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Chemical Gas Sensors and the Characterization, Monitoring and Sensor Technology Needs of the U. S. Department of Energy

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The Office of Technology Development within the Dept. of Energy (DOE) has the responsibility of providing new technologies to aid the environmental restoration and waste management (ER/WM) activities of the DOE. There is a perception that application and judicious development of chemical sensor technologies could result in large cost savings and reduced risk to the health and safety of ER/WM personnel. A number of potential gas sensor applications which exist within DOE ER/WM operations will be described. The capabilities of several chemical sensor technologies and their potential to meet the needs of ER/WM applications in the present or near term future will be discussed.

In 1989, the U. S. Department of Energy (DOE) committed to rapidly bringing all operating facilities into compliance with applicable laws and regulations and to cleaning up the contaminated sites and facilities by the year 2019[1] (U. S. Department of Energy 1991). The Office of Environmental Restoration and Waste Management (EM), within DOE, is responsible for fulfilling this commitment.

Within EM, the Office of Environmental Restoration (ER) has jurisdiction for an estimated 3700 hazardous waste sites at DOE facilities; the Office of Waste Management (WM) is responsible for management of approximately 100 million gallons of high-level radioactive waste in 327 tanks and more than 14 million 55-gallon drums of various waste forms including radioactive waste. The Office of Technology Development, also within EM, is responsible for providing new technologies to ER and WM, when needed, so the commitment can be fulfilled.

The current emphasis in ER is on assessment of the nature and extent of contamination so there is great interest in characterization, monitoring, and sensor technologies. In the future, these technologies will also be needed for remediation and post-closure monitoring. WM is focusing on ensuring adequate, permitted storage capacity for existing waste, much of which will have to be processed before disposal. Characterization, monitoring, and sensor technologies will also be required before and during the processing and following disposal.

Characterization and monitoring are typically accomplished by taking samples of air, water, soil, waste, and waste process material, and sending them to analytical laboratories for analysis. Although this practice is effective, it is expensive and time-consuming, in part because transportation and maintenance of sample integrity and identity are necessary. Some radioactive samples cannot be shipped off site. Because of the large size of the DOE commitment mentioned above and the projected enormous characterization and monitoring costs, there is a perception that application and judicious development of chemical sensor technologies could result in large cost savings and reduced risk to the health and safety of personnel.

Within the Characterization, Monitoring and Sensor Technology Integrated Program (CMST-IP), chemical sensors are defined as the components of characterization and monitoring systems that produce different, measurable, and reproducible responses when exposed to different levels of specific chemicals or classes of chemicals. In addition, the following criteria are believed to be applicable to chemical sensors:

- Field deployable
- Selective detection of analyte
- Adequate sensitivity for application
- Capable of unattended operation
- Capable of long-term and continuous operation
- Real time response
- Inexpensive.

Activities to support the characterization and monitoring efforts of the DOE have been organized to focus upon five critical problem areas:

- Remediation of High-Level Waste Tanks
- Containment of Existing Landfills
- Characterization, Treatment, and Disposal of Mixed Waste
- Migration of Contaminants
- Decommissioning and Final Disposal

Table 1 summarizes the potential sensor applications within each of these problem areas.

Table 1

Remediation of High Level Waste Tanks Tank Safety Issues Monitoring of Headspace Gas Concentrations Hydrogen; N_2O; NH_3; Organics
Characterization, Treatment, and Disposal of Mixed Waste Waste Stream/Process Monitoring Waste Streams During Processing Waste Effluents (e.g. Off-Gas Monitoring for VOCs; PICs; Metals
Containment of Exisitng Landfills In Situ Determination of Contaminants Beneath Landfills Organics; Metals
Migration of Contaminants Location, Type, and Concentration of Subsurface Contaminants Chlorinated Hydrocarbons Petroleum Hydrocarbons Explosives; Pesticides; Herbicides
Decommissioning and Final Disposition Long Term, Post Closure Monitoring Organics

