

TENTH MEASUREMENT AND MONITORING LITERATURE UPDATE

2002 Student Projects: Environmental Remediation
NASA Langley Research Center, DEVELOP Program, 15 pp, Mar 2003

The Department of Defense asked the DEVELOP Environmental Remediation Team to use earth science to investigate pollution around military bases and to identify possible cleanup sites. Remote sensing data could be especially useful because of it has the ability not only to search a wide area but also to gather extensive data on specific locations. Six FUDS (Formerly Used Defense Sites) in Louisiana were selected for the project. Runoff from military installations on the NPL and FUDS Environmental Project list includes PCB, metal, and PAH contamination. An additional goal was to use remote sensing to observe any hull corrosion contamination that might be emanating from a fleet of 100 surplus ships moored in the estuary. The project relies a variety of remote sensing data to determine the extent of pollution near each military installation and to formulate a predictive model of pollution scope and concentration. These data include water, sediment, and aquatic life samples analyzed by the USGS and by the Virginia and Louisiana Departments of Environmental Quality. NASA's AVIRIS (Airborne Visual InfraRed Imaging Spectrometer) technology and Landsat TM (Thematic Mapper) data will facilitate analysis. The health effects and characteristics of each pollutant will be thoroughly researched. Disease data sets will be evaluated for the populations surrounding each site. All data will be incorporated into a three-dimensional visualization, allowing the customer to estimate the status of the environmental situation without sorting through lists of data. A predictive model will be developed, enabling visuals to illustrate the ecological future of each military installation. DEVELOP is a student-run applications, outreach, and workforce development project led by NASA Langley Research Center. Students bridge the gap between earth science information and communities through the use of immersive visualizations. The pilot projects employ remote sensing and other earth science information to create 3D visuals that aid communities in solving local problems. DEVELOP "layers" multiple sources of information to create one meaningful visualization.

<http://develop.larc.nasa.gov/projects/2002/env-rem/>
<http://develop.larc.nasa.gov/projects/2002/env-rem/develop-2002-envremediation.pdf>

Advanced Fuel Hydrocarbon Remediation National Test Location: Site Characterization and Analysis Penetrometer System

Heath, J.; E. Lory, U.S., Naval Facilities Engineering Service Center, Port Hueneme, CA.
NFESC-TDS-2016-ENV(REV), NTIS: ADA323566, 2 p, Mar 1997

The site characterization and analysis penetrometer system (SCAPS) with laser induced fluorescence (LIF) sensors are being demonstrated as a quick field screening techniques to determine the physical and chemical characteristics of subsurface soil and contaminants at hazardous waste sites. SCAPS is a collaborative development effort of the Navy, Army, and Air Force under the Tri-Service SCAPS Program. The current SCAPS configuration is designed to quickly and cost effectively distinguish areas contaminated with petroleum products (hydrocarbons) from unaffected areas.

<http://handle.dtic.mil/100.2/ADA323566>

Advances in Cone Penetrometer Technology
Yilmaz, Recep, Fugro Geosciences Inc., Houston, TX.

CIGMAT 2000. University of Houston, Center for Innovative Grouting Materials and Technology (CIGMAT).

Cone penetration testing (CPT) has been routinely used as a site investigation tool in Europe for almost 75 years and is now recognized throughout the world as a viable method of obtaining soils information. The principal reasons for acceptance and increased use of the CPT in recent years are the accuracy and detailed nature of CPT data, the fact that the test is conducted in-situ eliminating sample disturbance and changed stress conditions, and the relative speed and economy of the method as compared to conventional drilling and sampling.

Static cone penetration testing equipment consists of four major components:

- [1] a thrusting mechanism (usually hydraulic) for pushing the cone into the ground,
- [2] a thrust reaction system consisting of screw anchors or dead weight,
- [3] the electronic cones and associated push rods, and
- [4] a resistance measurement system.

The cone penetrometer normally contains two resistance strain gauge load cells for independent measurements of tip and friction resistances. Electric signals from the load cells are transmitted through an electrical cable running inside the hollow push rods and are recorded by a computer acquisition system at the surface. The cone is pushed into the ground at a rate of 2 cm/sec to depths in excess of 100 feet. Recent advances include the ROST(TM) technology and GeoVIS (Soil Video Imaging System).

http://cigmat.cive.uh.edu/content/conf_exhib/00_present/5.htm

Alternatives for Landmine Detection

MacDonald, Jacqueline, et al.

The Rand Institute, Washington, DC. ISBN: 0-8330-3301-8, 350 pp, 2003

The United States currently invests about \$100 million annually in humanitarian mine clearance—the largest commitment of any country. Despite this investment and the funding from many other developed nations and nongovernmental organizations, at the current rate clearing all existing mines could take 450–500 years. This report addresses the following questions:

What innovative research and development (R&D) is being conducted to improve antipersonnel mine detection capabilities?

What is the potential for each innovative technology to improve the speed and safety of humanitarian demining?

What are the barriers to completing development of innovative technologies?

What funding would be required, and what are the options for federal investments to foster development of promising mine detection technologies?

The report focuses on close-in detection of antipersonnel mines rather than on airborne or other remote systems for identifying minefields. The report was written by RAND S&TPI staff and a task force of eight experts in mine detection from universities and U.S. and Canadian government agencies. In addition, 23 scientists provided background papers with details on 13 specific mine detection technologies; these papers are published in this report as separate appendixes.

<http://www.rand.org/publications/MR/MR1608/>

Ammonia Detection by Use of Near-Infrared Diode-Laser-Based Overtone Spectroscopy

Claps, R.; F.V. English; D. Leleux; D. Richter; F.K. Tittel; R.F. Curl, Rice Univ., Houston, TX.

Applied Optics, Vol 40, p 4376-4386, 2001

The authors describe the performance of a trace gas sensor based on overtone absorption spectroscopy at 1.53 μm , applied to ammonia and carbon dioxide detection in a bioreactor exhaust line, with a time resolution of 30 s and a sensitivity of 0.7 ppm at a signal-to-noise ratio value of 3. This sensor has advantages compared with other methods in that it is compact, portable, simple to operate, and can perform near-real-time measurements. The ammonia concentration measurements reveal a dynamic behavior of the bioreactor that could not be detected and measured otherwise. These measurements also indicate that during the period of the study ammonia emissions into the environment remained below harmful levels. The sensor performed simultaneous NH_3 and CO_2 measurements in real time. A clear anti-correlation between the concentrations of these two gases was observed, which is in agreement with the expected operating conditions of the NASA JSC bioreactor. The diode-laser-based ammonia sensor can be used to monitor other gases in other applications, especially those with concentration levels of 1 ppm and higher, that need to be monitored with a fast response. The DFB diode laser or a tunable multi-wavelength DFB diode-laser source provides additional wavelength channels for multispecies gas detection.

<http://www-ece.rice.edu/lasersci/detectio.html>

Anticipating Sediment Bed-to-Water Column Exchanges of Toxic Organic Compounds in Naval Harbors

Geyer, W.R.; P.M. Gschwend, Woods Hole Oceanographic Inst., MA.

Report No: ADA408137, 13 pp, Oct 2002

This study explored the importance of sediment resuspension on the distribution of hydrophobic organic contaminants in urban estuaries. The study consisted of three components. (1) A passive in situ sampler, the polyethylene device (PED) was developed and tested. (2) The desorption rate of pyrene, a polycyclic aromatic hydrocarbon, was quantified from native Hudson River sediments. And (3) a field study was conducted to quantify the influence of sediment resuspension in the lower Hudson estuary on the distributions of pyrene and PCB 52.

<http://handle.dtic.mil/100.2/ADA408137>

Application of Compound Specific ^{13}C Isotope Investigations of Chlorinated Hydrocarbons in Contaminated Groundwaters

Osenbrueck, K.; M. Heidinger; A. Voropaev; S. Ertl; L. Eichinger, Hydroisotop GmbH, Schweitenkirchen, Germany.

Proceedings of the Study of Environmental Change Using Isotope Techniques. International Atomic Energy Agency, Vienna (Austria). IAEA-CSP-13/P, 476-477, 2002 [Paper No: IAEA-CN-80/36P, OSTI: DE20328892]

The determination of the stable isotope ratio C-13/C-12 of chlorinated hydrocarbons in ground water offers a promising tool to investigate the origin and the biodegradation characteristics of complex contamination situations with overlapping contaminant plumes. The application of the method is based on characteristic isotope fingerprints, which differ in chlorinated solvents. The isotope fingerprint derives from different production pathways and is not influenced by transport or by retardation processes in the underground. Due to the fact that two different contaminants can be distinguished by isotope ratios, an improved distinction of spatially and temporally different contamination plumes is possible. During biologically mediated degradation processes such as denitrification or sulfate reduction, a shift of the isotope ratios between the precursor and the product often can be observed. The

isotope fractionation is due to a preferential reaction of the bonds formed by the lighter isotopes and leads to a progressive enrichment of the heavy isotopes in the precursor, while the product becomes depleted in the heavy isotopes. Biological degradation of highly chlorinated hydrocarbons results from co-metabolic dechlorination. Isotope ratios can be used to assess and quantify the degradation of the organic compounds at field sites. This application holds great interest for remediation strategies, including monitored natural attenuation. The author examined the results of 21 field studies where compound-specific C-13 isotope ratios had been applied. Isotope fractionation processes of chlorinated hydrocarbons due to biodegradation were not seen in all cases, and the author concludes that the occurrence and the degree of significant isotope fractionation of chlorinated hydrocarbons is still an open question whose answer may vary with the activity and type of the microbiological species, availability of cosubstrates, and hydrochemical and hydrogeological conditions. NOTE: the URL links to the Proceedings in their entirety and the file may be very slow to load.

http://www-pub.iaea.org/MTCD/publications/PDF/CSP-13-P_web.pdf

Applications of Kalman Filtering to Real-Time Trace Gas Concentration Measurements

Leleux, D. (Rice Univ., Houston, TX); R. Claps; W. Chen; F.K. Tittel; T.L. Harman.

Applied Physics B, Vol 74, p 85-93, 2002

The researchers demonstrated an automated trace gas sensor in which the use of a Kalman filter significantly improved the detection sensitivity of the diode-laser-based gas sensor by a factor of two to six when using 1.5 μm overtone absorption lines and by a factor of 7.5 when performing ammonia concentration measurements at 10 μm with fundamental absorption lines. The sensor required no operator intervention during data collection. This paper discusses both the theory and implementation of a practical Kalman filter and analyzes limitations of certain aspects of this technique. In the operation of the Kalman filter with two different dynamic ranges corresponding to the two gases used, detection sensitivity factor improvements of six and two were observed at concentration levels of 4 and 1500 ppm for NH_3 and CO_2 , respectively. One limitation of the Kalman filtering technique as presented in this paper is the fact that it must operate on concentration values after a data processing algorithm has reduced them. A potentially more accurate method would be to operate the filter directly on the absorption profile output of the detector prior to the non-linear least-squares fitting routine.

<http://www-ece.rice.edu/lasersci/detectio.html>

Assessment of Perchlorate Releases in Launch Operations

Lang, V.I.; K.R. Bohman; J.T. Tooley; E.W. Fournier; B.B. Brady, Aerospace Corp., El Segundo, CA. Report No: TR-2001(1306)-3, NTIS: ADA396842. 44 pp, Oct 2001

An overall approach to the assessment of potential perchlorate releases from launch operations is presented. Two particular aspects of the assessment have been addressed to date. Laboratory studies to determine the effects of salinity and temperature on the chemical kinetics of perchlorate release from solid rocket motor propellant were conducted. The results showed an increase in the rate of perchlorate loss with increasing temperature and a decrease in the rate with increasing salinity. Second, a methodology developed for evaluating solid rocket motor propellant dispersal in the event of a catastrophic failure was applied to several failed historic launches, as well as to Delta IV and Atlas V cases.

<http://handle.dtic.mil/100.2/ADA396842>

Benzene Concentration Measurements Using Difference Frequency Laser Absorption Spectroscopy
Chen, Weidong (Univ. du Littoral, Dunkerque, France); F. Cazier; F.K. Tittel; D. Boucher.
Applied Optics, Vol 39 No 33, p 6238-6242, 20 Nov 2000

Benzene vapor has been successfully detected and quantified with a tunable DFG-based spectrometer in the ν_4 band at $\sim 15\ \mu\text{m}$. The signal-to-noise ratio of ~ 15 deduced from this spectroscopic measurement corresponds to a minimum detectable concentration of ~ 11.5 ppm. Increased sensitivity at ppm levels should be attainable by long-path absorption spectroscopy in combination with software signal filtering and enhanced data-acquisition techniques.

<http://www-ece.rice.edu/lasersci/detectio.html>

Bio-Agent Identification Based on Tandem Mass Spectrometry of Protein Biomarkers
McLuckey, S.A.; G.E. Reid; J.M. Hogan; M. He; K.A. Newton; H. Shang; G.U. Lee, Purdue Univ.,
West Lafayette, IN.
224th ACS National Meeting, 18-22 August 2002, Boston, MA.
American Chemical Society. Division of Analytical Chemistry: Abstract No 223, 2002

The authors are developing an approach for the detection and identification of toxins, viruses, and pathogenic bacteria based on the use of proteins as bio-markers. The approach relies on the formation of gaseous protein ions via electrospray ionization followed by dissociation of mass-selected ions. A key aspect to the approach is the use of gas-phase proton transfer chemistry to manipulate precursor and product ion charge states. This chemistry simplifies product ion interpretation and enables the concentration and purification of protein ions present in complex mixtures of ions derived from multiple proteins. The success of the overall approach depends upon a variety of key elements. These include, among others, ion/ion reactions for charge state manipulation, protein ion fragmentation chemistry, mass analysis figures of merit, and the derivation of protein information from mass spectral data. Significant progress has been made in these and other areas. Examples will be given for the concentration/ purification/dissociation of protein ions derived from mixtures of proteins comprised of at least thirty components. Furthermore, strategies for using whole protein ion MS/MS data for protein identification will be described along with examples of the identification of a priori unknown proteins in mixtures derived from HPLC fractions of whole cell lysates.

Bright Light Source Monitors Bacterial Chromium Reduction
Wilson, Elizabeth, Univ. of Massachusetts, Amherst.
Chemical & Engineering News, 30 Aug 1999

New insight into the ability of certain bacteria to reduce toxic Cr(VI) to less harmful Cr(III) comes from staff scientist Hoi Ying Holman and colleagues at Lawrence Berkeley National Laboratory in Berkeley, CA. Using LBNL's bright Advanced Light Source (ALS), they monitored in real time and with unprecedented resolution a bacterial colony and the disappearance of Cr(VI) and corresponding appearance of Cr(III). Their study shows that the bacterial process is by far the most important pathway for Cr(VI) reduction in geological materials. Thanks to the $10\text{-}\mu\text{m}$ spatial resolution afforded by the brightness of IR light obtained from the ALS, the group could produce spectromicroscopic "images" whose peaks and valleys show the locations of the action. Fortuitously, a protein in the bacteria, the chromium species, and toluene all have well-characterized IR absorption bands. Most important, the IR

light, despite its brightness, doesn't destroy the bacteria, as many other analytical techniques used to study these types of systems do.

<http://zdna.micro.umass.edu/press/1999-08-30-chemeng.pdf>

Broadband LIBS: A Powerful New Tool for Chemical Analysis in the Field

Miziolek, Andrzej (U.S. Army Research Laboratory); Richard Wainner; Kevin L. McNesby; Russell Harmon, Patrick French.

The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana.

Laser-induced breakdown spectroscopy (LIBS) is a relatively simple and elegant technique where a high-power laser pulse is focused on a material of interest resulting in a spark which is spectrally analyzed for information concerning the chemical composition and concentration of the analyzed material. Traditionally, the spectral detection has focused on emission from a particular element. This is partly due to resolution requirements and the fact that the full emission spectrum (say, 200-900 nm) is a virtual sea of information, in which nearly every element emits. However, such a broadband spectral profile provides an excellent signature for interrogated compounds, as well as concentration information on particular elements, both useful for molecular identification. Also, the advent of LIBS systems coupled with echelle spectrographs is eliminating any issues of resolution for broadband detection. Narrowband work in our lab has included the detection of Pb contamination in soil, groundwater, and paint and have assisted in the development of fieldable prototypes. Quasi-broadband LIBS has been used in our laboratory to detect and identify trace amounts of hazardous compounds such as explosives (organo- nitro and inorganic, e.g. RDX and black powder), chemical warfare agent simulants (e.g., DMMP), several halocarbon fire inhibitors, refrigerants, and candidate halon alternatives (e.g., Halon 1301 and FM-200), as well as various other materials (e.g., plastic and steel). The plasma emission spectra have shown a high degree of sensitivity with single laser shots. With the advent of wider-scale use of broadband-LIBS, the application range of this already powerful field analytical sensor technology will be greatly increased.

Capabilities and Limitations of a Cone Penetrometer Deployed Fiber Optic Laser Induced Fluorescence (LIF) Petroleum Oil and Lubricant (POL) Sensor

McGinnis, W.C.; M. Davey; K.D. Wu; S.H. Lieberman, U.S. Naval Command, Control and Ocean Surveillance Center, San Diego, CA.

NTIS: ADA350581, 16 pp, 1995

This paper presents data from a new field-screening technique using a fiber-optic laser-induced fluorescence (LIF) petroleum, oil, and lubricant (POL) chemical sensor deployed from a truck-mounted cone penetrometer. The system provides real-time, in situ measurement of petroleum hydrocarbon contamination and soil type to a maximum depth of 150 feet with a vertical spacing of two inches. Each depth measurement records the fluorescent spectrum from 350 to 720 nm. Spectral signatures can be used to track single or multiple contaminants across a site. Real-time measurement permits on-site interpretation and "plume chasing." Field data from SCAPS (Navy) field operations are presented to show how the system can be used for rapid three-dimensional delineation of a POL contaminant plume.

<http://handle.dtic.mil/100.2/ADA350581>

A Chemical-Detecting System Based on a Cross-Reactive Optical Sensor Array

Dickinson, T.A.; J. White; J.S. Kauer; D.R. Walt.

Nature, Vol 382, p 697-700, 1996

The vertebrate olfactory system has long been recognized for its extraordinary sensitivity and selectivity for odours. Chemical sensors have been developed recently that are based on analogous distributed sensing properties¹⁻⁴, but although an association between artificial devices and the olfactory system has been made explicit in some previous studies^{4,5}, none has incorporated comparable mechanisms into the mode of detection. Here we describe a multi-analyte fibre-optic sensor modeled directly on the olfactory system, in the sense that complex, time-dependent signals from an array of sensors provide a 'signature' of each analyte. In our system, polymer-immobilized dye molecules on the fibre tips give different fluorescent response patterns (including spectral shifts, intensity changes, spectral shape variations⁶ and temporal responses) on exposure to organic vapours, depending on the physical and chemical nature (for example, polarity, shape and size) of both the vapour and the polymer. We use video images of temporal responses of the multi-fibre tip as the input signals to train a neural network for vapour recognition. The system is able to identify individual vapours at different concentrations with great accuracy. 'Artificial noses' such as this should have wide potential application, most notably in environmental and medical monitoring.

