soil venting. The ability to retrieve quantified information from the in-situ sensors such as contaminant characteristics and location may prove useful for the end user to make informed decisions regarding treatment and remediation.

For example, commercial gas stations are required by the U.S. EPA to have monitoring and leak-detection systems for their underground storage tanks. However, the systems are set to trigger an alarm when the sensor detects a change in the baseline signal. Additional testing and methods are required to verify the leak and the characteristics of the leak (location, amount, etc.). We believe that integrated systems involving data acquisition, data interpretation, and processing can be developed to quantify some of these issues from the in-situ sensor data. Characterization of the contaminant (species, source location, and extent) can potentially be evaluated from the sensor data directly to avoid additional costly and time-consuming sampling methods. Laboratory studies in controlled environments, as initiated as part of this LDRD project, can help to interpret the sensor data in actual geologic environments. These tests and models can provide a better understanding of the impacts of geologic, hydrologic, and contaminant features and processes on real-time, in-situ sensing. Improved sensors for geologic environments can then be developed and refined to address such issues as durability, sensitivity, and selectivity.

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