Other applications for gas sensors may arise in response to needs for monitoring or characterizing a wide variety of chemicals in the air and in the headspace over different types of samples. Some of these needs may derive from legislative mandates such as:

Clean Air Act

Safe Drinking Water Act

Resource Conservation and Recovery Act

Clean Water Act

Toxic Substances Control Act

State and Local laws

Chemical gas sensors are not the only technology with the potential to meet DOE needs for characterization and monitoring. Currently large number of samples are collected in the field and sent to central laboratories for analysis. While this practice is expensive, it may be expected to continue indefinitely. It is also possible to build analytical laboratories into trailers which can be field deployed on site. Samples would still need to be taken, but sample transport and disposal would be simplified.

Field deployable instrumentation presents the strongest competition to chemical gas sensors. For example, conventional optical spectrometers, gas chromatographs, and mass spectrometers are all being adapted for field deployment. This route to field assay may be the most expeditious in the near future although the deployment of large numbers of these instruments may be cost prohibitive.

The chemical gas sensor technologies which have the potential to meet DOE characterization and monitoring needs may be classified into at least three categories:

Fiber Optic

Piezoelectric Mass

Electrochemical

Two reports discussing these categories have recently been produced under DOE sponsorship[2,3].

Fiber Optic Sensors

Chemical sensors that employ fiber optics exist in several forms[4-6]. The simplest types determine an analyte through observation of an intrinsic spectroscopic property of the analyte. In these sensor types, the optical fibers serve only as light guides. The spectroscopies commonly employed are optical absorption, fluorescence, Raman, and surface-enhanced Raman. Other spectroscopies beginning to be investigated for sensor applications include infrared, near-infrared, and ultraviolet reflection. Surface plasmon resonance is attracting commercial interest for biosensor applications.

A more sophisticated class of fiber optic sensors employs recognition chemistry. A chemical layer acts as a transducer or indicator in conjunction with an optical fiber. The layer may either be placed at the distal end or on an unclad portion of the optical fiber. The recognition chemistry may be reversible or irreversible. Presently these chemistries are deployed by coupling polymers, indicators, or combinations of the two, to detect such things as metal ions, ammonia, hydrogen ion, oxygen, carbon dioxide, and hydrocarbons. Sensors for all these analytes have been demonstrated with different levels of success and work is continuing. Enzymes can also be coupled to the chemical layers to provide additional sensitivity.

Sensors based on irreversible recognition chemistries use reagents rather than indicators. Such sensors respond only to a single analyte exposure unless additional reagent is released or otherwise delivered to regenerate the sensor. Such a reagent-based fiber optic sensor for trichloroethylene has already been field demonstrated.

Antibodies are also in the category of irreversible recognition chemistry. The highly selective binding of an antibody can be coupled with an optical sensing scheme to quantify the antibody/antigen interaction. Commercial immunoassay systems already employ such schemes. Fiber optic immunoassay techniques for clinical and other applications have been under development, for example, by Ciba Corning Diagnostics (Medfield, MA).

Considerable development work is in progress. Prototype systems that employ a variety of spectroscopic techniques are being evaluated for environmental monitoring, and commercial devices are available for selected applications. Issues of stability and selectivity remain to be solved. Internal calibration capability is a significant advantage of some fiber optic sensors[7]. Table 2 provides a rough indication of the current state of the technology.

Table 2.

Analytes	Estimated Dynamic Range
Trichloroethylene (TCE)	Low ppb to ppm
Polynuclear Aromatic Hydrocarbons	Tens to Hundreds of ppm
Hydrocarbons	Tens to Hundreds of ppm

There is a great need to develop improved recognition chemistries for fiber optic and other types of chemical sensors. The development of sensor coatings that have greater selectivity and sensitivity is expected to be a dominant research direction. For irreversible indicating chemistries, development of systems to continuously deliver reagents is possible and is presently an area of active investigation.