Chemical Sensing Applications with Pulsed QC-DFB Lasers Operating at 15.6 μm

Kosterev, A.A. (Rice Univ., Houston, TX); F.K. Tittel; R.F. Curl; M. Rochat; J. Faist.

Applied Physics B, Vol 75, p 351-357, 2002

Researchers characterized pulsed thermoelectrically cooled QC-DFB lasers operating at 15.6 μm for spectroscopic gas sensing applications and developed a new method for wavelength scanning based on repetition rate modulation. A non-wavelength-selective pyroelectric detector was incorporated in the sensor configuration, which promoted the advantage of room-temperature operation and low cost. The lasers were used to scan CO_2 and H_2O in ambient air, providing information about the concentration of these species.

http://www-ece.rice.edu/lasersci/ApplPhysB_Kosterev.pdf

Chemical Sensors Based on Quantum Cascade Lasers

Kosterev, Anatoliy A.; Frank K. Tittel, Rice Univ., Houston, TX.

IEEE Journal of Quantum Electronics, Vol 38 No 6, p 582-591, June 2002 [Special Issue on Quantum Cascade Lasers]

Since 1998, the usefulness of gas sensors based on mid-infrared CW and pulsed QC-DFB lasers has been demonstrated to be potentially capable of numerous applications in areas such as environmental monitoring (atmospheric chemistry, volcanic plume emissions), industrial emission measurements (e.g., fenceline perimeter monitoring, combustion sites, waste incinerators, gas down-well monitoring, and gas-pipe and compressor-station safety). The authors have employed QC-DFB lasers for the monitoring and quantification of several trace gases and isotopic species in ambient air at ppmv and ppbv levels by means of direct absorption, wavelength modulation, and cavity enhanced and cavity ringdown spectroscopy.

<http://www-ece.rice.edu/lasersci/detectio.html>

Chemical Sensors Using Quantum Cascade Lasers

Kosterev, A.A.; R.F. Curl; F.K. Tittel.

Laser Physics, Vol 11, p 39-49, 2001

Detection of trace gases in ambient air was demonstrated with both cw and pulsed Quantum Cascade Distributed Feedback lasers. Pulsed QC-DFB lasers can be used at near room temperature for high-sensitivity detection of simple molecules when a spectral resolution of ~ 300 MHz is sufficient. The cw-operated laser showed a sensitivity of 3.5×10^{-5} absorption, and the pulsed QC-DFB laser-based spectrometer a sensitivity of 1.7×10^{-4} . For detection of complex molecules with congested spectra the use of cryogenically cooled cw lasers offer an advantage of high spectral resolution. This mode of operation is preferable if accurate spectroscopic information is required.

<http://www-ece.rice.edu/lasersci/detectio.html>

Combined imaging and chemical sensing of fertilization-induced acid release from single sea urchin eggs

Michael, K.L.; D.R. Walt.

Analytical Biochemistry, Vol 273, p 168-178, 1999

We demonstrate a microarray sensor capable of obtaining both chemical and visual information on multiple cells simultaneously with single-cell resolution. The array was fabricated by covalently immobilizing a thin, pH-sensitive polymer layer on the distal end of an optical imaging fiber. The sensor's ability to measure localized chemical dynamics in real-time was evaluated using sea urchin fertilization biochemistry as a model system. Following sea urchin fertilization the Na^+/H^+ transporter is activated to exchange extracellular sodium ions for intracellular hydrogen ions, causing a release of hydrogen ions at the egg's surface. By placing the pH sensor proximal to the egg and switching between a fluorescence image and a white light image, we were able to observe both localized pH changes following fertilization as well as morphological transformations during cell division.

Compact Diode Laser-Based Wave-Mixing Spectroscopy for High-Resolution Gas-Phase Hyperfine Applications

Briggs, Ron D.; Wendy J. Lyons; William G. Tong, San Diego State Univ., San Diego, CA.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 178, 2002

Gas-phase atomic species play important roles in atmospheric processes including ozone depletion and the formation of many pollutants such as acid rain. Traditional optical measurement of these species has proven to be difficult due to the fact that the strongest resonance lines lie in the far ultraviolet region. Using a home-made hollow cathode discharge atomizer, an inexpensive diode laser excitation source, and a simplified nonlinear absorption optical setup, we can detect many important elements with hyperfine-level spectral resolution using convenient visible wavelengths.

Compact Mid-Infrared Trace Gas Sensor Based on Difference-Frequency Generation of Two Diode Lasers in Periodically Poled LiNbO_3

Richter, D. (Rice Univ.); D.G. Lancaster; R.F. Curl; W. Neu; F.K. Tittel.

Applied Physics B, Vol 67 No 3, p 347-350, 1998

The advent of novel enabling technologies involving room-temperature diode lasers, efficient nonlinear optical materials, optical fibers, and non-cryogenic infrared detectors has made it possible to investigate a new device architecture for laser-based difference frequency generation (DFG) gas sensors that is particularly suited for the 3-5 μm spectral region. This paper reports on the development and characterization of a compact mid-infrared source for high-resolution spectroscopic detection of trace gases such as methane and water vapor at 3.3 μm in ambient air. This source utilizes DFG in a periodically poled LiNbO₃ (PPLN) crystal pumped by two single-frequency diode lasers. A maximum DFG power of 1.6 μW at 3.6 μm was generated with a pump power of 61.4 mW at 832 nm and a signal power of 41.5 mW at 1083 nm incident on a 19-mm-long PPLN crystal.

<http://www-ece.rice.edu/lasersci/detectio.html>

Comparison of Methods for Particulate Phase Mercury Analysis: Sampling and Analysis

Lynam, Mary M.; G.J. Keeler, Univ. of Michigan Air Quality Laboratory, Ann Arbor.

Analytical and Bioanalytical Chemistry, Vol 374 No 6, p 1009-1014, Nov 2002 [NTIS: DE20314753]

Accurate and reliable sampling and analysis of mercury forms is an overriding aim of any atmospheric monitoring effort which seeks to understand the fate and transport of the metal in the environment. Although a fraction of the total mercury forms found in the atmosphere, particulate phase mercury, Hg, is believed to play a prominent role in both wet and dry deposition to the terrestrial and aquatic environments. Currently, microwave acid extraction and thermoreductive methodologies for analysis of Hg samples are widely used. We report on the potential for the use of a thermoreductive method for Hg analysis to evaluate and optimize it for use in routine monitoring networks. Pre-baked quartz filters can be placed in particulate samplers with well-characterized size cuts, such as dichotomous samplers and microorifice impactors. The thermoreductive methodology facilitates rapid analysis after sample collection. It requires no chemical extraction thereby eliminating the potential for contamination and generation of hazardous waste. Our results indicate that, on average, the thermoreductive method yields 30% lower values for fine fraction Hg when compared with microwave acid digestion. This may be due to matrix interferences that reduce the collection efficiency of mercury onto gold preconcentration traps. Results for total particulate mercury samples indicate that on average the thermoreductive method yields 56% lower values for the coarse fraction when compared with microwave acid digestion.

A Comparison of Ultra-Short and Nanosecond Laser Pulses for LIBS

Eland, Kristine L. (Univ. of South Carolina); Dimitra N. Stratis; S. Michael Angel; Mark A. Berg; David M. Gold.

The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana. Presentation 1398, 2001

Laser-induced breakdown spectroscopy (LIBS) is a relatively simple and rapid form of elemental analysis that employs a pulsed laser to create a plasma on virtually any type of sample surface. With LIBS, minimal sample preparation is needed and the sample only needs to be optically accessible, making remote and on-line analysis feasible, but the processes involved in laser-induced plasma formation are complex, and LIBS suffers from poor precision and detection limits compared to other forms of elemental analyses. Ultra-short laser pulses, <10 ps, have been used in materials processing and micro-machining applications because of the ability to more precisely control ablation of materials, resulting in more reproducible hole formation. This results, in part, because the energetic pulse removes material before thermal conduction can heat the surrounding material leading to minimal thermal

damage and melting. The advantages of ultra-short laser pulses have never been extended to analytical applications of LIBS; thus we have begun LIBS studies using ultra-short, 1.3 ps and 140 fs, laser pulses on a variety of materials including conductors, non-conductors and semi-conductors. The plasma created by the use of ultra-short pulses is qualitatively different compared to the use of ns pulses. For example, the plasma is smaller, and atomic-line and background intensities decay much more rapidly than with ns pulse excitation. We have also seen that the plasma seems to dissipate relatively quickly, and because of this LIBS spectra can be obtained using a non-gated detector, with very little continuum background emission. We present results obtained using 1.3 ps and 140 fs pulses on samples including copper, steel and glass, and compare those results to those obtained using ns pulses for excitation. Non-gated LIBS spectra are also shown using ultra-short laser pulses.

Conjugated Polymers as Fluorescent Explosives Detectors

Anderson, J.E. (U.S. Army Engineer Research and Development Center, Alexandria, VA), R.L. Fischer, C.B. Smith; S.P. Gardner (Physical Sciences, Inc., Andover, MA).
23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, EP-18, 2 pp, 2002

Unexploded ordnance (UXO) from buried landmines and waste munitions are a threat to both military and civilian populations. The goal was to develop a polymer-based formulation through which the presence of nitro-aromatic compounds could be detected by active fluorescence. The design goal for the fluorescent polymer was fluorescence quenching of at least 2% upon interaction with explosive materials and that its fluorescence is detectable from a distance of at least 30 m at night. The fluorescent polymer, MBS-PPV, demonstrates a 15% reduction in fluorescence upon interaction with soil containing 5 ppm TNT. This level of contrast is significantly higher than the 2% contrast needed to detect the presence of explosive material in soil. The Stern-Volmer relationship indicates that the detection of explosive compounds in soil at concentrations of >0.5 ppm is feasible and that the fluorescence can be easily detected from 30 m in daylight and >500 m at night. By gaining a better understanding of the interaction between soil components and the explosives detection formulation, we can develop a highly sensitive, explosive material detection formulation.

<http://www.asc2002.com/>

Convergent, Self-Encoded Bead Sensor Arrays in the Design of an Artificial Nose

Dickinson, T.A.; K.L. Michael; J.S. Kauer; D.R. Walt.
Analytical Chemistry, Vol 71, p 2192-2198, 1999

The authors report a new approach to designing an artificial nose based on high-density optical arrays that directly incorporate a number of structural and operational features of the olfactory system. The arrays are comprised of thousands of microsphere (bead) sensors, each belonging to a discrete class, randomly dispersed across the face of an etched optical imaging fiber. Beads are recognized and classified after array assembly by their unique, "self-encoded" response pattern to a selected vapor pulse. The high degree of redundancy built into the array parallels that found in nature and affords new opportunities for chemical-sensor signal amplification. Since each bead is independently addressable through its own light channel, it is possible to combine responses from same-type beads randomly distributed throughout the array in a manner in the mammalian olfactory system. Signal-to-noise improvements of approximately $n^{1/2}$ have been achieved using this method.

Demonstration of a Multi-Metal CEM

Hay, K.J. (U.S. Army Engineer Research and Development Center); J.A. Cooper and B.E. Johnsen (Cooper Environmental Services).

23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, EP-02, 2 pp, 2002

A multi-metal CEM has been developed using x-ray fluorescence as the analytical method and an automated sampling system that provides extractive batch sampling on to a resin impregnated filter tape (XCEM). An isokinetic sample is taken from the stack using a probe and transported to three-inch diameter stilling chamber. A representative sub-sample is then drawn through a 1/4-inch diameter extraction tube to a 0.3 square cm spot on the tape, which is then advanced to the detector. There are two sampling cassettes that contain filter tape that can be easily exchanged for continuous operation. The monitor is capable of measuring 19 elements simultaneously once every 20 minutes. The system has been integrated with user-friendly Wonderware® software that provides sensor integration, automation, quality assurance routines, calibration routines, and report generation. The equipment includes the quality control automated features such as a stability check with every sample, daily zero and span checks, a filter seal check with each sample, flags and alarms when data are outside of specifications, a backup flow meter for flow controller verification, and programmed fixed interelement relationships. Because the x-ray fluorescence analysis is nondestructive, post-analysis verification can take place by analyzing the spent filter tape.

<http://www.asc2002.com/>

Design of a Highly Lead Selective Fluorionphore Sensor

Fitch, Alanah; Audrius Zukas, Loyola Univ., Chicago, IL.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 30, 2002

A highly selective lead fluorionophore sensor was developed. The starting point was the identification of structural characteristics of lead binding to a common calcium fluorometric reagent. Based on the differences in binding between Calcein Blue with calcium and lead the structure of Calcein Blue was altered to increase lead selectivity while maintaining a change in the fluorescence output of the reagent. The reagent is selective only to lead and copper and the selectivity ratio of lead to copper is between 200 to 300. The reagent was subsequently functionalized with an aliphatic tail and immobilized within a PVC membrane. The reagent retains the desired lead selectivity within the membrane.

Detection and Measurement of Explosives in Groundwater Using In Situ Electrochemical Sensors

Olsen, Khrist B.; Joseph Wang, Battelle Pacific Northwest National Labs., Richland, WA.

NTIS: ADA409108, 27 pp, May 2002

The results of this study demonstrate that remotely-deployable submersible sensors are capable of monitoring explosive compounds both temporally and spatially in ground water and can be more cost-effective than conventional sampling and analysis. Such new remote-sensing capability can bring significant changes to the way in which nitro-based explosives are monitored. This technology can be deployed in standard ground-water wells that are 1.5 inches or greater in diameter. Future modification of the sensor probe could decrease the probe size to less than 3/4 inch to accommodate installation with minimally invasive direct-push technologies, such as a cone penetrometer or GeoProbe system. The

sensor measurement frequency can be easily changed from a remote location, enabling the investigator to tailor the measurement cycle to the speed at which the parameter in question is or may be changing. During the course of this SERDP SEED project, various working electrode materials and voltammetric waveforms were compared, and relevant experimental parameters were optimized. Based on initial testing, the researchers developed a submersible electrochemical probe using a carbon-fiber electrode assembly connected to a 50-foot-long shielded cable for the real-time monitoring of nitro-organic explosives in natural water. The facile reduction of the nitro moiety group allowed convenient and rapid square-wave voltammetric measurements of trace levels of nitroaromatic explosives (TNT, TNB, and Tetryl) down to levels of 50 to 100 pb.

<http://handle.dtic.mil/100.2/ADA409108>

Detection of Chemical Warfare Agents by Catalytic Hydrolysis Based on a Porous Silicon Interferometer

Sohn, Honglae; Michael J. Sailor; William C. Trogler, Univ. of California, San Diego.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Colloid and Surface Chemistry: Abstract No 362, 2002

Incorporation of catalysts for hydrolysis of phosphonate esters into the surface oxidized layer of a porous silicon thin-film Fabry-Perot interferometer produces a sensor selective for the detection of diisopropylfluorophosphonate (DFP), which is a simulant for the closely related fluorinated CW agents Sarin, Soman, and GF. Hydrolysis of the nerve agent produces HF gas, which removes the silicon oxide as SiF₄ (g) and induces both a blue shift and a decrease in intensity of the Fabry-Perot fringes. The intensity of the reflectivity fringes decreased about 10% and blue shift in the optical thickness are detected after 5 min of DFP vapor (800 ppm) exposure with TMEDA[Cu(II)] catalyst. This implies that the predominant change in the refractive index occurs at the surface of the porous layer. With micellar TMEDA[Cu(II)] catalyst, we observed a significant blue shift in the optical thickness without decreasing intensity in the reflectivity fringes, indicating that the predominant change occurs in pores of the porous silicon. Detection of DFP using other catalysts will be addressed.

The Determination of Perchlorate Anion in High Ionic Strength Samples

Thomas, D.H.; J.S. Rohrer, Dionex Corporation.

International Labmate, Vol 27 No 2, Apr 2002

Problems of perchlorate anion contamination in drinking and groundwater require a reliable and accurate means of measurement both to identify contaminated water directly and to understand the sources of the contamination. This article focuses on an application of ion chromatography with on-line eluent generation and suppressed conductivity detection for the determination of perchlorate contamination in water derived from materials such as fertilizers and inorganic salts.

<http://www.product-search.co.uk/internationallabmate.com/features/april2002/dionex.shtml>

Determination of Perchlorate in Drinking Water by Ion Chromatography

Saari-Nordhaus, R. (Alltech Associates, Inc., Deerfield, IL); D.R. Douglas, P. Despres.

The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana. Abstract 2284P, 2001

Ammonium perchlorate is used as an oxidizer in solid propellant of rockets, missiles, and fireworks. Recently, trace amount of perchlorate is found in drinking water in areas where these devices have been manufactured and tested. Since perchlorate interferes with the utilization of iodine and disrupts the production of thyroid gland, it's present in drinking water is a health hazard. Regulatory agencies have started to develop methods for the analysis of perchlorate in drinking water. U.S. Environmental Protection Agency (US EPA) method 314.0 determines perchlorate in drinking water using ion chromatography. The perchlorate ion is very hydrophobic and it usually retains very strongly on most anion exchange columns used in ion chromatography. A new column that is hydrophilic has been developed to reduce the retention time and improve the peak shape. This paper describes the analysis of perchlorate in drinking water using the new column and discusses the optimized mobile phase conditions, method detection limits, and linearity of the calibration curves.

Determination of Trace-Level Perchlorate According to U.S. EPA Method 314.0 Using a Polyvinyl Alcohol Gel Resin

De Borba, Brian M.; Derrick W. Rowe, Metrohm-Peak, Inc., Houston, TX.
American Laboratory News, p 22-24, Apr 2001

No National Primary Drinking Water Regulation (NPDWR) for has been determined for perchlorate as of 2001. In 1996, perchlorate was placed on the Contaminant Candidate List, which is not currently subject to the NPDWR. Data from the U.S. EPA suggest an action level from 4 to 18 $\mu\text{g/L}$ in order to provide adequate human health protection. Levels exceeding this range will require removal and proper treatment of the contaminated water source. In 1997, the California Department of Health Services and the Nevada Division of Environmental Protection established an action level of 18 $\mu\text{g/L}$. In 1999, Arizona and Texas set provisional action levels of 31 and 22 $\mu\text{g/L}$, respectively. This article discusses an improved method for the determination of trace levels of perchlorate. The method discussed required a large sample loop with a Metrosep A Supp 5 column, a hydroxide eluent modified with p-cyanophenol, and suppressed conductivity to quantitate down to the 2 $\mu\text{g/L}$ level. Other parameters, such as calibration linearity, method detection limit, matrix conductivity threshold, and recovery of perchlorate in various matrices also are discussed. In addition, the performance of a dedicated IC system (Metrohm 761 Compact IC, Metrohm-Peak, Inc., Houston, TX) is discussed briefly.

<http://www.iscpubs.com/articles/entirealn.html>

Development of a Soil Video Imaging System (SoilVIS) in Conjunction with a Profile Cone Penetrometer (PCP)

Lieberman, S.H. (SPAWAR Systems Center, San Diego, CA); D.J. Rooney (Univ. of Wisconsin-Madison), and B. Lowery.

1998 annual American Society of Agronomy/Crop Science Society of America/Soil Science Society of America Meeting, 18-22 October 1998, Baltimore, MD

A soil video imaging system has been designed for use in the soil environment. Rapid visualization of various soil attributes such as texture or color can have a dramatic impact on the efficiency and accuracy of soil sampling techniques. A truck-mounted, hydraulically driven cone penetrometer is used to push the system through the soil profile to view the soil strata. Soil in contact with the side of the probe is imaged through a sapphire window and lens with a miniature CCD color camera. The soil is illuminated with a diode emitting an array of white light and located in the probe. The video signal from the camera is returned to the surface in real time where it is displayed on a video monitor, recorded on a

video cassette recorder, and/or captured digitally with a frame grabber installed in a microcomputer system. The system images an area that is 2 x 2.5 mm, which provides a magnification factor of approximately 100 when viewed on a standard computer monitor. Contact: D.J. Rooney, (608) 262-0415, djrooney@students.wisc.edu.

Development of a Tunable Mid-IR Difference Frequency Laser Source for Highly Sensitive Airborne Trace Gas Detection

Richter, Dirk (National Center for Atmospheric Research, Boulder, CO); Alan Fried, Bryan P. Wert, James G. Walega, and Frank K. Tittel
Applied Physics B, Vol 75, p 281-288, 2002

The authors report on the development of a compact tunable mid-IR laser system at 3.5 μm for quantitative airborne spectroscopic trace gas absorption measurements. The mid-IR laser system relies on difference frequency generation (DFG) in periodically poled LiNbO₃ and utilizes optical fiber amplified near-IR diode and fiber lasers as pump sources operating at 1083 nm and 1562 nm, respectively. This paper describes the optical sensor architecture, performance characteristics of individual pump lasers, and DFG, as well as its application to wavelength modulation spectroscopy employing an astigmatic Herriott multipass gas absorption cell. This compact system permits detection of formaldehyde with a minimal detectable concentration of 74 parts per trillion by volume (pptv) for 1 minute of averaging time using calibrated gas standards, zero air background, and rapid dual-beam subtraction.

<http://www-ece.rice.edu/lasersci/detectio.html>

Development of Fluorescent Ion-Exchange Optode System Based on the "Host-Guest" Interaction and Their Applications in Metal Analysis

Chan, Wing Hong (Hong Kong Baptist Univ., Kowloon, Hong Kong), Albert W. M. Lee, Yiu Sing Lam; Ke-Min Wang (Hunan Univ.), Rong-Hua Yang.
224th ACS National Meeting, 18-22 August 2002, Boston, MA.
American Chemical Society. Division of Analytical Chemistry: Abstract No 159, 2002

Two new proton-selective fluorescing indicator, fluorescein octadecyl ether octadecyl ester (FODEE) and 3,3',5,5'-tetramethyl-N-(9-anthrylmethyl)benzidine (TMANB) were synthesized and applied in the optode membrane fabrication for the determination of sodium and lead ion, respectively on the basis of a cation-exchange mechanism. The membrane cocktails contain a lipophilic anionic site (potassium tetrakis(4-chlorophenyl)borate), the fluorescing indicator and metal ion ionophore in a plasticized poly(vinyl chloride) (PVC). Tert-butylcalix[4]arene tetraester and tert-butylcalix[4]arene-tetrakis(N,N-dimethylthio-acetamide) were used as the metal selective ionophore rendering a "host-guest" type interaction for the optical sensory systems and the metal analytes. Optodes exhibited reversible response to metal ions in the concentration range of 1.0×10^{-6} to 0.1 mol/L. The selectivity, response time, reproducibility and lifetime of the optode membrane were examined. The sodium-selective optode was used in the real sample analysis in beverage and urine samples whereas the lead-selective optode was applied for the environmental samples. The results were found in good agreement with those obtained by atomic spectrometry. Acknowledgements: The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong SAR, China (Project No. HKBU 2054/98P).

Development of Radon-222 as Natural Tracer for Monitoring the Remediation of NAPL in the Subsurface

Davis, Brian M.; Lewis Semprini; Jonathan Istok, Oregon State Univ.

Report No: DOE/ER/62523, 121 pp, Feb 2003

Naturally occurring 222-radon in ground water can potentially be used as an in situ partitioning tracer to characterize dense nonaqueous phase liquid (DNAPL) saturations. The static method involves comparing radon concentrations in water samples from DNAPL-contaminated and non-contaminated portions of an aquifer. During a push-pull test, a known volume of test solution (radon-free water containing a conservative tracer) is first injected ("pushed") into a well; flow is then reversed and the test solution/groundwater mixture is extracted ("pulled") from the same well. In the presence of NAPL, radon transport is retarded relative to the conservative tracer. Assuming linear equilibrium partitioning, retardation factors for radon can be used to estimate NAPL saturations. The utility of this methodology was evaluated in laboratory and field settings.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=809809&queryId=1&start=0

DNAPL Characterization Using the Ribbon NAPL Sampler: Methods and Results

Riha, B.D. (Savannah River Site, Aiken, SC); J. Rossabi; C. Eddy-Dilek; D. Jackson; C. Keller.

Treating Dense Nonaqueous-Phase Liquids (DNAPLs): Remediation of Chlorinated and Recalcitrant Compounds, 22-25 May 2000, Monterey, CA. Battelle Press, Columbus, OH. Also available as Paper No: WSRC-MS-2000-00182, 6 pp, Apr 2000

The Ribbon NAPL Sampler (RNS) is a direct sampling device that provides detailed depth discrete mapping of non-aqueous phase liquids (NAPLs) in a borehole. This characterization method provides a yes-or-no answer to the presence of NAPLs and is used to complement and enhance other characterization techniques. Several cone penetrometer deployment methods are in use and methods for other drilling techniques are under development. The RNS has been deployed in the vadose and saturated zones at four different sites. Three of the sites contain DNAPLs from cleaning and degreasing operations and the fourth site contains creosote from a wood preserving plant. A brief description of the process history and geology is provided for each site. Where available, lithology and contaminant concentration information is provided and discussed in context with the RNS results.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=754455

DNAPL Site Characterization: the Evolving Conceptual Model and Toolbox Approach

Rossabi, J., Savannah River Site, Aiken, SC.

Remediation of Chlorinated and Recalcitrant Compounds, 22-25 May 2000, Monterey, CA.

Paper No: WSRC-MS-2000-00183, 6 pp, 2000

In natural subsurface systems dominated by heterogeneity, the delineation and even the detection of sparingly soluble, dense contaminants can be extremely difficult. The performance assessment of cleanup at these sites is therefore more complex. Several technologies for the characterization of sites contaminated with dense non aqueous phase liquids have recently been developed. These include geophysical techniques, tracer tests, and direct sampling or sensing methods.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=755217

Electrochemical Sensors for the Transuranics

Russell, Dale D.; Jon M. Scaggs; Michael W. Hill, Boise State Univ., Boise, ID.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 150, 2002

Electrochemical sensors for the transuranics have been demonstrated, based a chelating group covalently bound to a conductive polymer. When the probe contacts a solution of the target ion, such as uranyl, it is preconcentrated in the polymer coating. Selectivity is achieved by both the large formation constant of the metal-chelate complex, and also by its electrochemistry. Binding the analyte on the surface changes several electrochemical properties of the polymer, including the characteristic i-E curve. In amperometric mode, current is proportional to uranyl ion concentration through a range of several orders of magnitude. The chelating molecule is calix[6]arene, which also binds other transuranics. The various species are distinguished based on their redox potentials. The sensing surface is integrated into a hand held instrument.

“Electronic Nose” Chip Microsensors for Chemical Agent and Explosives Detection

Lewis, Nathan S., Noyes Laboratory, Pasadena, CA.

23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, JP-02, 2 pp, 2002

Arrays of conducting polymer composite vapor detectors have been evaluated for performance in the presence of the nerve agent simulants dimethylmethylphosphonate (DMMP) and diisopropylmethylphosphonate (DIMP). Arrays of these vapor detectors were easily able to resolve signatures due to exposures to DMMP from those due to DIMP or due to a variety of other test analytes in a laboratory air background. In addition, DMMP at 27 mg/cubic meter could be detected and differentiated from the signatures of the other test analytes in the presence of backgrounds of potential interferents in the background.

<http://www.asc2002.com/>

Environmental Monitoring and Remediation Analysis of Explosives

Zakikhani, Mansour; D.W. Harrelson; J.C. Pennington; J.M. Brannon; M.K. Corcoran; J. Clark; W.A. Sniffen, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, EP-16, 2 pp, 2002

Waste disposal practices associated with manufacturing and loading, assembling, and packaging explosives during and before World War II and the Korean Conflict have resulted in contamination of soil and ground water with explosives. Monitored natural attenuation (MNA) is a relatively inexpensive approach to site cleanup compared to engineered remediation. Natural attenuation of explosives can take place through microbial mineralization, microbial transformation, and/or immobilization. Natural attenuation of explosives was studied at the Louisiana Army Ammunition Plant (LAAP) to establish through appropriate site monitoring that natural attenuation was occurring, to develop guidance for selecting monitored natural attenuation as a remediation alternative, and to develop a protocol for implementing MNA. Trends in contaminant concentration were generally static to declining over time. Results of batch and column tests indicated that the soils at LAAP have low sorptive capacity and slow transformation rates for the explosives. Biomarker results indicated low levels of direct and cometabolic

microbial activity against explosives. This paper discusses the protocol for MNA selection and implementation, and addresses regulatory issues associated with MNA for explosives cleanup.

<http://www.asc2002.com/>

Evaluation of Solid Phase Batch Extraction for Environmental Analysis

Furlong, Melanie R. (Univ. of Massachusetts, North Dartmouth, MA); John C. Schaumlöffel (SUNY College at Oneonta).

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 61, 2002

Solid phase extraction (SPE) has long been utilized for the quantitation of organic compounds in environmental samples. Traditional methods of implementing a solid phase extraction require bringing the sample to the laboratory for extraction, or performing lengthy extraction procedures in the field. This does not facilitate long term monitoring and would require numerous trips to the test site for sample collection. Our novel application of solid phase extraction can be used as a passive-sampling device in the field. This method is a variation of what is generally known as solid phase batch extraction. Initial, probative experiments demonstrate the reproducibility of the method for the extraction of xylenes under controlled, laboratory conditions. The experiments were conducted at various temperatures and analyte concentrations, using a commonly available solid phase prepared using relatively simple methods.

Evanescent Wave Immunosensors for Detection of Biohazards

Taitt, Chris Rowe; Frances S. Ligler; George P. Anderson, Naval Research Lab., Washington, DC.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 212, 2002

Researchers at the Naval Research Laboratory have developed fiber optic and array biosensors capable of detecting multiple analytes simultaneously in less than 15 minutes. Antibodies are immobilized on optical fibers or in patterned arrays on planar waveguides and are used to “capture” analyte present in the samples. The presence of bound analyte(s) is determined by interrogating the waveguide with fluorescently labeled tracer antibodies. Using evanescent excitation of the fluorescent “sandwiches”, we can detect, identify, and quantify a number of inactivated pathogens, toxins, viruses, simulants for biohazardous agents, and physiological markers in a variety of sample matrices, including body fluids (urine, blood, nasal swabs, fecal extracts), clay and sand suspensions, and smoke extracts. Up to 9 analytes can be detected simultaneously. Furthermore, we have been able to demonstrate real time binding of analyte and have determined antibody-antigen association rates. The fiber optic biosensor, still a laboratory prototype, is currently being automated and minimized.

A Far-Field-Viewing Sensor for Making Analytical Measurements in Remote Locations

Michael, K.L.; D.R. Walt.

Analytical Chemistry, Vol 71, p 2766-2773, 1999

The authors demonstrate a far-field-viewing GRINscope sensor for making analytical measurements in remote locations. The GRINscope was fabricated by permanently affixing a micro-Gradient index (GRIN) lens on the distal face of a 350- μm -diameter optical imaging fiber. The GRINscope can obtain

both chemical and visual information. In one application, a thin, pH-sensitive polymer layer was immobilized on the distal end of the GRINscope. The ability of the GRINscope to visually image its far-field surroundings and concurrently detect pH changes in a flowing stream was demonstrated. In a different application, the GRINscope was used to image pH- and O₂-sensitive particles on a remote substrate and simultaneously measure their fluorescence intensity in response to pH or pO₂ changes.

Feasibility Study of Using High-Temperature Raman Spectroscopy for On-Line Monitoring and Product Control of the Glass Vitrification Process

Windisch, C.F. Jr.; G.F. Piepel; H. Li; M.L. Elliott; Y. Su.

Report No: PNNL-12037, 63 pp, Jan 1999

A pulse-gating Raman spectroscopy setup was developed in this project. The setup was capable of performing in situ high-temperature Raman measurements for glasses at temperatures as high as 1412 degrees C. Vitrification is a method DOE uses to solidify high-level waste into blocks of glass. In the literature, high-temperature Raman measurements have only been performed on thin films of glass to minimize black-body radiation effects. The pulse-gating Raman setup allows making high-temperature measurements for bulk melts while effectively minimizing black-body radiation effects. A good correlation was found between certain Raman characteristic parameters and glass melt temperature for sodium silicate glasses measured in this project. Comparisons were made between the high-temperature Raman data from this study and literature data. The results suggest that an optimization of the pulse-gating Raman setup is necessary to further improve data quality (i.e., to obtain data with a higher signal-to-noise ratio). An W confocal Raman microspectrometer with continuous wave laser excitation using a 325 nm excitation line was evaluated selectively using a transparent silicate glass and a deep-colored high-level waste glass in a bulk quantity. The data were successfully collected at temperatures as high as approximately 1500 degrees C. The results demonstrated that the UV excitation line can be used for high-temperature Raman measurements of molten glasses without black-body radiation interference from the melt for both transparent and deep-color glasses. Further studies are needed to select the best laser system that can be used to develop high-temperature Raman glass databases.

<http://www.osti.gov/dublincore/gpo/servlets/purl/2520-Pc6apC/webviewable/>

Field Demonstration and Transition of SCAPS Direct Push VOC In-Situ Sensing Technologies

Davis, William M., U.S. Army Engineer Research and Development Center, Waterways Experiment Station.

Report No: DOE/OR/22663-1-Vol.1, NTIS: DE00763299, 47 pp, 1999

This project demonstrated two in-situ volatile organic compound (VOC) samplers in combination with the direct sampling ion trap mass spectrometer (DSITMS). The technologies chosen were the Vadose Sparge and the Membrane Interface Probe (MIP) sensing systems. Tests at two demonstration sites showed the newer VOC technologies capable of providing in situ contaminant measurements at two to four times the rate of the previously demonstrated Hydrosparge sensor. The results of this project provide initial results supporting the utility of these new technologies to provide rapid site characterization of VOC contaminants in the subsurface.

<http://www.osti.gov/dublincore/gpo/servlets/purl/763299-9kd0Gf/webviewable/>

Field Demonstrations Using the Waterloo Ground Water Profiler

Pitkin, Seth E. (Stone Environmental, Montpelier, VT); J.A. Cherry (Univ. of Waterloo, Canada); R.A. Ingleton; M. Broholm.

Ground Water Monitoring & Remediation, Vol 19 No 2, p 122-131, 1999

The Waterloo Profiler is a new direct-push (DP) ground-water sampling tool developed by researchers at the University of Waterloo in Ontario, Canada. The Profiler is the only DP tool designed to collect depth-discrete ground-water samples in a single hole with one probe entry. With the Waterloo Profiler, site investigators can quickly delineate vertical profiles of contaminants dissolved in ground water.

Field Portable Electrochemical Sensors for Heavy Metals

Scaggs, Jon M.; Dale D. Russell; Michael W. Hill, Boise State Univ., Boise, ID.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 149, 2002

Electrochemical sensors for heavy metal species such as mercury and uranium have been demonstrated, based on a chelating group covalently attached to a conductive polymer. When the surface contacts a solution of the target species, it is preconcentrated in the polymer. Selectivity is achieved by both large formation constant of the metal-chelate complex, and also by its electrochemistry. Binding the analyte on the surface changes several electrochemical properties of the polymer, including the characteristic i-E curve. In amperometric mode, current is proportional to target species concentration through a range of several orders of magnitude. The various species can be distinguished based on their redox potentials. The sensing surface is integrated into a hand held or autonomous field portable instrument.

Field Raman Spectrograph for Environmental Analysis

Sylvia, J.M.; J.W. Haas; K.M. Spencer; M.M. Carrabba; R.D. Rauh; R.W. Forney; T.M. Johnston.

Report No: DE-AC21-92MC29108-01, 94 pp, Jul 1998

The researchers have developed and demonstrated in the field a transportable, high performance Raman spectrograph that can be used to detect and identify contaminants in a variety of scenarios. With no moving parts, the spectrograph is rugged and can perform many Raman measurements in situ with flexible fiber-optic sampling probes. The instrument operates under computer control and a software package has been developed to collect and process spectral data. A collection of Raman spectra for 200 contaminants of importance to DOE has been compiled in a searchable format to assist in the identification of unknown contaminants in the field.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=3969&queryId=1&start=0

Field Validation of Real Time Airborne Lead Analyzer: ESTCP Cost and Performance Report

U.S. DoD, Environmental Security Technology Certification Program. CU-9905, 41 pp, Nov 2002

The objective of this project was to demonstrate and validate a personal breathing zone (PBZ) lead analyzer/single sample ambient air monitor (AAM), which will report occupational airborne lead levels in near real time. The first field site where the analyzer was tested was the indoor firing range

located at Naval Amphibious Base Little Creek, VA, in January 2000. Based on the field results, further work was conducted on the unit before going to the second demonstration site in June 2000, an outdoor firing range located at MCAGCC Twentynine Palms, CA. Both facilities provided real-world materials created by live fire rifle and pistol shooting exercises. The AeroLead™ failed to meet all of the performance criteria during this program, and therefore, was not validated. Had the objective been accomplished, significant improvements to occupational safety and decreases in the cost of OSHA compliance would be realized. Current OSHA protocols require sending PBZ samples to a laboratory for analysis, resulting in delayed report times (24 hours to 3 days) and an increased potential for sample integrity breaches due to shipping and handling. It was expected that the AeroLead™ analyzer would provide an improved method of airborne lead sampling and analysis, providing nearly instantaneous feedback. Cost estimates indicated that sampling costs would have been reduced from \$25 to less than \$3 per sample.

<http://www.estcp.org/documents/techdocs/index.cfm>

Fluorescent, Langmuir and Langmuir-Blodgett Sensors For Copper Ions

Leblanc, Roger M.; Yujun Zheng, Univ. of Miami, Coral Gables, FL.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Colloid and Surface Chemistry: Abstract No 369, 2002

The researchers are aimed at constructing highly efficient, surface-oriented fluorescent sensors for copper ions. Selective detection of Cu²⁺ plays an important role in life and environment. Much of recent effort has been placed on exploring fluorescent sensors for the detection of copper ions in bulk solution phase. An artificial design is presented of fluorescent sensors for copper ions by simulating the models in natural copper-binding proteins having glycine-glycine-histidine or glycine-histidine motifs. Several fluorescent peptide lipids were synthesized using solid phase peptide synthesis protocol and found to form stable monolayers at the air/water interface. The interesting thermodynamic and fluorescent properties of the monolayer in the presence and absence of copper ions were investigated especially in terms of selectivity. The monolayers can be transformed to solid substrates to form Langmuir-Blodgett (LB) films. The sensing performances of the solid films toward copper ions were demonstrated.