Specific sensors will become available for some priority analytes but the development of a large number of highly selective indicators or coatings is not likely in the near term. Development of sensors which can determine compounds as a class is clearly possible. Such sensors would indicate, for example, that a certain class of contaminants is present and could measure the total concentration. In the short term, it should also be useful to deploy sensors that are capable of indicating concentrations to only within an order of magnitude of the actual value for various chemical classes. Such sensors could provide valuable data on trends and significant concentration changes.

Among the recognition chemistries needed by DOE, but not yet available, are indicators for a variety of volatile organic compounds and some volatile explosives. If suitable recognition chemistries were developed, chemical sensors for these materials could be available in three to five years.

The establishment of an extensive field testing program is also needed. Too few field tests are currently being performed. An important aspect of such field testing is the packaging of the sensors for field use. A related issue is obtaining measurements that are representative of the material of interest. If a fiber is simply placed in the environment or material of interest, the sensor response depends on location. If the sensor is reversible, it can be moved to profile the environment. Otherwise, sensors must be placed at a number of different locations.

Piezoelectric Chemical Sensors

Piezoelectric chemical sensors are a special class of piezoelectric mass sensors, small electronic devices which quantitatively respond to the amount of mass deposited or sorbed on their surface. When such devices are coated with materials that selectively sorb a particular chemical or class of chemicals, they function as chemical sensors[8-10].

Piezoelectric chemical sensors currently exist as bulk acoustic resonators (BARs) and acoustic wave guides (AWGs). The BARs are made from thin piezoelectric crystals or thin layers of piezoelectric material on a supporting substrate. BARs operate with acoustic wave propagation perpendicular to the surface and are commonly referred to as quartz crystal microbalances (QCMs), thin film resonators (TFRs), quartz crystal resonators, and piezoelectric resonators. The AWGs are made from the same materials as BARs but involve acoustic wave propagation parallel to the surface. Various AWG types are surface acoustic wave (SAW), flexural plate wave (FPW), Lamb wave (LW), and shear horizontal (SH) acoustic plate mode (SH APM) devices.

Piezoelectric chemical sensors are under development at many laboratories; some are being commercially produced in limited quantities for a number of applications. A prototype system for VOCs is being field tested. Information on some known developers and potential suppliers of piezoelectric chemical sensors for various applications is given in Table 3.

Table 3. Developers and potential suppliers of piezoelectric chemical sensors.

Developer/Supplier	Application
Microsensor Systems Bowling Green, KY	SAW detectors with gas chromatographs, for industrial hygiene and environmental control
Femtometrics Costa Mesa, CA	SAW sensors for the measurement of ozone and detection of air borne particulates
Amerasia Technology Inc. Westlake Village, CA	Prototype SAW sensors for the detection of explosives such as TNT and RDX
Universal Sensors Metaire, LA	BARs with and without coatings for R&D use and for several sensing applications
Xsensor Delft, Netherlands	Manufactures SAWs, FPWs, and their support electronics in integrated circuit form
Vaisala Finland	SAW devices as dew point sensors
Ciba GeigySwitzerland	SAW sensors for internal process control applications
Sandia National Laboratories (DOE) Albuquerque, NM	SAW detectors, used with a gas chromatograph to measure VOCs
Ames Laboratory (DOE) Ames, IA	BARs and AWGs for gaseous species (combustion gases, formaldehyde)

Current piezoelectric chemical sensors can measure vapor concentrations (e.g. for VOCs) in the range of 10 ppm or higher; this sensitivity is thought to be adequate for many DOE needs. In selected applications, the sensitivity and/or selectivity of piezoelectric chemical sensors has been enhanced by the addition of a concentration and/or separation stage for treatment of sample material before it is exposed to the sensor. Such work is in progress, for example, at Sandia National Laboratories, Albuquerque, NM and Microsensor Systems, Inc., Bowling Green, KY.