Fundamentals of Explosives Detection

Fetterolf, Dean D., FBI Laboratory, FBI Academy, Quantico, VA.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 220, 2002

The field screening, laboratory confirmation and detailed characterization of explosives represent unique analytical challenges. An understanding of the fundamental chemical and physical properties of explosives is critical to the design of instrumentation and successful sampling strategies. For example, the equilibrium vapor pressures for the common explosives varies by nearly 8 orders of magnitude. The screening for trace explosive is done using ion mobility spectrometers (IMS) and chemiluminescence detectors. For example, explosive residue on surfaces is collected using wipe samples and thermally desorbed into the detectors. Laboratory confirmation requires robust analytical protocols. It was observed that 1 mM ammonium nitrate enhanced molecular ion or adduct formation in LC/MS resulting in detection limits of about 1 ng. Finally, the legal system places its own requirements on the analysis.

The techniques must be tested, accepted by the relevant scientific community, have known or measurable error rates, and have been peer reviewed.

Generating Sensor Diversity through Combinatorial Polymer Synthesis

Dickinson, T.A.; D.R. Walt; J. White; J.S. Kauer.

Analytical Chemistry, Vol 69, p 3413-3418, 1997

A new approach for rapid, simple generation of uniquely responding sensors for use in polymer-based sensor arrays has been developed. Polymerization reactions between different combinations of two starting materials have been found to lead to many new, unique sensors with responses not simply related to the proportion of the starting and ending monomer concentrations. Gradient sensors were fabricated using two different binary monomer systems, with both systems showing regions of broadly diverse fluorescence responses to organic vapor pulses.

GeoVis Video Camera System for CPT

U.S. DOE. Summary Sheet, Tech ID 2399. 2000

The GeoVIS Probe is an in situ video imaging system developed by DoD's SPAWAR Systems Center in San Diego. GeoVIS is deployed with a cone penetrometer and used to acquire visual information about the subsurface. The GeoVIS probe consists of a CCD color camera, lens/focusing system, and white LED illumination system. The camera, mounted inside the probe, uses a sapphire window viewport. During several field applications, the GeoVIS Probe has successfully delineated DNAPL and other colored compounds in the subsurface. The GeoVIS can resolve features as small as 10 μm .

http://www.cmst.org/Projects/pp_2399.html

Guidance on the Use of Passive-Vapor-Diffusion Samplers to Detect Volatile Organic Compounds in Ground-Water-Discharge Areas, and Example Applications in New England

Church, P.E. (U.S. Geological Survey), D.A. Vroblesky, F.P. Lyford; R.E. Willey (U.S. EPA).

U.S. Geological Survey, Denver, CO. Water-Resources Investigations Report 02-4186, 90 pp, 2002

Polyethylene-membrane passive-vapor-diffusion (PVD) samplers consist of an empty glass vial enclosed in two layers of polyethylene membrane tubing. When samplers are placed in contaminated sediments, the air in the vial equilibrates with VOCs in pore water. Analysis of the vapor indicates the presence or absence of VOCs and the likely magnitude of concentrations in pore water. Examples of applications at nine hazardous-waste sites in New England demonstrate the utility of PVD samplers in a variety of hydrologic settings, including rivers, streams, ponds, wetlands, and coastal shorelines. Results of PVD sampling at these sites have confirmed the presence and refined the extent of VOC-contaminated ground-water discharge areas where contaminated ground water is known, and identified areas of VOC-contaminated ground-water discharge where ground-water contamination was previously unknown. The principal VOCs detected were chlorinated and petroleum hydrocarbons. Vapor concentrations in samplers range from not detected to more than 1,000,000 parts per billion by volume. These results provided insights about contaminant distributions and ground-water-flow patterns in discharge areas, and have guided the design of focused characterization activities.

<http://water.usgs.gov/pubs/wri/wrir024186/>

Heavy Metals Analyzer: ESTCP Cost and Performance Report
U.S. DoD, Environmental Security Technology Certification Program. CU-9606, 43 pp, Jan 2003

The Space and Naval Warfare Systems Center (SPAWAR) developed an Automated Trace Metals Analyzer (ATMA), which is based on Potentiometric Stripping Analysis (PSA). This automated instrument is designed for unattended near real-time (one sample/5 min) collection and analysis of trace levels of heavy metals (multiple metals) in water. The ATMA can be set up to take measurements at timed intervals or in response to an external trigger. ATMA's Windows-based interface enabled non-technical personnel to set up the instrument and collect data with minimal training. The instrument continually monitors performance and will automatically notify the operator and log any problems that it cannot correct. While in operation, the instrument is sealed from the external environment, excluding the possibility of sample contamination. The instrument also allows non-technical personnel to operate it in an on-site, discrete analyses mode. This capability will permit expanded monitoring in support of efforts where diverse sources must be monitored frequently over extended periods at a low cost. The ATMA was used in two types of wastewater treatment systems. The first was a traditional manual batch tank treatment process where flocculent is manually added to a tank of wastewater and the precipitates containing the metals are allowed to settle out. The second system was a continuous flow-through system utilizing advanced Molecular Recognition Technology (MRT). The objective of the demonstration was to provide performance, cost, and field data and validate these results with laboratory analyses.

<http://www.estcp.org/documents/techdocs/index.cfm>

High Speed Fluorescence Detection of Explosives-Like Vapors
Albert, K.J.; D.R. Walt.
Analytical Chemistry, Vol 72 No 9, p 1947-1955, May 2000

In this paper, we report on the preparation of novel cross-reactive optical microsensors for high-speed detection of low-level explosives and explosives-like vapors. Porous silica microspheres with an incorporated environmentally-sensitive fluorescence changes during nitroaromatic compound (NAC) vapor exposure. The porous silica-based sensor materials have good adsorption characteristics, high surface areas, and surface functionality to help maximize analyte-dye interactions. The interactions occur immediately upon vapor exposure, i.e. in less than 200 milliseconds (ms), and are monitored with a high-speed charge coupled device (CCD) camera to produce characteristic and reproducible vapor response profiles for individual sensors within an array. Employing thousands of identical microsensors permits sensor responses to be combined which significantly reduces sensor noise and enhances detection limits. Normalized response profiles for 1,3-dinitrobenzene (DNB) are independent of analyte concentration, analyte exposure time, or sensor age for an array of one sensor type. Explosives-like NACs such as 2,4-dinitrotoluene (DNT) and DNB are detected at low part-per-billion (ppb) levels in seconds. Sensor-analyte profiles of some sensor types are more sensitive to low-level NAC vapor even when in a higher organic vapor background. We show that single-element arrays permit the detection of low-level nitroaromatic compound vapors because of sensor-to-sensor reproducibility and signal averaging.

High-Speed Fluorescence Detection of Explosives Vapor
Albert, K.J.; M.L. Myrick; S.B. Brown; F.P. Milanovich; D.R. Walt.
Proceedings of SPIE, Vol 3710, p 308-314, 1999

High-density optical arrays of fluorescent micrometer sized sensors show promise for detecting low level vapor phase explosives and explosives-like compounds. Imaging software and a high-speed CCD detection system are used to capture changes in a temporal response pattern upon pulsatile vapor delivery to the sensors. Nitroaromatic compounds (NAC's) such as 2,4-dinitrotoluene (DNT) and 1,3-dinitrobenzene (DNB), which are often present on the soil surface above buried landmines, are used to train patterns recognition networks for vapor phase detection. We have demonstrated previously that -9ppb 2,4 DNT can be detected when signal processing schemes are employed.

Identification of Multiple Analytes Using an Optical Sensor Array and Pattern Recognition Neural Networks

Johnson, S.R.; J.M. Sutter; H.L. Engelhardt; P.C. Jurs; J. White; J.S. Kauer; T.A. Dickinson; D.R. Walt. Analytical Chemistry, Vol 69, p 4641-4648, 1997

The further development of a vapor-sensing device utilizing an array of broadly distributed optical sensors is detailed. Data from these optical sensors provided input to pattern-recognizing networks, which successfully identified and quantified a collected of 20 analyte vapors. The optical sensor array consisted of 19 optical fibers whose tips were coated with Nile Red immobilized in various polymers matrices. Responses consisted of the changed in fluorescence with time resulting from the presentation of a vapor to the sensor array. Numerical descriptors calculated from these responses were then used to highlight important temporal and spatial features. Learning vector quantization neural network models were constructed using subsets of these descriptors, and they accurately identified and quantified each of the presented analytes. Successful classification was achieved for both the training set data (89%) and for the external prediction set data (90%). Relative concentrations were correctly assigned for 90% of the prediction set data.

Induced Fluorescence Sensors for Direct Push Systems. Innovative Technology Summary Report
U.S. DOE, Office of Environmental Management, Office of Science and Technology.
Report No: DOE/EM-0638, 34, Sep 2002

In the subsurface, DNAPLs tend to form blobs and ganglia that disperse and sink; their subsurface migration is less directly connected to ground-water flow than is the case with more soluble pollutants. Once introduced into the subsurface they can remain as sources of contamination for extremely long periods. Delineating the extent of contamination is a necessary first step toward remediation. This delineation is a major challenge due to the typically dispersed nature of the contamination. The goal is to locate and then remediate or isolate the nonaqueous phase sources; once this is done, ground-water contamination by these constituents can be remediated. Induced fluorescence sensors can be efficient screening tools for the presence of certain POLs and NAPLs. The subsurface media adjacent to the probe are illuminated with ultraviolet light. Polycyclic aromatic hydrocarbons (PAHs), if present, will fluoresce in response to this illumination. This fluorescence is usually transmitted via a fiber-optic cable to a spectrometer or other sensor at the surface. PAHs are commonly found in POLs and certain other organic constituents such as coal tar derivatives. DNAPLs themselves WILL NOT fluoresce when excited at feasible wavelengths. In many cases, however, PAHs are found in DNAPLs that have been used in cleaning or degreasing operations. The induced fluorescence will have distinct frequency and time spectra depending on the PAHs present and on the exciting frequency. Frequency and/or time domain analyses of the observed fluorescence can be used to distinguish among categories of

fluorescing compounds, such as distinguishing fuels from coal tar residues and distinguishing hydrocarbon contamination in general from natural mineral fluorescence. Recent developments utilizing multiple excitation and response frequencies show promise at both identifying and quantifying multiple individual constituents of concern.

Imprinted Polymer Sensors for Pesticide Detection

Jenkins, Amanda L., Applications Development, Jasco Inc., Easton, MD.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 156, 2002

Antibodies and enzymes are often used as molecular recognition elements in chemical sensors. However, their lack of stability and signal transduction mechanisms limits their use as sensors. Advances in the field of molecularly imprinted polymers (MIPs) have created synthetic materials that can mimic the function of biological receptors with less stability constraints. These polymers provide high sensitivity and selectivity while maintaining thermal and mechanical stability. The advantages of the MIP are enhanced by a fluorescent component which provides chemical affinity and signal transduction. A fiber-optic spectrom-eter monitors the reversible binding of the analyte to the reporter molecule that invokes a spectral signature between 550-700nm. Detection limits are less than 10 parts per trillion with long linear dynamic ranges. The sensors exhibit the same recognition characteristics over several months of use with response times of less than 15 minutes. Selectivity of the sensors against other similar compounds will be demonstrated.

In-Situ Characterizations of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

Pope, G.A. (Texas Univ. at Austin); D.C. McKinney; A.D. Gupta; R.E. Jackson; M. Jim.

Report No: DOE/ER/14720, NTIS: DE2002-793613, CD-ROM or 219 pp, Mar 2002

Major advances have been made during the past three years in the research on interwell partitioning tracers tests (PITTs). These advances include (1) progress on the inverse problem of how to estimate the three-dimensional distribution of NAPL in aquifers from the tracer data, (2) the first ever partitioning tracer experiments in dual porosity media, (3) the first modeling of partitioning tracers in dual porosity media, (4) experiments with complex NAPLs such as coal tar, (5) the development of an accurate and simple method to predict partition coefficients using the equivalent alkane carbon number approach, (6) partitioning tracer experiments in large model aquifers with permeability layers, (7) the first ever analysis of partitioning tracer data to estimate the change in composition of a DNAPL before and after remediation, (8) the first ever analysis of partitioning tracer data after a field demonstration of surfactant foam to remediate DNAPL, and (9) experiments at elevated temperatures.

<http://www.osti.gov/dublincore/gpo/servlets/purl/793613-kUJy7A/native/793613.pdf>

Integrated Raman-pOH Sensor for In-Tank Corrosion Monitoring: Raman Feasibility Study Report

Haas, J.W.; T.M. Johnston, EIC Laboratories, Inc., Norwood, MA.

U.S. DOE CMST Program, 13 pp, 1998[?]

This project addresses the need to monitor species related to corrosion in high-level liquid waste tanks at the Savannah River Site (SRS). Ultimately, the method will be applicable at Hanford and other DOE facilities. A primary source of corrosion is the nitrate ion, often present at high concentrations in the

tanks, but which can be controlled (inhibited) by maintaining adequate levels of hydroxide and nitrite ions. The ideal sensor for this application is one that accurately and safely monitors all three anions directly in the tank liquid, eliminating the need for traditional grab sampling and analysis. The researchers have identified fiber-optic Raman spectroscopy as a leading candidate for simultaneous, in-tank monitoring of nitrate, nitrite, and hydroxide. Raman spectroscopy is an optical technique that produces a unique "fingerprint" spectrum for every molecule. Its spectral features are sharp, so multiple components of mixtures can often be differentiated without physically separating them. Although a full Raman instrument is unsuitable for in-tank deployment, small, flexible fiber-optic probes connected to the instrument can be readily delivered into the tanks for in situ monitoring.

The objective of the first 6-month phase of this program was to establish the feasibility for Raman detection of nitrate, nitrite, and hydroxide at concentrations relevant to hazardous waste tanks. This report presents the results of the tests, which demonstrate that Raman monitoring of nitrate, nitrite, and hydroxide at relevant waste tank concentrations is feasible.

http://www.cmst.org/PubPages/p_pubs-pres.html

Ion Mobility Spectrometry as Detector and Sensor for Chemical Warfare Agents and Toxic Industrial Chemicals

Eiceman, Gary A., New Mexico State Univ., Las Cruces, NM.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 211, 2002

Principles of response in ion mobility spectrometers were recognized early as advantageous for the detection of organophosphorus compounds (OPCs) including nerve agents. The favorable gas phase chemistry of OPCs at ambient pressure resulted in the development of the Chemical Agent Monitor, one of the most widely used sophisticated analytical instruments. In the past decade, the relationship between gas phase ion chemistry and the resultant mobility spectrum has been explored and a model exists to describe the appearance of spectra. Response to a wide range of organic compound classes demonstrates that IMS could be used as a detector of numerous chemical threats including toxic industrial chemicals and markers from bacteria. The strengths of IMS include field portability and low detection limits; limitations include complexity of gaseous ionization at ambient pressure and resolution. Recent advances in IMS will be discussed. Also, attempts to miniaturize drift tubes will be reviewed and will include micro-machined drift tubes based upon concepts of ion separation using high field mobility.

Laboratory-on-a-Cable for Pollution Control and Prevention

Wang, Joseph, New Mexico State Univ., Las Cruces.

New Mexico Waste-management Education and Research Consortium (WERC), 9 pp, Oct 2000

This research has addressed the urgent needs for providing timely analytical data on priority inorganic and organic pollutants through the development of remote electrochemical sensors. Our work resulted in novel protocols and powerful sensing tools for in-situ and on-site monitoring of major contaminants. In particular, remotely deployable submersible sensors, capable of monitoring priority pollutants both in time and location, were shown advantageous for environmental monitoring. The new devices were optimized, characterized, and tested under relevant conditions. Their high sensitivity is coupled to good selectivity and stability, and absence of carry-over effects. The new technologies offer great promise for performing environmental testing more rapidly, easily, and inexpensively in a field setting.

<http://www.werc.net/researchers/pdf/wang2000.pdf>

Landfill Construction Quality: Lessons Learned from Electrical Resistivity Testing of Geomembrane Liners

Phaneuf, Robert; Ian Peggs.

Geotechnical Fabrics Report, p 21-26, Apr 2001

The use of summarized electrical resistivity leak location data allows us to take a focused proactive approach to improving upon the quality of environmental containment system construction. This focused approach should include the following considerations:

- Designers, specifiers and installers need to minimize extrusion welded seams. Consideration should be given to the configuration of necessary extrusion welds to ease non-destructive testing, especially in critical containment areas such as pipe penetrations.
- Specifications should call attention to the need for taking more care with extrusion bead stop/starts and at "T" junctions. These locations should also be the subject of careful non-destructive testing of the entire weld.

<http://www.ifai.com/File.php?ID=24>

LIBS: A New Versatile, Field Deployable, Real-Time Detector System for Force Protection and Anti-Terrorism Applications

Miziolek, A.W. (U.S. Army Research Lab., Aberdeen Proving Ground, MD), K.L. McNesby, B.E. Homan, F.C. DeLucia; R.S. Harmon (U.S. Army Research Lab., Research Triangle Park, NC); R.J. Winkel, Jr. (USMA, West Point, NY); S. Grossman (NVESD, Ft. Belvoir, VA), A. LaPointe; N. Melikechi (Delaware State Univ., Dover); R.A. Walters (Ocean Optics Inc., Winter Park, FL).

23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, 2 pp, 2002

Laser Induced Breakdown Spectroscopy (LIBS) is a sensor technology undergoing rapid growth in application areas and in instrumentation. In particular, LIBS possesses great potential for use in many applications related to force protection and anti-terrorism. It is a straightforward and relatively simple technique which utilizes a pulsed laser to create a microplasma on the target material as well as an array spectrometer to capture the transient light for elemental identification and quantification. The simplicity of the technique and the technological maturity of the components that comprise a LIBS sensor attest to the fact that this technology is both rugged and robust, and therefore particularly suitable for field use. LIBS attributes include: (1) no sample preparation required, (2) it is very sensitive (nanograms), (3) has been made briefcase size for man-portable field use and could be made smaller, (4) response is real-time, and (5) can be operated as both a point sensor or in a standoff detection mode (distances of 100 meters and greater have been demonstrated). The ARL LIBS researchers have worked in this field for over 12 years. Recently a number of potential military applications have been identified and actively pursued. Some examples include: (1) trace explosives detection, (2) chem-bio detection, (3) robotics applications (ground and airborne), (4) buried landmine and UXO detection, and (5) RCRA/toxic metal detection and identification. Recent progress in instrumentation includes the development of a compact multispectrometer system which allows for very broad spectral coverage (200-950+ nm) with high resolution (0.1 nm). In particular, over the past year ARL collaborated with Ocean Optics Inc. to develop a new commercial instrument (LIBS 2000+) which allows for real-time detection of all elements of any unknown target. Thus LIBS is now sensitive to molecular and biological materials. The reason for this is that all chemical elements emit light in the 200-950 nm region. Thus, molecular

detection and identification is based on sensing all of the constituent elements of an unknown material as well as their relative abundances, and comparing the LIBS spectrum of an unknown with a library of reference spectra. This advance in technology has made possible the use of LIBS to discriminate between different explosive formulations and different types of plastics, which has the potential to make LIBS an important new sensor for demining. Yet another application for LIBS is the determination of chemical composition of particles of interest in advanced energetics applications.

<http://www.asc2002.com/>

Long-Term Monitoring Sensor and Analytical Methods Workshop, 13-15 June 2001, Orlando, FL
U.S. DOE, Office of Science and Technology, Characterization, Monitoring, and Sensor Technology
Crosscutting Program (CMST-CP) & Subsurface Contaminants Focus Area.
34 pp + 171 pp Appendix, 2001

One hundred and twenty people participated in the workshop, which was conducted to evaluate available and newly emerging sensors and analytical instruments for use in long-term monitoring (LTM) of contaminants in the subsurface. DOE site-identified LTM needs were used as the basis for determining functional requirements for sensors and for assessing current technologies and approaches. From this assessment, technology gaps were determined and opportunities for LTM research and development (R&D) were identified. While workshop discussions were originally intended to focus on chemical sensors and/or chemical field analytical methods that can be used to monitor contaminants for LTM programs, participants maintained that surrogate measurements or alternative approaches to measuring contaminants directly are equally, if not more, important for monitoring programs. Participants expressed uncertainty regarding the ability of point chemical measurements to provide an accurate assessment of site conditions, even with numerous measurements. Instead, the primary interest was in the broader goal of identifying what measurements need to be taken to support monitoring decisions. Participants with monitoring program experience stated that monitoring subsurface parameters such as moisture, pH, or oxygen levels can provide critical information about the condition and integrity of a remedial system, even to early warning of remedial system failure. The workshop participants concluded that most technologies needed for measuring surrogate parameters are well developed today. Thus, the near-term R&D focus in this area should be demonstrating the integration of these existing sensors and analytical methods for the purposes and objectives of environmental monitoring. In contrast, chemical environmental contaminant sensors are largely under-developed, and recently emerging techniques were discussed. The primary focus, however, was identification of requirements for contaminant sensors. Requirements for each contaminant class were developed to guide the future R&D program. The report's appendix comes in a separate volume.

<http://www.cmst.org/lrm/index.html>

Low-Power Reconfigurable Microfluidic Chips For Chem-Bio Detection And Monitoring
Garrell, Robin L.; J.-Y. Yoon; H. Moon; J. Fowler; C.-J. Kim, Univ. of California at Los Angeles.
224th ACS National Meeting, 18-22 August 2002, Boston, MA.
American Chemical Society. Division of Analytical Chemistry: Abstract No 224, 2002

Moving liquids rapidly through micron-scale channels by pushing (pressure) is difficult, as friction at the channel walls and the high surface-to-volume ratio lead to large pressure drops and large power requirements. Electrophoresis and electroosmotic flow require charged or highly polarizable solutes and the ability to dissipate heat rapidly to the surrounding medium. We report the feasibility of using

electrowetting on dielectrics (EWOD) to manipulate protein and nucleic acid solutions, as well as serum, in micron-scale channels on-chip. EWOD involves applying a potential between a liquid and a dielectric-coated electrode. Charge redistributes at the solid-liquid interface, leading to a change in contact angle and droplet motion. The system has been optimized to decrease the power requirement to below 15 V, and to minimize fouling of the substrate by biomacromolecules. These results demonstrate that EWOD is a practical method for moving biofluids through microfluidic devices.

Measurement of Available Cyanide Using USEPA Method OIA-1677 and the Flow Solution® IV
OI Analytical, College Station, TX. Application Note 1843-0802, 6 pp, 2002

A method is described for determining available cyanide in water and wastewater by ligand exchange, flow injection analysis (FIA), and amperometric detection according to EPA Method OIA-1677. Cyanide ion (CN^-), hydrogen cyanide in water (HCN(aq)), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver can be determined by this method.

<http://www.oico.com/appniaca.htm>

Measurement of Cyanide in Water Using On-line Distillation, UV Digestion, and the Flow Solution® IV
OI Analytical, College Station, TX. Application Note 1828-0802, 4 pp, 2002

Cyanide is released from cyanide complexes by UV digestion and on-line distillation. The liberated hydrogen cyanide is converted to cyanogen chloride by reaction with chloramine-T trihydrate at a pH of less than 8. The cyanogen chloride then reacts with the pyridine-barbituric acid reagent to form a red-colored complex, which is measured at 570 nm^3 . The OI Analytical Flow Solution IV (FS-IV), a high-throughput, automated system for ion analysis employing segmented flow analysis, is used with this method. The FS-IV uses advanced Expanded Range (ER)TM detection allowing single calibration ranges of 3 to 4 orders of magnitude, which significantly reduces sample reruns due to off-scale samples. The system's WinFLOWTM software package allows random access sampling, automatic recalibration, real-time results, and QC monitoring.

<http://www.oico.com/appniaca.htm>

Measurements of NH_3 and CO_2 with Distributed-Feedback Diode Lasers Near $2.0\text{ }\mu\text{m}$ in Bioreactor Vent Gases

Webber, M.E. (Stanford Univ.); R. Claps; F.V. Englich; F.K. Tittel; J.B. Jeffries; R.K. Hanson.
Applied Optics, Vol 40 No 24, p 4395-4403, 20 Aug 2001

Sensors were designed for detection of trace ammonia and varying concentrations of carbon dioxide in the vent gases of a bioreactor. A DFB laser operating near $2\text{ }\mu\text{m}$ offered significant gains in accessible absorption intensities, so the optimum transitions in that region were selected for use with an automated and portable sensor system developed at Rice University. The Rice sensor system employed a multipass cell, which increased sensitivities and allowed for low-pressure operation to isolate the different absorption transitions, and allowed as well for direct absorption. The researchers adapted the sensor system for operation at 2 mm by changing the laser and the detector and operating it over a 45-h period for quasi-continuous measurements of NH_3 and CO_2 concentration at detection limits of 0.25-ppm and 40-ppm, respectively.

<http://www-ece.rice.edu/lasersci/detectio.html>

Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group:
Determination of Triazine and Phenylurea Herbicides and Their Degradation Products in Water Using
Solid-Phase Extraction and Liquid Chromatography/Mass Spectrometry
Lee, E.A.; A.P. Strahan; E.M. Thurman, U.S. Geological Survey.
U.S. Geological Survey, Lawrence, KS. Open-File Report 02-436, 19 pp, 2002

This report presents an analytical method for the determination of seven triazine and phenylurea herbicides and 12 of their degradation products in natural water samples using solid-phase extraction and liquid chromatography/mass spectrometry. Special consideration was given during the development of the method to prevent the formation of degradation products during the analysis. Filtered water samples were analyzed using 0.5 gram graphitized carbon as the solid-phase extraction medium followed by liquid chromatography/mass spectrometry. Three different water-sample matrices—ground-water, surface-water, and reagent-water samples—spiked at 0.2 and 2.0 micrograms per liter were analyzed. Method detection limits ranged from 0.013 to 0.168 microgram/liter for the parent triazine herbicides and the triazine degradation products. Method detection limits ranged from 0.042 to 0.141 microgram per liter for the parent phenylurea herbicides and their degradation products. Mean recoveries for the triazine compounds in the ground- and surface-water samples generally ranged from 72.6 to 117.5 percent, but deethyl-cyanazine amide was recovered at 140.5 percent. Mean recoveries from the ground- and surface-water samples for the phenylurea compounds spiked at the 2.0-micrograms-per-liter level ranged from 82.1 to 114.4 percent. The mean recoveries for the phenylureas spiked at 0.2-microgram per liter were less consistent, ranging from 87.0 to 136.0 percent. Mean recoveries from reagent-water samples ranged from 87.0 to 109.5 percent for all compounds. The triazine compounds and their degradation products are reported in concentrations ranging from 0.05 to 2.0 micrograms per liter, with the exception of deethylcyanazine and deethylcyanazine amide which are reported at 0.20 to 2.0 micrograms per liter. The phenylurea compounds and their degradation products are reported in concentrations ranging from 0.20 to 2.0 micrograms per liter. The upper concentration limit was 2.0 micrograms per liter for all compounds without dilution.

<http://ks.water.usgs.gov/Kansas/pubs/abstracts/of.02-436.html>

Mid-IR DFG Source Pumped by a 1.1 mm/1.5 m Dual Wavelength Fiber Amplifier for Trace Gas Detection

Goldberg, L.; D.G. Lancaster; J. Koplow; R.F. Curl; F.K. Tittel.
Optics Letters, Vol 23 No 19, p 1517-1519, 1998

The authors describe a compact DFG source based on mixing of 1.1- and 1.5- μm outputs of a dual-wavelength fiber amplifier. The amplifier uses a high-power Yb-doped fiber to produce optical gain near 1.1 μm and to pump an Er/Yb co-doped fiber for amplification at 1.5 μm . With a 19-mm-long PPLN crystal, a maximum DFG power of 11 μW is measured at 3.4 μm , and wavelength tunability is demonstrated from 3.3 to 3.5 μm (pumping at 1064 nm). The source offers the advantages of compactness, low cost, a robust all-fiber design, and a large tuning range made possible by wide gain bandwidth of the fiber amplifier. In addition, the large optical gains provided by the amplifiers make it possible to use low-power diode seed lasers, and spatial overlap between the two pump beams in the crystal is ensured by the single fiber output of the pump source. Using the DFG source, the researchers demonstrated spectroscopic detection of CH_4 and H_2CO .

<http://www-ece.rice.edu/lasersci/detectio.html>

MIME Chemical Vapor Microsensors

Snow, A.W. (NRL Chemistry Div.); H. Wohltjen and N.L. Jarvis (Microsensor Systems, Inc.).
2002 NRL Review, NRL/PU/5211-02-442, p. 45-55, May 2002

A nanocluster metal-insulator-metal ensemble (MIME) chemical vapor sensor is a solid state sensor composed of nanometer-size gold particles encapsulated by a monomolecular layer of alkanethiol surfactant deposited as a thin film on an interdigital microelectrode. The principle by which this sensor operates is that vapors reversibly absorb into the organic monolayer, which causes a large modulation in the electrical conductivity of the film. The tunneling current through the monolayer between gold particle contacts is extremely sensitive to very small amounts of monolayer swelling and dielectric alteration caused by absorption of vapor molecules. The nanometer scale of the particle domains and correspondingly large surface area translate into a very large vapor sensitivity range, extending to sub-ppm concentrations. Selectivity of the sensor is regulated by incorporation of chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. The current focus of research is in mapping the selectivity and sensitivity of sensor elements made by incorporating these functionalities into the shell of the nanocluster. Targeted applications include detection of chemical warfare agents and explosives, and residual life indication of carbon filters and protective clothing.

<http://www.nrl.navy.mil/content.php?P=02REVIEW45>

Miniaturized Mass Spectrometers for Bioagent Detection

Cotter, Robert J., Johns Hopkins Univ., Baltimore, MD.
224th ACS National Meeting, 18-22 August 2002, Boston, MA.
American Chemical Society. Division of Analytical Chemistry: Abstract No 213, 2002

Many recent studies have shown that the mass spectra of microorganisms and other biological agents reveal characteristic biomarkers, which in many cases can now be referenced to genomic and proteomic databases for the organism. In conjunction with such studies there has been an effort to develop small, fieldable mass spectrometry detectors; however, the task is to maintain performance for these instruments. In time-of-flight mass spectrometers, a smaller drift region generally results in lowered mass resolution, because the effects of the time spent in the source become significant. A miniaturized instrument is described which addresses mass resolution problems using pulsed extraction and a flight tube biased at the detector voltage. Mass resolution of greater than 1/1000 is realized using a 3-inch drift region. In addition, mass-correlated acceleration reduces the dependence of pulsed extraction parameters on mass and provides a means for recording biomarkers over a broad mass range. Atmospheric pressure matrix-assisted laser desorption ionization (AP MALDI) provides the opportunity to analyze biological samples external to the mass spectrometer and has been implemented on an ion trap.

NASA Develops Smallest, Lightest Chemical Analyzer

National Aeronautics and Space Administration, Office of Biological and Physical Research.
Space Research: Transforming Tomorrow Today, 2003

Detecting trace levels of toxic chemicals before they reach harmful levels in the atmosphere is crucial to human health. One highly accurate and reliable tool that can quickly and automatically analyze complex mixtures of gases is the mass spectrometer, but mass spectrometers are large, expensive devices demanding large power supplies. Ara Chutjian and his colleagues at NASA's Jet Propulsion Laboratory (JPL) in Pasadena, CA, revolutionized the mass spectrometer by developing a miniature version just three inches tall and weighing about four ounces (a world record). With its associated gear, the system weighs only three pounds. This new Trace Gas Analyzer (TGA) debuted in February 2001. It can detect leaks of ammonia from cooling systems, propellant from thrusters, and air leaks from seals and micrometeorite holes in the spacecraft structure. The U.S. EPA uses mass spectrometers to monitor contamination from hazardous sites and factory emissions. These devices have been used sparingly because of their large size and high cost, and the samples are often brought back to labs for analysis. Chutjian and his colleagues hope to make their small, inexpensive unit available for readily detecting contaminants in the field. They are working with Consolidated Edison to develop field-deployable prototypes to detect PCBs (polychlorinated biphenyls) at contaminated sites. Chutjian and his colleagues are designing a second-generation mass spectrometer with 50 times the sensitivity and three times the resolution of the current model. NASA contact: Dr. Charlie Barnes, 202-358-2365. <http://SpaceResearch.nasa.gov/2003.html>

NASA Success Story: Advanced Wideband Electromagnetic Sensors
NASA Office of Technology Transfer, John C. Stennis Space Center.
Success Story ID # 2400471, Nov 2000

Geophex has developed a prototype airborne sensor that can measure variations in the electrical conductivity in the Earth. The technology developed under this project produced the GEM-2, an airborne electromagnetic sensor to find mineral deposits. Geophex also developed a handheld version, known as the GEM-3, which has been successfully used for investigating soil and ground-water contamination. The handheld GEM-3 has been applied for detecting and identifying buried unexploded ordnance and landmines. The cleanup cost related buried unexploded bombs for the U.S. alone is estimated to exceed \$10B. Two GEM-2s have flown in Australia for mining companies looking for diamond deposits (known as Kimberlite pipes), precious metal (gold and silver), and base metals (copper, nickel, etc.). They expect to start a similar airborne geophysical operation out of the U.S. using the same sensors. Geophex received US Patent # 5,557,206, entitled "Apparatus and Method for Detecting a Weak Induced Magnetic Field by Means of Two Concentric Transmitter Loops." The patent has wide applications in geology, geophysics and biophysics.
Contact: NASA IP Manager, (228) 688-1929.

NASA Success Story: AVIR, LLC Licenses Technology For Remote Sensing of Chemical Weapons Agents and Illicit Drug Manufacturing
Technology Commercialization Center, Inc., NASA Langley Research Center.
Success Story ID # 202394, Dec 2001

AVIR, LLC has obtained an exclusive field of use license to commercialize NASA technology and is working on development of these new applications. The objective of the commercialization effort is to develop sensors for detecting chemical weapons agents and illicit drugs. It would use differential absorption radiometry to identify the infrared spectroscopy of chemicals while correcting for background interferences that might cause false readings. Once developed, these sensors would provide

early warning of chemical weapon attack for counter-terrorism and military use and provide improved ability to detect illicit drug manufacturing. Contact: Rosemary Rallo Baize, Technology Commercialization Project Manager, NASA Langley Research Center, Hampton, VA, (757) 864-7717, Fax: (757) 864-8314, r.r.baize@larc.nasa.gov.

NASA Success Story: NASA Licenses Air Quality Monitoring Technology
Technology Commercialization Center, Inc., NASA Langley Research Center.
NASA Success Story ID # 202086, Jul 1998

A sensor originally developed to measure gases in the Earth's atmosphere from an aircraft or satellite, now offers an economical solution to many ground-based monitoring applications. MERCO Inc., an air quality consulting firm, has licensed NASA Langley Research Center's (LaRC) remote gas sensor. Under the agreement, the sensor will be used to monitor gaseous pollutants emitted from petroleum refineries and chemical manufacturing facilities. The gas filter correlation radiometer, called GFCR, accurately measures concentrations of key gas species, including carbon monoxide (CO), methane (CH₄), and nitrogen oxides (NO_x). The device relies upon electro-optical techniques, rather than mechanical techniques, to switch its internal optical paths. This offers distinct advantages such as a faster response rate, higher reliability, lower weight, and a more compact design. Contact: Moe Bonakdar, MERCO, Inc., Golden, CO, (303) 274-9686.

NASA Success Story: Plant Fluorescence Sensor
NASA Office of Technology Transfer, John C. Stennis Space Center.
Success Story ID # 2400455, October 2000

The Plant Fluorescence Sensor is a real-time, direct monitor of plant health that is manifested by chlorophyll fluorescence. This simple, rugged and field deployable device uses a spectral (Fraunhofer) line discriminator for the passive sensing of sunlight excited fluorescence, suitable for observing vegetation canopies. The plant fluorescence sensor has both ground-based and low-altitude airborne applications. The target market segments identified by Aerodyne are site-specific agriculture; irrigation on demand; hydroponic growing environments; and ecological monitoring, including soil remediation and coastal remote sensing. The core components of the PFS are passive, with minimal moving parts, relatively inexpensive, and simple in design. The PFS sensing concept is based upon the fundamental process of photosynthesis. Aerodyne has received U.S. Patent #5,567,947 for a "spectral line discriminator for passive detection of fluorescence." All components of the PFS are based on established technology and readily available at competitive prices. Contact: Herman Scott, Aerodyne Research, Inc., Billerica, MA, (978) 663-9500 x267, Fax: (978) 663-4918.

NASA to Aid Con Edison's Environmental Operations
Jet Propulsion Laboratory News Release 2002-152, 29 July 2002

Consolidated Edison of New York, Inc. (Con Edison) recently signed a technology affiliates agreement with NASA's Jet Propulsion Laboratory in Pasadena, Calif., to gain access to JPL researchers with experience in developing sensors. By becoming a technology affiliate member, Con Edison will work directly with JPL researchers to develop the sensors, which will search for two specific chemical families: polychlorinated biphenyl compounds (PCBs) and perfluorocarbon tracers (PFTs). The current

method of identifying PCB concentrations at an environmental incident takes up to eight hours because a crew take a sample in the field, transport it to a laboratory, and then analyze the samples using a gas chromatograph system. A truck-mounted JPL Reversal Electron Attachment Detection system would allow workers to take a sample and analyze it on the spot in about 30 minutes. The system will detect other chemical vapors as well, such as explosives and nerve-agents. Another application of the JPL system is the detection of PFTs. Con Edison injects trace amounts of PFTs into the insulating oil used in its high-voltage transmission lines routed under the streets of New York City. These trace amounts of PFTs are used to pinpoint insulating-oil leaks from underground power lines. The current detection system uses a slower PFT detector on a truck, which requires the crew to go through a time-consuming processing of noting whether the detection hits are "colder" or "hotter" and backtracking until they gradually home in on the leak. The JPL system would be faster, with no lag time. A "hit" would be made in close proximity to the actual leak, requiring minimal backtracking, saving worker time. JPL and Con Edison will make the sensors compact and portable, and compatible for use by Con Edison. The sensor technology being applied to help Con Edison was first developed through two separate partnerships with the Federal Aviation Administration to detect explosive vapors at airports and with the U.S. Navy to detect unexploded ordnance on the ocean floor.