The inability to selectively determine a single chemical in the presence of interfering chemicals is a current limitation of piezoelectric, and most other types of chemical sensors. Selectivity improvements are being sought through sample pretreatment to remove interferents and through pattern recognition analysis of the responses from piezoelectric sensor arrays in which each array element has a different coating.

At Iowa State University (Analytical Instrumentation Center and Ames Laboratory) thin film resonator (TFR) measurement systems are being developed in a field deployable form. Support electronics for the

TFRs in the form of oscillator and mixer circuits have been developed as customized integrated circuits on a single chip. The small size and low power requirements of the TFRs and their support circuitry should make deployment of sizable arrays of these sensors quite feasible.

As in the case of fiber optic chemical sensors, major research will be directed to finding sensor coatings that will interact selectively with specific chemicals. Some coatings may be found via Edisonian experimentation based on known chemical interactions. Advances should also be made in the ability to predict interactions between coatings and species of interest via computational and other models founded on the rapidly increasing understanding of such interactions.

Additional development of arrays of piezoelectric chemical sensors, for which coating requirements are less demanding, is expected; new coatings and improved pattern recognition methods will also be sought. Also in the near term, efforts will be made to produce and couple more sophisticated sample treatment systems (chromatographs, etc.) with highly sensitive but not necessarily very selective sensors. Such chemical sensor systems would be both highly sensitive and selective.

Improvements in packaging for field deployment and optimization of the support electronics and noise reduction techniques are needed. Such improvements, addressed most efficiently by interdisciplinary teams of scientists and engineers, will certainly advance the application of piezoelectric chemical sensors.

Electrochemical Sensors

Electrochemical sensors determine analytes through measurements of their influence on the voltage, current, or conductance of an electrochemical cell[11-13]. For gas sensor applications, the most common types of electrochemical sensors are the semiconductor metal oxide sensor, which operates on the basis of changes in conductivity, and amperometric sensors.

Selectivity of response with semiconductor metal oxide sensors is obtained by mixing the oxide with a variety of dopants and by operation at different elevated temperatures. Amperometric gas sensors normally include a membrane where gases come into contact with the electrolyte of an electrochemical cell.

Electrochemical sensors exist and/or are under development for the measurement of gases such as CO, CO_2, H_2, SO_2, hydrocarbons, and chlorinated hydrocarbons. Improvements in selectivity and sensitivity may be required for many potential DOE applications.

Business Opportunities

A number of federal programs have been created to encourage private sector development of new technologies and the transfer of technologies developed in government laboratories. Cooperative Research and Development Agreements (CRADAs) require the private sector to provide in-kind matching funds to collaborate with government laboratories. Within the DOE, a program known as the Partnership for Global Competitiveness has been implemented to streamline the process of establishing CRADAs. Funding authority has been delegated to selected DOE contractors and the legal process has been standardized.

Three other programs provide grants for the development of commercializable technologies and do not require participation of government laboratories or contractors. These programs are:

Program Research and Development Announcements (PRDAs)

Research Opportunity Announcements

Small Business Innovation Research (SBIR) Program

These programs often focus on specific areas. Details and application procedures are published in the Federal Register and Commerce Business Daily.

The transfer of existing technology is encouraged by other programs as well. Within the Office of Technology Development of the DOE there is a Technology Integration Program designed for this purpose. Contact can be made via the following toll-free telephone number:

Technology Integration Program
Matt Cain
800 845-2096

A second program is the American Alliance for Environment and Trade. Its mission is to foster public/private partnerships for national technology development and applications. Contact may be made by calling:

American Alliance for Environment and Trade
Sheila Conway
303 279-2700

Finally, there is a mechanism for locating technology experts and special technical facilities within the federal laboratories. The Locator of the Federal Laboratory Consortium for Technology Transfer is the designated point of contact for all the federal laboratories. Inquiries can be made by calling:

Locator of the Federal Laboratory Consortium for
Technology Transfer
800 775-7445

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