Contacts: Carolina Martinez, JPL, 818-354-9382; Michael Braukus, NASA HQ, 202-358-1979; Brenda Perez, Con Edison, 212-460-4111.

Near-Infrared Diode Based Spectroscopic Detection of Ammonia: a Comparative Study of Photoacoustic and Direct Optical Absorption Methods

Bozoki, Zoltan (Research Group on Laser Physics of the Hungarian Academy of Sciences, Szeged, Hungary); Arpad Mohacsi; Gabor Szabo; Zsolt Bor; Miklos Erdelyi; Weidong Chen; Frank Tittel. *Applied Spectroscopy*, Vol 56 No 6, p 715-719, 2002

Cross-calibration of a photoacoustic and an optical absorption spectroscopic system, both based on fiber-coupled telecommunication DFB diode lasers, proved that both sensors can operate with sub-ppm level sensitivity. Both analyzer systems are capable of automatic, unattended operation, although the PAS system is less sensitive to optical alignment and in some applications offers the advantage of small size, ease of operation, and minimum maintenance.

<http://www-ece.rice.edu/lasersci/detectio.html>

Neural Network Classification and Quantification of Organic Vapors Based on Fluorescence Data from a Fiber-Optic Sensor Array

Sutter; J.M.; P.C. Jurs.

Analytical Chemistry, Vol 69, p 856- , 1997

Computational neural networks have been developed to classify and quantify nine organic vapors. The neural network analyses used data that consisted of the change in fluorescence of a sensor array that was patterned after the mammalian olfactory system. The sensor array consisted of 19 fiber optics that contained a polymer and dye mixture on one end. Plots of change in fluorescence intensity versus time were measured as pulses of analyte were presented to the sensor array. Important features derived from the intensity versus time plots were used to build neural network models that accurately classified and quantified each analyte. Most of the data were used to train the neural networks (training set members), some were used to assist termination of training the neural networks (cross-validation set members), and some were used to validate the models (prediction set members). Classification rates approaching 100%

were achieved for the training set data, and 90% of the members in the prediction set were correctly classified. In addition, 97% of the prediction set observations were assigned a correct relative concentration.

New Cetyltrimethylammonium Methods of Determination of Perchlorate

Cyganski, A.; P. Kowalczyk; J. Krystek; B. Ptaszynski.

Chemical Analysis, Vol 45 No 6, p 911-919, Nov-Dec 2000

In the presence of cetyltrimethylammonium bromide (CTA) perchlorates form a sparingly soluble compound. The analysis has proved that it is cetyltrimethyl-ammonium perchlorate. In the present work gravimetric, nephelometric and turbidimetric methods of determination of perchlorates have been worked out. Measurements can be made in the pH range from 1.5 to 11.5. For 5 to 20 mg of perchlorate the gravimetric method and for 0.05 to 1.0 mg of perchlorate the nephelometric and turbidimetric methods can be used. The effect of foreign ions has been examined. Only large anions (e.g. MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, J^-) interfere with the determination.

New Technique Monitors Chromium Contamination In Groundwater

University Of Illinois News Release, 18 Mar 2002

Widely used in electroplating, hexavalent chromium, aka chromate or Cr(VI) , is a suspected carcinogen and a common contaminant in ground water. Researchers at the University of Illinois have discovered a simple, but effective, method for monitoring this pollutant. Thomas Johnson, a geologist at the University of Illinois, graduate student Andre Ellis at the UI, and hydrologist Thomas Bullen at the U.S. Geological Survey in Menlo Park, CA, have developed a means for measuring how fast, and to what extent, hexavalent chromium is changing to the less hazardous trivalent chromium at a given site. Chromium has four stable (non-radioactive) isotopes. By measuring the isotope fractionation in laboratory experiments and in natural waters, the researchers found that lighter isotopes reacted preferentially during the reduction reaction. Trivalent chromium, or Cr(III) , becomes enriched in lighter isotopes as the reduction proceeds, while the remaining Cr(VI) becomes enriched in heavier isotopes. By measuring the relative abundances with an isotope-ratio mass spectrometer, investigators can determine how much reduction has taken place, and then estimate the long-term reduction rate. The partitioning of the lighter isotopes into the reduction product, Cr(III) , provides a convenient and effective monitoring technique. As the reduction reaction proceeds, the ratio of heavier to lighter isotopes will change. At some sites, there are naturally occurring reducing agents in the subsurface – such as iron-bearing minerals like magnetite – that will convert hexavalent chromium to trivalent chromium. If the reaction rate is fast enough, the contaminant can be naturally attenuated. Such an approach is much less expensive and disruptive than active remediation. At other sites, chemical reducing agents must be injected in the ground to mitigate the pollution. Knowing how fast the reaction is occurring within a contaminant plume can help investigators decide whether natural attenuation is a viable approach at a site, or if active remediation is required. The National Science Foundation funded the research.

<http://www.sciencedaily.com/releases/2002/03/020315072021.htm>

Novel Neural Network Technology for Very Fast Analysis of Hyperspectral Imagery, Opto-Knowledge Systems, Inc., Torrance, CA
Goddard Space Flight Center, Success Story #5-026, Jan 1999

An integrated benchtop hyperspectral sensor and analysis system was developed for use in laboratory and field applications in a NASA STTR Phase I project funded in 1995. The project demonstrated the application of a compact hyperspectral camera system utilizing a liquid crystal tunable filter for ground truth collection and analysis in support of remote sensing applications. It also demonstrated a novel algorithmic paradigm for neural network training specifically optimized for computationally intensive applications such as hyperspectral analysis. The researchers developed a Toolbox of additional algorithms for hyperspectral analysis and integrated the benchtop sensor and Toolbox to form a turnkey system. The first commercial use of the system was by Ford Motor Company. Scientists at the NIH, USDA, and NASA have expressed interest in testing the sensor for a wide range of applications ranging from real-time medical, food, and other produce inspections, to process control. The system is now in use in the NASA EOCAP-Hyperspectral program for development of hyperspectral precision agriculture applications. Points of Contact: Robert Crompt, NASA, 301-286-4351; Linda Papermaster, Opto-Knowledge Systems, 310-371-4445 ext 228.

Online Sensing of Volatile Organic Compounds in Groundwater Using Mid-Infrared Fibre Optic Evanescent Wave Spectroscopy: a Pilot Scale Test

Steiner, H. (Vienna Univ. of Technology, Vienna, Austria); K. Staubmann; R. Allabashi; N. Fleischmann; A. Katzir; Y. Reichlin; B. Mizaikoff.
Water Science & Technology, Vol 47 No 2, pp 121-126, 2003

A prototype sensing system for in situ monitoring of volatile organic compounds in contaminated ground water was tested at a pilot-scale plant. The sensor consists of a commercially available Fourier transform infrared spectrometer connected to a 6 m long infrared transparent silver halide fiber-optic cable. A 10 cm long core-only section at the center of the fiber is mounted on a sensor head and coated with a hydrophobic polymer layer, while the remaining fibre is protected by Teflon tubing and thus not in contact with the surrounding media. The sensor head was immersed in the monitoring wells of the pilot plant under circumstances close to field conditions. The pilot plant consists of a 1 cubic meter tank filled with gravel. Pumped water circulates horizontally through the tank, simulating a natural aquifer. The prototype sensing system monitored the evolution of the concentration of analytes injected into the system over time, and the results were validated by corresponding sampling and analysis with headspace gas chromatography.

Optical Fiber Microarrays for Chem/Bio Detection

Walt, David R.; S.E. Stitzel; J. Epstein; S. Bencic; A.P.K. Leung, Tufts Univ., Medford, MA.
224th ACS National Meeting, 18-22 August 2002, Boston, MA.
American Chemical Society. Division of Analytical Chemistry: Abstract No 221, 2002

Micrometer- and nanometer-sized sensors have been fabricated by etching the cores of optical imaging fibers to create wells and loading them with micro and nanospheres. Such arrays can be employed for making genosensors with high sensitivity and reproducibility. Genosensors have been prepared for identifying different bacterial strains by coupling gene expression profiles with pattern recognition. We have also created optical sensors based on cross-reactive arrays of sensors. In this approach, specificity

is distributed across the array's entire reactivity pattern rather than contained in a single recognition element. The ability to use such information-rich assemblies for broad-based chemical sensing will be discussed.

Optical Multi-Bead Arrays for Simple and Complex Odor Discrimination

Albert, Keith J. and David R. Walt (Tufts Univ., Medford, MA); Daljeet S. Gill and Tim C. Pearce (Univ. of Leicester, Leicester, UK).

Analytical Chemistry, Vol 73 No 11, p 2501-2508, 2001

A fiber optic bead-based sensor array platform has been employed to discriminate between six different odors and air carrier gas. Six different bead sensor types, with over 250 replicates of each, were monitored before, during, and after odor exposure to produce time dependent fluorescence response patterns that were unique for each sensor-analyte combination. A total of 2683 sensors were analyzed with respect to changes in their fluorescence and signals from identical sensor beads were averaged to improve signal-to-noise ratios. 100% analyte classification rates were achieved for three complex (coffee bean) odors and three pure (simple) odors (toluene, acetone, and 1,3-dinitrotoluene) measured at their highest relative concentrations. When lower odor concentrations were employed, the system exhibited better than 85% classification rates for analyte discrimination. Sensor response repeatability to these odor stimuli has also been quantified statistically, which is vital in defining the detection limit of the overall system. These results demonstrate, for the first time, the utility of our bead array technology for discriminating between different odor types at various dilution levels.

Organic tracers identification as a convenient strategy in industrial landfills monitoring

Benfenati, E.; E. Porazzi; R. Bagnati; F. Forner; M. Pardo Martinez; G. Mariani; R. Fanelli.

Chemosphere, Vol 51 No 8, p 677-683, June 2003

Industrial landfills, especially aging ones, can release toxic compounds into the environment. A good strategy for early evaluation of contamination involves injection of tracers into the landfill, so that their detection in adjacent monitoring wells will signal the escape of leachate. The protocol suggested here for well-water characterization is based on solid phase extraction combined with GC-MS and HPLC-MS/MS. The authors present some specific examples of monitoring landfills for organic industrial pollutants.

Partitioning Tracers for In-Situ Measurement of Nonaqueous Phase Liquids in the Subsurface

Brusseu, Mark L., Univ. of Arizona, Tucson.

Report No: DOE/ER/14722, 37 pp, Sep 2000

The overall goal of the proposed project is to explore the use of partitioning tracers to characterize dense nonaqueous phase liquids (DNAPLs) in aquifer systems. Bulk-phase partitioning tracers will be investigated to detect and determine DNAPL saturation, while interface partitioning tracers will be investigated to measure the area of the DNAPL-water interface. The following specific objectives will be addressed to accomplish this goal: (1) Investigate the use of partitioning tracers to detect and determine both the saturation and interfacial area of DNAPLs in saturated porous media. (2) Investigate the effect of rate-limited mass transfer on the transport behavior of partitioning tracers. (3) Investigate the effect of porous-media heterogeneity on the transport behavior of partitioning tracers. (4) Develop

and evaluate mathematical models capable of simulating the transport of partitioning tracers in complex systems. This proposal outlines an integrated approach for the development and testing of a unique method for detecting and measuring DNAPL in aquifer systems. The approach combines one-dimensional laboratory experiments, three-dimensional intermediate-scale flow cell experiments, physical methods for DNAPL description (including dual-energy gamma radiation), and advanced modeling techniques.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=790174

Pre-Ablation Spark Dual-Pulse LIBS

Eland, Kristine L. (Univ. of South Carolina); Dimitra N. Stratis; S. Michael Angel.

The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana.

The researchers have developed a new dual-pulse laser-induced breakdown spectroscopy (LIBS) technique using a pre-ablation spark to obtain signal enhancements up to 60-fold, as well as greatly enhanced sample ablation. They have seen enhancements on a variety of sample types including conductors, semi-conductors and non-conductors. The pre-ablation spark technique is different from other dual-pulse techniques in that a first laser pulse is focused above the sample surface to form an air-spark or air plasma, before a second pulse is brought in to the sample surface and used to ablate the sample. The plasma generated using the new dual-pulse technique is being characterized using a variety of approaches including time-resolved spectral imaging. Time-resolved spectral imaging of plasmas using a tunable filter along with an intensified charge coupled device (ICCD) is useful for studying LIBS since the character of the plasma changes dramatically over time. Time-resolved spectral images show an overall larger plasma volume when using the pre-ablation spark method compared to single-pulse excitation. In this paper, dual-pulse enhancement and plasma imaging results are presented.

Preliminary Assessment of Using Tree-Tissue Analysis and Passive Diffusion Samplers to Evaluate Trichloroethene Contamination of Ground Water at Site SS-34N, McChord Air Force Base, Washington, 2001

Cox, S.E, U.S. Geological Survey, Tacoma, WA.

U.S. Geological Survey, Water-Resources Investigations Report 02-4274, 21 pp, 2002

Two low-cost innovative sampling procedures for characterizing trichloroethene (TCE) contamination in ground water were evaluated in 2001 for use at McChord Air Force Base (AFB) by the U.S. Geological Survey, in cooperation with the U.S. Air Force McChord Air Force Base Installation Restoration Program. Previous attempts to characterize the source of ground-water contamination in the heterogeneous glacial outwash aquifer at McChord site SS-34N using soil-gas surveys, direct-push exploration, and more than a dozen ground-water monitoring wells met with limited success. The procedures assessed in this study involved analysis of tree-tissue samples to map underlying ground-water contamination and deploying passive-diffusion samplers to measure TCE concentrations in existing monitoring wells. These procedures have been used successfully at other DoD sites and have resulted in cost avoidance and accelerated site characterization. Despite the presence of TCE in ground water at site SS-34N, TCE was not detected in any of the 20 trees sampled at the site during either early spring or late summer sampling. The reason the tree tissue procedure was not successful at the McChord AFB site SS-34N may have been due to an inability of tree roots to extract moisture from a water table 30 feet below the land surface, or concentrations of TCE in ground water were not large enough to be detectable in the tree tissue at the sampling point. Passive-diffusion samplers were placed near the top,

middle, and bottom of screened intervals in three monitoring wells and TCE was observed in all samplers. Concentrations of TCE from the passive-diffusion samplers were generally similar to concentrations found in samples collected in the same wells using conventional pumping methods. In contrast to conventional pumping methods, the collection of ground-water samples using the passive-diffusion samples did not generate waste purge water that would require hazardous-waste disposal. In addition, the results from the passive-diffusion samplers may show that TCE concentrations are stratified across some screened intervals. The overall results of the limited test of passive-diffusion samplers at site SS-34N were similar to more detailed tests conducted at other contaminated sites across the country and indicate that further evaluation of the use of passive-diffusion samplers at McChord site SS-34N is warranted.

<http://water.usgs.gov/pubs/wri/wri024274/pdf/wri024274.pdf>

Quantitative Analysis of the Detection Limits for Heavy Metal- Contaminated Soils by Laser-Induced Breakdown Spectroscopy

Alexander, Dennis R.; Dana E. Poulain, Nebraska Univ., Lincoln

NTIS: ADA328435, 34 pp, Jun 1997

Laser-induced breakdown spectroscopy (LIBS) is a rapid remote measurement method for detection of metals in the environment. A major factor in the quantitative use of this technique involves the minimum detection limits under both laboratory and field operations, on which research has been carried out on limits of detection of heavy metals in different types of soils under various conditions using LIBS. Pulses from a Nd:YAG laser operating at 125 mJ at $\lambda = 1.06$ micrometers are focused on sample surfaces to produce laser sparks (plasmas). Atomic emissions from the plasmas are recorded using an optical multichannel analyzer after delays of a few microseconds when interference from broad-band emissions is reduced. Research has been performed on the detection limits of arsenic, cadmium, chromium, mercury, lead, and zinc in soil matrices. This report presents results on the lower detection limits of these six elements in sand, silt, clay, and kaolin matrices. Detection limits are significantly lower for heavy metals in sand matrices than silt and clay matrices due to differences between surface and volume contamination.

<http://handle.dtic.mil/100.2/ADA328435>

Rapid Ultrasensitive Chemical-Fingerprint Detection of Chemical and Biochemical Warfare Agents

Ashby, Carol I.; T.J. Shepodd; W.G. Yelton; D.J. Muron, Sandia National Labs.

Report No: SAND2002-4055, 39 pp, Dec 2002

Vibrational spectra can serve as chemical fingerprints for positive identification of chemical and biological warfare molecules. The required speed and sensitivity might be achieved with surface-enhanced Raman spectroscopy (SERS) using nanotextured metal surfaces. Systematic and reproducible methods for preparing metallic surfaces that maximize sensitivity have not been previously developed. This work sought to develop methods for forming high-efficiency metallic nanostructures that can be integrated with either gas or liquid-phase chem-lab-on-a-chip separation columns to provide a highly sensitive, highly selective microanalytical system for detecting current and future chem/bio agents. In addition, improved protein microchromatographic systems have been made by the creation of acrylate-based porous polymer monoliths that can serve as protein preconcentrators to reduce the optical system sensitivity required to detect and identify a particular protein, such as a bacterial toxin.

<http://www.osti.gov/dublincore/gpo/servlets/purl/808603-bh9ieO/native/>

Recent Advances in Characterization of Vadose Zone DNAPL in Heterogeneous Media
Rossabi, J.; B.D. Riha; C.A. Eddy-Dilek; B.B. Looney; W. K. Hyde, Westinghouse Savannah River
Company, Aiken, SC.
Report No: WSRC-MS-2001-00230, 2001

One of the most important technological developments for characterization of unconsolidated sediments in the past twenty years is the direct push method for accessing and probing the subsurface. The cone penetrometer and related direct push technologies, such as the Geoprobe(R), have been increasingly used for geologic and chemical characterization at sites throughout the United States and abroad. In addition to its standard suite of sensors (i.e., tip pressure, sleeve friction, capillary pressure) to determine soil type, the cone penetrometer has been used with innovative sensors and samplers to perform contaminated site assessments and has also been used to install wells, sampling points, and geophysical tools and arrays. By integrating geologic information from the standard cone penetrometer sensor with the depth-discrete chemical and physical information obtained from innovative cone penetrometer-based samplers and sensors, an accurate, rapid and cost-effective characterization can be accomplished. Cone penetrometer tests (CPT) provide quality, high-resolution data. The tests are minimally invasive, rapid, and produce a minimum of investigation derived waste. These attributes are critical to investigative and cleanup operations at large hazardous waste sites with heterogeneous sediments.

<http://www.srs.gov/general/pubs/fulltext/ms2001230/ms2001230.html>

Remote Measurement of Volcanic Gases by Fourier Transform Infrared Spectroscopy
Oppenheimer, C. (Univ. of Cambridge); P. Francis; M. Burton; A.J.H. Maciejewski; L. Boardman.
Applied Physics B, Vol 67 No 4, p 505-515, 1998

Scientists have been applying Fourier transform infrared (FTIR) spectroscopy to volcanological field studies only fairly recently, but the method has remarkable potential for rapid, remote surveillance of a wide range of volcanic gases. This paper reviews the application of FTIR spectroscopy to volcanological studies, and considers some of the challenges that must be met if the technique is to be fully utilized. The compilation of volcanic gas data obtained by field spectroscopy presented here can assist in design of future gas measurement campaigns by FTIR or related spectroscopic techniques.

Remote Sensing Tutorial
Short, Nicholas M.

Hosted by the Remote Sensing Education and Outreach Laboratory at NASA's Goddard Space Flight Center, 1998 [updated]

This extensive and lavishly illustrated site that explains the science behind remote sensing from space has been updated repeatedly between 1998 and 2003. The Tutorial begins with an introduction that covers the principles of physics (especially electromagnetic radiation) underlying remote sensing, then considers the main kinds of observing platforms, and includes the history of satellite systems, with a focus on Landsat. Many of the subsequent sections and topics center on Landsat because it continues to be a kingpin among the current remote sensing systems. The introduction also delves into three special topics: Use of satellites for geophysical measurements of Earth's force fields; a survey of satellite programs (military and security agencies) employed in monitoring activities detrimental to a country's

safety (these are often called "spy satellites), and the applications of instruments and techniques within the purview of remote sensing that are used in medical diagnosis.

<http://rst.gsfc.nasa.gov/start.html>

Remote Tank Monitoring and Inspection Methods

Lemieux, E. (NRL Chemistry Div.) A. Webb, K.E. Lucas, P.F. Slebodnick, M. Krupa, F. Martin; E.A. Hogan (NRL Materials Science and Technology Div.).

2002 NRL Review, NRL/PU/5211-02-442, p. 110-112, May 2002

Preservation of tanks and voids on U.S. Navy ships expends more than 25% of maintenance funds annually. The MIL-P-24441 system that has been installed in most tanks and voids has a 5- to 7-year service life. Two major thrusts have been made to reduce maintenance costs of tank and void preservation: (1) replacement with high solid epoxy coating systems that are approximately 98% solids, are edge-retentive, and have a service life of 20 years; and (2) implementation of condition-based maintenance technology via electrochemical in situ sensors and remote optical inspection technologies for routine assessment of the "state of preservation" of shipboard tanks and voids. This article reviews improvements in technology currently being developed with regard to the second thrust area. Various inspection techniques, including the Insertable Stalk Imaging System (ISIS), the Remotely Operated Paint Inspector (ROPI), and the Corrosion Detection Algorithm (CDA) are discussed.

<http://www.nrl.navy.mil/content.php?P=02REVIEW110>

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

Ho, Clifford K.; M.T. Itamura; M.J. Kelley; R.C. Hughes, Sandia National Labs., Albuquerque, NM.
Report No: SAND2001-0643, 33 pp, Mar 2001

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. The particular focus of this project is limited to the detection and monitoring of volatile organic compounds (VOCs), such as aromatic hydrocarbons (e.g., benzene, toluene, xylenes), halogenated hydrocarbons (e.g., trichloroethene (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. As part of this project, a literature search was conducted to survey available technologies and identify the most promising methods for sensing and monitoring subsurface contaminants of interest. 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.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=780299

Sample Collection Systems for the Determination of Airborne Chemical or Biological Materials
Graham, P.W.; C.A. Weiss, Jr.; S.L. Larson; D.B. Ringelberg; P.G. Malone, U.S. Army Corps of Engineers, Vicksburg, MS, and Hanover, NH.

23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts, 2 pp, 2002

In order to avoid problems associated with pump-through samplers, a rugged sampler was developed to rapidly trap a known volume of air using a large-orifice (12 mm-diameter) automated valve mounted on an evacuated, stainless steel cylinder. The result is a sampler that can be placed near a blast environment and can collect a sample, before, during, or after, a blast event. The valve system used is electrically triggered with a 24-volt signal and the valve is rapidly opened and closed using a pneumatic system powered with a cylinder of compressed nitrogen. The length of time over which sampling occurs can be determined using a timing circuit and by varying the size of the sampling orifice and the volume of the evacuated cylinder. The development efforts have produced a versatile sampler that is inexpensive to manufacture and can be adapted to sampling particulates or gases under extreme environmental conditions. The automated evacuated cylinder system is all stainless steel and Teflon resulting in a system that is tough enough to survive the pressure from a nearby blast, but simple to clean and decontaminate for reuse. Additionally, the large thermal mass of the metal cylinder and the cooling effect that occurs as the gaseous sample is pulled into a vacuum lowers the temperature of the sample reducing thermal degradation. Generally there is no need to pre-cool the gases entering the sampler. The entry orifice can have multiple small openings in front of the valve opening into a single larger orifice. Any particulates entering the smaller openings can pass through the wide-throated ball valve and into the cylinder with little risk of clogging.

<http://www.asc2002.com/>

Selective Determination of Airborne Hexavalent Chromium Using Inductively Coupled Plasma Mass Spectrometry

Li, Yarong; Narayan K. Pradhan; Roy Foley; Gary K.C. Low.

Talanta, Vol 57 No 6, p 1143-1153, 2002

A new method for determining ultra-trace levels of hexavalent chromium in ambient air has been developed. The method involves a 24-h sampling of air into potassium hydroxide solution, followed by silica gel column separation of chromium (VI), then preconcentration by complexation and solvent extraction. The chromium (VI) complex was dissolved in nitric acid. The resultant chromium ions were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a dynamic reaction cell (DRC) with ammonia as the reactive gas to reduce polyatomic interferences. The interconversion of chromium in potassium hydroxide solution and air sample matrix were investigated under ambient conditions. It was found that there was no conversion of chromium (VI) into chromium (III) species. However, it was observed that some chromium (III) species were converted into chromium (VI) species.

SERS Detection of Chemicals Using an AOTF-Based Detection System

Stokes, David L. (Oak Ridge National Lab.); Brian M. Cullum; Joel Mobley; Tuan Vo-Dinh.

The Pittsburgh Conference: PITTCON 2001, 4-9 March 2001, New Orleans, Louisiana.

The SERS detection of various compounds of health and environmental interest using an acousto-optic tunable filter (AOTF)-based instrument is reported. AOTF's are compact, solid-state devices used for rapid, tunable wavelength discrimination. Advantages to using AOTF's include compactness, robustness

(afforded by the no-moving-parts design), rapid random bandpass access, and slitless apertures that can facilitate imaging spectroscopy. The recent development of AOTF's having resolution as high as 7.5 cm^{-1} in the 600-900 nm range has now made them practical for Raman analysis. In this study, an AOTF is used with an avalanche photodiode in the single-channel scanning mode for the generation of SERS spectra. Various SERS-inducing media developed in our laboratory are described and evaluated for use with compact lasers, such as a low-power, 632.8-nm helium-neon laser and a 785-nm diode laser. Both of these excitation sources are amenable to field studies. Furthermore, the resulting SERS spectra are collected in the red-to-near-IR region, where the possibility of interfering fluorescence from an analyte or sample matrix is relatively low. The narrow features of Raman spectra, combined with the high resolving power of the AOTF-based instrument, permit the analysis of complex samples. Moreover, the SERS effect enables trace level detection of a variety of compounds of health and environmental interest. As a whole, the instrument is lightweight, field portable, and capable of generating 200-1650 cm^{-1} spectra in less than a minute. Fiberoptic SERS detection is demonstrated with this compact, robust instrument.

Single Mode Tunable Diode Lasers from 1.9 to 2.3 Microns, Focused Research, Inc., Santa Clara, CA
Goddard Space Flight Center, Success Story #5-025, Jan 1999

An external-cavity diode laser that emits single-mode radiation tunable from 1.87-2.06 and operates at room temperature was developed in a NASA SBIR Phase II project funded in 1994. The tunable diode lasers provide greater than 1 milliwatt of narrow linewidth (less than 1 MHz, full width half maximum) infrared light for spectroscopic and molecular sensing applications and rapid single-mode scanning (greater than 6 nanometer per second) over the greater than 80 nm tuning range. Developed in cooperation with the High Temperature Gas-Dynamics Laboratory at Stanford University, one laser is currently being used to analyze CO_2 and H_2O for combustion diagnostics. The new laser system is available as a commercial product and has been highlighted at a topical meeting of the Optical Society of America and at CLEO. Commercial orders in excess of \$100K have been received, with an estimated product revenue of \$1M over four years. Tunable lasers from 1.8 to 2.3 microns can monitor gaseous molecular and transient species that are not amenable to probing with standard diode lasers (0.6 to 1.6 microns). Rapid tuning and narrow-linewidth facilitate direct absorption spectroscopy. The lasers have been used at NASA Goddard Space Flight Center for laboratory spectroscopy, e.g., low temperature linewidth and linestrength measurements of CO_2 transitions. The laser is used as a calibration source for ongoing work with tunable acousto-optic filters. Contact: John Allen, NASA, 301-286-5896; Timothy Day, Focused Research, 408-980-8088.

Site Characterization and Analysis Penetrometer System (SCAPS) Field Investigation at the Building 4020 Site, Aberdeen Proving Ground, Maryland

Davis, W.M.; L.T. Lee; J.F. Powell, U.S. Army Corps of Engineers, Waterways Experiment Station, Environmental Lab, Vicksburg, MS.

Report No: WES/TR/EL-96-17, NTIS: ADA320251. 87 pp, 1996

The U.S. Army Engineer Waterways Experiment Station site characterization and analysis penetrometer system (SCAPS) investigated suspected fuel leaks from removed underground storage tanks at the Building 4020 site on Aberdeen Proving Ground, Maryland. Fifty-one penetrations were made with the SCAPS soil sensor and the laser-induced fluorescence sensor during a period of 12 working days. The suspected contamination was detected, and its limited extent delineated.

<http://handle.dtic.mil/100.2/ADA320251>

Solid-Phase Extraction for the Determination of Dimethoate in Environmental Water and Soil Samples by Micellar Electrokinetic Capillary Chromatography (MEKC)

Sanchez, M.E.; B. Rabanal; M. Otero; J. Martin-Villacorta, Univ. of Leon, Spain.

Journal of Liquid Chromatography and Related Technologies, Vol 26 No 4, p 545-557, 2003

A micellar electrokinetic chromatography (MEKC) procedure has been developed for the analysis of dimethoate (DM) in environmental water and soil samples, using solid phase extraction (SPE) as a clean-up and pre-concentration technique to improve selectivity and DM detection limits. The limit of quantification (LOQ) was 1 $\mu\text{g/mL}$ for direct injection and 3 ng/mL after the SPE pre-concentration procedure. Within-run and between-day reproducibility studies performed at 0.02, 0.05, and 0.2 $\mu\text{g/mL}$ indicated that the procedure was indeed reproducible. Quantification was by UV detection at 200 nm. The capillary electrophoresis (CE) method proposed uses sodium borate 100 mM with sodium dodecyl sulfate 50 mM, pH 8.4 as a buffer. The method was simple and fast, with good recoveries, which on average ranged from 82 to 92% with a relative standard deviation of 7% or less for water and soil samples fortified at 10, 20, 30, and 300 ng/mL . Our results show CE to be a powerful analytical tool for the determination of DM in environmental water and soil samples.

Soil Gas Survey and Analysis of the Rose-Hulman Institute of Technology Campus Using a Portable Gas Chromatograph

Jones, Harvey B., III, Rose-Hulman Inst. of Technology, Terre Haute, IN.

NTIS: ADA307874, 214 pp, May 1996

This project focused on a method used to discover hidden contamination: soil gas surveying. The Rose-Hulman Institute of Technology campus in Terre Haute, IN, is on the site of an old farm. The campus has an old gasoline station on its border, a chemical storage building on the grounds, and areas where fuel, oil, and solvents are used and stored by the physical plant operation. There was a possibility that underground contamination might be present from these operations. Contaminants typical of these types of operations include benzene, toluene, ethylbenzene, and m-, p-, and o-xylenes, a combination of chemicals usually known as BTEX. BTEX chemicals are used in the processing of petroleum products and other manufacturing. The researchers also looked for the chlorinated solvents trichloroethene and tetrachloroethene. No significant areas of contamination were found. This report contains a detailed description of the method and test results and concludes with recommendations for improved management of potential contamination areas.

<http://handle.dtic.mil/100.2/ADA307874>

Solid Phase Microextraction of Polycyclic Aromatic Hydrocarbons from Soil

Sedukiene, I.; V. Vickackaite; R. Kazlauskas.

Chemical Analysis, Vol 45 No 6, p 835-841, Nov-Dec 2000

The authors suggest a headspace solid-phase microextraction technique for the determination of polycyclic aromatic hydrocarbons in soil. The optimum extraction conditions from the headspace of humic soil are temperature at 60 degrees C for 30 min and desorption at 250 degrees C for 2 min. The

researchers estimated the precision and linearity of determination as well as detection limits for acenaphthene, fluorene, and anthracene. The extraction efficiency depends strongly on soil humidity.

Spectroelectrochemical Sensor with a Chelating Agent For Cu(en)^{2+}

Rarog, Tanya; William R. Heineman; Carl J. Seliskar, Univ. of Cincinnati, Cincinnati, OH.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 151, 2002

Spectroelectrochemical determination of copper-ethylenediamine complex (Cu(en)^{2+}) in aqueous solution is demonstrated. The cation-selective Nafion-SiO₂ composite film spin-coated on ITO (indium tin oxide)-glass electrode was used for electrochemical sensing. Neocuproine (nc) dye (2, 9-dimethyl-1, 10-phenantroline) was incorporated into the film. In order to be detected Cu(en)^{2+} partitions into the cation-selective Nafion-SiO₂ film, it undergoes a reduction/oxidation processes at ITO-glass electrode, en is replaced reversibly by nc, and spectral absorption during cyclic voltammetry under attenuated total internal reflection (ATR) at 450 nm is recorded. Cu(en)^{2+} complex has suitable chemical, optical, and electrochemical properties. The potential was cycled between 0.8 V and -0.9 V. Peak absorbance enhancement was observed using Nafion-SiO₂-modified ITO-glass electrode comparing with the bare ITO-glass electrode under the same conditions. The effect of potential scan rate on the absorbance-time profile for electrochemical modulation was studied. The calibration curve for Cu(en)^{2+} was made and it is linear in the $5 \times 10^{-6} \text{ M}$ – $1 \times 10^{-3} \text{ M}$ concentration range.

Standard Practice for Cone Penetrometer Technology Characterization of Petroleum Contaminated Sites with Nitrogen Laser-Induced Fluorescence (LIF)

American Society for Testing and Materials (ASTM), West Conshohocken, PA. D6187-97, 7 pp, 1998

This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Ground Water and Vadose Zone Investigations.

Standoff Detection of Chemicals Using Nanoencoded Porous Silicon Photonic Crystal “Smart Dust” Particles

Sailor, Michael J.; T.A. Schmedake; F. Cunin; J.R. Link; Y.Y. Li, Univ. of California, San Diego.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Colloid and Surface Chemistry: Abstract No 361, 2002

Small particles of microporous Si are used to detect chemicals by measurement of the intensity of reflected light from a remote laser probe. The particles contain a periodic porous nanostructure that is generated in an electrochemical etch. Periodic structures such as Bragg stacks and Rugate reflectors can be generated. These structures display sharp features in the optical reflectivity spectrum at wavelengths that are controlled by the etch parameters. The intensity and wavelength of reflected light is determined in part by the refractive index of the porous nanostructure, which can be modified by adsorption of vapors within the hydrophobic porous matrix. Using a 10 mW laser as an optical probe and telescope collection optics, detection of ethanol, acetone and toluene vapors has been achieved at a distance of 20 m. Control experiments using water vapor at comparable partial pressures show very little response, demonstrating selectivity towards the hydrocarbon analytes with the hydrophobic particles used in the study.

Subpixel Target Detection for Hyperspectral Images Using ICA-Based Feature Extraction
Kwon, Heesung; Sandor Z. Der; Nasser M. Nasrabadi, Army Research Laboratory, Adelphi, MD.
23rd Army Science Conference, 2-5 December 2002, Orlando, Florida. Extended Abstracts

The basic premise of hyperspectral target detection is that the spectral signatures of target materials are measurably different than background materials. The proposed algorithm is based on subpixel target detection where a reflectance spectrum of each pixel is assumed to be a linear mixture of constituent spectra from the two disparate material types – the target and background. Each pixel spectrum is projected onto the orthogonal background subspace to remove the background spectral portion from the corresponding pixel spectrum. The abundance of the remaining target portion within the pixel spectrum is estimated through matched filtering of the background-removed spectra. Independent component analysis (ICA) is used to generate a target matched filter. A target filter is also generated by simple averaging of the target sample spectra, and detection performance for both the target extraction techniques are compared using a set of HYDICE hyperspectral images.

<http://www.asc2002.com/>

Subsurface Soil Analysis Using an In Situ Video Imaging System
Lieberman, Stephen H., Space and Naval Warfare Systems Center/San Diego.
Publication No: EPA 542-N-01-004, Tech Trends, p 1-2, Nov 2001.

A novel system has been developed by the Space and Naval Warfare Systems Center/San Diego (SSC San Diego) to obtain detailed information about subsurface soil characteristics on very small spatial scales. Known as GeoVIS, this system uses a miniature charge-coupled device (CCD) color video camera coupled with magnification and focusing lens systems integrated into a cone penetrometer probe. The system is designed to characterize soil properties involved in estimating subsurface water flow and contaminant transport, and to characterize complex contaminants such as non-aqueous phase liquid (NAPL). The article is available in the Tech Trends archive through the URL listed.

<http://www.clu-in.org/products/newsletters/trend/default.cfm>

Successful Technology Commercialization: NASA Plant Stress Technology Available Commercially
NASA Office of Technology Transfer, John C. Stennis Space Center.
NASA Success Story ID # 2400503, 2001

NASA and Spectrum Technologies, Inc., Plainfield, IL, have worked together to transfer a plant stress detection technology originally developed for Stennis Space Center to the commercial marketplace. The product, the Spectrum Chlorophyll Meter, can detect plant stress up to 16 days before plant deterioration is visible by measuring chlorophyll content through the amount of light energy reflected from the plant. Early detection of plant stress through chlorophyll loss has obvious application to agriculture and can also provide a means of monitoring phytoremediation projects. The hand-held, portable Spectrum Chlorophyll Meter makes instant, non-destructive chlorophyll measurements of a plant's reflected light energy. Two high-powered lasers outline the sample area and the measurement is automatically corrected for varying ambient light conditions. A data logger facilitates data collection and permits geo-referenced measurements with Global Positioning System (GPS). Data can be downloaded to a personal computer for more statistical analysis. The meter allows for non-destructive field measurement of chlorophyll with no light source other than the sun with hand-held point-and-shoot

technology. In 2001, the unit sold for approximately \$2,190, excluding options. Contact: Spectrum Technologies, Inc., 800-248-8873; or NASA Office of Technology Transfer, Stennis Space Center, MS, 228-688-1929, technology@ssc.nasa.gov.

Technologies for Detection of Chemical and Biological Agents

Long, S. Randolph, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD.

224th ACS National Meeting, 18-22 August 2002, Boston, MA.

American Chemical Society. Division of Analytical Chemistry: Abstract No 209, 2002

In both battlespace and terrorism scenarios involving use of chemical or biological agents, there are clear needs for early warning/alarm, real-time detection and identification, and post-event diagnostic and forensic capabilities. No currently known technology has performance attributes that render it the ideal solution to meet all these requirements. This suggests a layered CB defense architecture in which a number of technology solutions will find use. We first review in generic terms the spectrum of potential CB agents and the background against which these agents must be detected or analyzed. The potency of potential agents at low concentrations places a premium on sensitivity and selectivity. The range of agents suggests a need for broad-spectrum detection capability. Some examples of technologies currently available to address the CB challenge will be provided to establish a context for discussion of the relative merits of next-generation detection technologies.

Test Methods for Available Cyanide with Flow Injection Analysis (FIA) Using Gas Diffusion and Amperometric Detection

OI Analytical, College Station, TX.

2003 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 9-14 March 2003, Orlando, FL. Application Note 1911-0203, 6 pp, 2003

This application note compares two methods incorporating amperometric detection. Results according to EPA Method OIA-1677 were obtained using the OI Analytical Flow Solution® IV and proprietary ligand-exchange reagents, WAD A and WAD B from OI Analytical. An alternative method was developed employing the same analysis principles as EPA Method OIA-1677. Diagrams illustrate the configuration of both methods. Data illustrating the operating range, detection limits, reproducibility, and recoveries of various cyanide-containing compounds are presented. This note illustrates how EPA Method OIA-1677 for Available Cyanide and the WAD A and WAD B ligand-exchange reagents from OI Analytical provide accurate and precise results over an exceptional concentration range. The ASTM D19 committee has adopted the Method OIA-1677 configuration and the OI Analytical ligand-exchange reagents in a newly proposed ASTM method.

<http://www.oico.com/appniaca.htm>

Testing of Continuous Sampling Air-ICP and Mercury Systems as Continuous Emission Monitors at the Diagnostic Instrumentation and Analysis Laboratory

Baldwin, D.P.(Ames Laboratory), S.J. Bajic, D.E. Eckels, D.S. Zamzow; G.P. Miller (DIAL), S. Tao, C.A. Waggoner.

Report No: IS-5144, 25 pp, Mar 2001 [revised]

The purpose of the project is to develop instrumentation and methods for spectroscopic field monitoring applications. During FY00 this included continued work on the development of the continuous sample introduction system and the multi-frequency AOTF-echelle spectrometer, used in conjunction with the reduced-pressure air-ICP-AES system as a multi-metal CEM. The assembly, development, and testing of an echelle spectrometer system for the detection of mercury (Hg) by atomic absorption was also completed during FY00. The continuous sampling system and the multi-metal air-ICP and mercury-monitor CEM systems were tested at Mississippi State University at the Diagnostic Instrumentation and Analysis Laboratory (DIAL) at the end of FY00. This report describes the characteristics and performance of these systems, and the results of the field tests performed at DIAL. The continuous sampling air-ICP and mercury-monitor CEM systems are being developed in response to the need of DOE and other organizations to monitor the heavy-metal or radioactive materials that may be released during the processing or combustion of hazardous or mixed-waste materials. The air-ICP system has been designed for the on-line detection and monitoring of heavy metals (beryllium, cadmium, chromium, and lead, in particular) in process or exhaust gas streams by optical emission spectroscopy. Due to the relatively poor limits of detection for Hg by optical emission techniques, the mercury-monitor CEM has been designed specifically for the detection of elemental Hg by optical absorption.

http://www.cmst.org/PubPages/p_pubs-pres.html

Transportable Automated Ammonia Sensor Based on a Pulsed Thermoelectrically Cooled Quantum-Cascade Distributed Feedback Laser

Kosterev, Anatoliy A. (Rice Univ.); Robert F. Curl; Frank K. Tittel; Rudeger Kohler; Claire Gmachl; Federico Capasso; Deborah L. Sivco; Alfred Y. Cho.
Applied Optics, Vol 41 No 3, p 573-578, 2002

The researchers designed a compact portable ammonia sensor based on a thermoelectrically cooled pulsed QC DFB laser that operates at 10 μm . This device was applied to real-world ammonia concentration measurements. The configuration of the sensor will serve as the basis for the design of future portable QC DFB laser-based gas sensors for single or multiple trace gas quantification. The current sensitivity can be considerably improved by the addition of a second reference infrared detector. Such a two-beam configuration will cancel the noise caused by laser shot-to-shot energy fluctuations. These shot-to-shot fluctuations are the predominant noise source in the test measurements. The use of such a reference channel would also eliminate baseline uncertainty.
<http://www-ece.rice.edu/lasersci/detectio.html>

Trends in Laser Sources, Spectroscopic Techniques and Their Applications to Trace-Gas Detection Applied Physics B: Lasers and Optics, Vol 75 No 2-3, 2002 [Special Issue]

Many research groups have made significant progress in the development of tunable laser sources, advanced spectroscopic techniques, and the range of new and effective trace gas absorption applications. As evident in this special issue, many of the reported technologies have started to move into commercial markets, clearly a sign of the mature status and unique advantages that can be gained by laser spectroscopy-based instrumentation. The papers in this special issue indicate the growth in the number of applications as well as the number of new approaches employing laser-based spectroscopic instruments. More applications are sure to emerge with the development of very robust, user-friendly, and reliable laser-based spectroscopic instrumentation. These instruments will find application in

medicine, agriculture, industrial process control, advanced fire detection and law enforcement, and the environment. This special issue indicates the progress that has been achieved in spectroscopic laser-based gas sensing, from the visible to the far-mid-infrared spectral regions. The papers of this issue have been assembled according to the wavelength region and their subject areas.

The Tri-Service Site Characterization and Analysis Penetrometer System--SCAPS: Innovative Environmental Technology from Concept to Commercialization
U.S. Army Engineering R&D Center Environmental Laboratory, Vicksburg, MS; Army Environmental Center, Aberdeen Proving Ground, MD.
Report No: SFIM-AEC-ET-TR-99073, 47 pp, Jan 2000

The Tri-Service Site Characterization and Analysis Penetrometer System, or SCAPS, program began in 1987 under sponsorship of the U.S. Army Toxic and Hazardous Materials Agency (now the U.S. Army Environmental Center) to address the need for rapid site characterization of soil contamination at U.S. Army facilities. The program evolved into a Tri-Service (Army, Air Force and Navy), multi-year research, development, and technology demonstration program with additional funding by the SERDP and ESTCP. The U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency (EPA) also participated in the program. The U.S. Army Environmental Center took the lead for SCAPS sensor development efforts among DoD, DOE and EPA and coordinated with regulatory agencies, as well as potential government and commercial users. SCAPS consists of a commercial cone penetrometer unit mounted on the custom-designed bed of a 20-ton truck. The truck houses a mechanical room for the cone penetrometer and a data analysis room for operational and diagnostic computers and instrumentation. A variety of sensor probes can be attached to the cone penetrometer to investigate soil geophysical properties, or that respond to classes of contaminants such as petroleum, solvent products, metals and explosives. SCAPS operators use a 20-ton hydraulic press mounted in the truck to push the sensors up to 150 feet into the soil. The SCAPS systems relay information on subsurface contaminants to the surface for immediate analysis and interpretation. The final display products SCAPS provides can range from individual push charts to cumulative 3-D depictions of the subsurface.
http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/scaps99073.pdf

Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Membrane Interface Probe: ESTCP Cost and Performance Report
U.S. DoD, Environmental Security Technology Certification Program. CU-9603, 35 pp, Nov 2002

Several demonstrations of the ion trap mass spectrometer-Membrane Interface Probe (ITMS-MIP) system for volatile organic compounds (VOCs) were completed between August of 1998 and May of 2000. The purpose of each demonstration was to show the ability of the ITMS-MIP vapor sampling system to characterize the extent of subsurface contamination during a single field deployment. Previous Site Characterization and Analysis Penetrometer System (SCAPS) ITMS-MIP field investigations include a demonstration at Alameda Naval Air Station (NAS) in 1998, Long Horn Army Ammunition Plant in 1998, and Lake City Army Ammunition Plant in 1999. Validation demonstrations for the SCAPS ITMS-MIP system took place at the NAS North Island, Coronado, CA, in 1999 and 2000 and at DOE's Savannah River Site in 1999. Results of the demonstration at the Savannah River Site are discussed briefly; however, the major emphasis of this report is the demonstration at NAS North Island, which was specifically carried out as a production deployment. The ITMS-MIP system uses the commercially available MIP to collect vapor samples from the

subsurface. The MIP collects VOC samples from the subsurface through a permeable membrane into a helium carrier gas that transports the sample above the ground surface for analysis. The analysis is performed in real time by a direct sampling ITMS in accordance with U.S. EPA draft Method 8265 (1994). Approximately 4 minutes elapse from the time the MIP reaches the sample depth of interest until the analysis results are available.

<http://www.estcp.org/documents/techdocs/index.cfm>

Tunable Infrared Laser Spectroscopy

Curl, R.F.; F.K. Tittel, Rice Univ., Houston, TX.

Annual Reports on the Progress of Chemistry, Section C: Physical Chemistry, Vol 98, p 217-270, 2002

This review covers recent developments in three areas: tunable infrared laser sources, techniques for tunable laser infrared spectroscopy, and applications of tunable infrared laser spectroscopy. The focus time period covers the years 1996 to 2001. This review focuses primarily on cw infrared lasers and pays little attention to most tunable pulsed infrared sources, such as free electron lasers, pulsed OPOs, and Raman shifting IR sources. These are important and valuable sources for spectroscopy, but outside the scope of this review.

<http://www-ece.rice.edu/lasersci/detectio.html>

Tunable Laser for Ground-Based and Airborne Submillimeter Radiometers: DeMaria Electro-Optics Systems, Inc., Bloomfield, CT.

Goddard Space Flight Center, NASA Success Story #5-029, Mar 2000

The integrated, turnkey, Graphical-User-Interface-driven, THz (far-Infrared) laser system comes in a rugged package and is capable of fully autonomous operation. Its development was supported by a 1995 NASA SBIR Phase II project. A commercial contract was in place with telecommunications company for a similar system at the same time a Phase III contract was in place with JPL for a non-folded version of the laser system. The system is applicable with or to THz local oscillators, THz receiver development, semiconductor spectroscopy, and chemical/biological agent detection. Contact: Gordon Chin, NASA, 301-286-8649; Eric Mueller, Demaria Electro-optics Systems, 860-243-9557.

The Use of Decision Support Systems to Address Spatial Variability, Uncertainty, and Risk Knowlton, Robert G.; D.M. Peterson; H. Zhang, Duke Engineering and Services, Inc., Albuquerque, NM.

Symposium on Spatial Methods for the Solution of Environmental and Hydrologic Problems: Science, Policy and Standardization, 25 January 2001, Reno, NV.

ASTM Special Technical Publication No 1420, p 109-121, 2002

Traditional methods of characterizing contaminated waste sites and evaluating cleanup alternatives generally rely on conservative methods that may not produce optimal results. With the advent of powerful desktop computers, advanced database management tools, sophisticated graphical display capabilities, new statistical methods, as well as decision analysis methods, there is a greater opportunity to employ decision support systems to address spatial variability, uncertainty, sampling efficiency, risk, and cost-benefit needs. Several decision support systems have been developed in the past few years that can address these needs directly, and help decision-makers evaluate their environmental liabilities and

alternatives for action in a more efficient manner. EPA recognized the value of these new tools in the decision making process and instituted a review of Decision Support Systems. Two decision support tools that were evaluated by EPA's Environmental Technology Verification (ETV) program, SamplingFX and GroundwaterFX, are discussed in this paper, along with examples of the use of the tools for decision-making purposes. The SamplingFX toolkit applies geostatistical analysis techniques and operations research methods to quantify uncertainty in the nature and extent of soil contamination, as well as optimizing the number and location of samples required for characterization. The GroundwaterFX toolkit utilizes Monte Carlo simulation techniques and operations research methods to quantify uncertainty in the nature and extent of ground-water contamination, as well as optimizing the number and location of monitoring wells required for characterization, and evaluating groundwater remediation strategies.

Use of Fluorophore/DNAPL Mixtures to Detect DNAPLs In-Situ

Keller, A.A.; M.L. Kram.

Physical, Chemical and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. Batelle Press, Columbus, OH. p 131-136, 1998

Fluorophores such as aromatic compounds (e.g. benzene, toluene, ethylbenzene and xylenes, as well as other constituents of petroleum fuels, oils, lubricants and greases) are present as co-contaminants in many Dense Non-Aqueous Phase Liquid (DNAPL) spills or may be extracted by the flowing organic phase from the soil organic matter. From 10 to 25% of the carbon present in humic and fulvic acids (a major component of soil organic matter) is in aromatic rings and these naturally occurring compounds have specific fluorescence spectra. Chlorinated solvents have been used extensively at many military, industrial and commercial installations precisely to degrease and clean surfaces which contain fluorophores. The fluorophore/DNAPL mixture may be detected in-situ using Laser Induced Fluorescence (LIF) probes, allowing the detection and delineation of the DNAPL source zone(s). We present results from laboratory investigations on the fluorescence of mixtures of these fluorophores in DNAPLs, characterized using a Luminescence Spectrometer. Concentration as low as 5% of fluorophore in the DNAPL solvent are easily detectable with the current instrument. Using the difference in characteristic fluorescence wavelengths for the various fluorophores, we are able to distinguish between naturally occurring fluorophores in the DNAPL solvent and introduced fluorophores. Preliminary field investigations using a LIF probe at a former Fire Fighter Training Facility located on a military installation situated in the Central Valley of California corroborate our laboratory results. Further field testing is planned to determine the detection limits of the optimized LIF probe, corroborating with traditional sampling methods. Results to date indicate that the LIF probe will not be applicable for a quantitative assessment of DNAPL saturation, but may be useful in combination with other probes in the cone penetrometer for DNAPL source delineation. The information generated by the probe will significantly extend the ability to characterize a contaminated site, improving modeling, risk assessment and site management.

http://www.esm.ucsb.edu/fac_staff/fac/keller/

Use of Laser Induced Fluorescence to Detect DNAPL and Fluorophore Mixtures In-Situ

Keller, Arturo A.; Mark Kram, Univ. of California, Santa Barbara.

Proceedings of the XXVIII IAHR Congress, Graz, Austria. 4 pp, 1999

The authors present results from laboratory investigations on the fluorescence of dense nonaqueous phase liquids (DNAPL) and fluorophore mixtures, characterized using a Luminescence Spectrometer. Fluorophores such as aromatic compounds (e.g., benzene, toluene, ethylbenzene and xylenes, as well as other constituents of petroleum fuels, oils, lubricants, and greases) are present as co-contaminants in many DNAPL spills. Concentration as low as 5% of fluorophore in the DNAPL solvent are easily detectable. Using the difference in characteristic fluorescence wavelengths for the various fluorophores, they are able to distinguish between naturally occurring fluorophores in the DNAPL solvent and introduced fluorophores. Field investigations using a Laser Induced Fluorescence (LIF) probe at several sites corroborate our laboratory results. Results to date indicate that the LIF probe will be applicable only for a qualitative assessment of DNAPL saturation, but may be useful in combination with other probes in the cone penetrometer for DNAPL source delineation.

http://www.esm.ucsb.edu/fac_staff/fac/keller/

Validation of a U.S. EPA Method for the Ion Chromatographic Determination of Perchlorate in Fertilizers Using a Polyvinyl Alcohol Gel Resin

De Borba, Brian M. (Metrohm-Peak, Inc., Houston, TX); Edward Todd Urbansky (U.S. EPA, Cincinnati, OH).

American Laboratory News, p 14-16, Jul 2002

This article describes the results of a study that demonstrated the suitability of a polyvinyl alcohol gel column for separating and quantitating perchlorate using a modified eluent of 4-cyanophenoxide salt as an additive to NaOH. Despite the high ionic strength present in many fertilizer products, a satisfactory separation of perchlorate from other anions found in fertilizers was obtained, allowing analyte detection and quantitation by suppressed conductivity. The column is robust in these matrixes, allowing them to be used to validate U.S. EPA Method 600/R-01/026 for screening fertilizers for perchlorate. The performance on fortifications, quality control standards, and precision are comparable to columns used in EPA's previous investigation.

<http://www.iscpubs.com/articles/entirealn.html>

Validation of the Low-Range Differential Pressure (LRDP) Leak Detection System for Small Leaks in Bulk Fuel Tanks. ESTCP Cost and Performance Report

U.S. DoD, Environmental Security Technology Certification Program. CU-9806, 51 pp, Nov 2002

The Naval Facilities Engineering Service Center (NFESC), Port Hueneme, California, and its industrial partners, Vista Research, Inc. and Vista Engineering Technologies, LLC, have demonstrated and validated (DEM/VAL) an innovative mass-based leak detection system for bulk fuel underground storage tanks (USTs). The Low-Range Differential Pressure (LRDP) system is a computer-controlled system that can reliably detect small leaks in bulk USTs ranging in size from 50,000 gal to 12,500,000 gal. As part of this project, it has been evaluated for performance by an independent third party in a 122.5-ft diameter, 2,100,000-gal tank following EPA's standard test procedures. The LRDP meets monthly monitoring and annual precision (tightness) test regulatory compliance requirements using either a 10-h (overnight) or 24-h test. All of the objectives of the project have been met, and the LRDP is ready for commercial use. Both (1) on-line, permanently installed monitoring systems and (2) tightness testing services using the LRDP can be obtained commercially through Vista Research, Inc. The LRDP system achieves a very high level of performance against small leaks because of its high precision (0.0002 in.) and its accurate methods of compensating for the thermal

expansion and contraction of the fuel, the instrumentation, and the tank. Because of its innovative design, the LRDP achieves this high level of precision and accuracy with an off-the-shelf, industrial-grade differential pressure sensor. Thus, the LRDP not only delivers high performance, but it is also rugged and field-worthy.

<http://www.estcp.org/documents/techdocs/index.cfm>

Wireline Cone Penetrometer System for Multiple Tool Usage. Innovative Technology Summary Report
U.S. DOE. Office of Science and Technology.
Report No: DOE/EM-0617, 21 pp, Sep 2001

Cone Penetrometer Technology is becoming more common for site characterization activities as its advantages (e.g., increased speed, lower cost, reduced drilling waste) over conventional drilling technologies has been demonstrated. Although CPT offers many benefits, it can be improved to offer increased utility and cost savings with the development of an innovative wireline system. The wireline cone penetrometer system consists of an assortment of tools that can be pushed using standard CPT rigs and equipment. The novel aspect of this approach is that various tools can be placed at the tip of the rod string depending on the time of information or sample desired. Tools can be swapped at any depth and different tools can be used for penetration or retraction. Wireline CPT allows nearly all work to be accomplished in a single penetration, as opposed to the multiple penetrations currently conducted if more than one kind of data is required.

http://www.osti.gov/bridge/product.biblio.jsp?osti_id=793548

The X-Ray, K-Edge Heavy Metal Detector

Jensen, Terrence; Joseph Gray, Ames Lab. and Center for NDE, Iowa State Univ., Ames, IA.
Report No: IS-5142, 27 pp, Aug 2000

Better quantification of heavy metal contamination in weapons lab facilities can yield savings in cleanup costs and benefits of reduced risk during dismantlement operations. The X-ray, K-edge heavy metal detector was developed under DOE's Characterization Monitoring and Sensor Technology Crosscutting Program [note: this program ended in 2002] to address these needs. The K-edge inspection technology is based on the measurement of the energy spectrum of a broadband X-ray beam transmitted through a sample. The X-ray source is an industrial X-ray tube, and the detector is a high purity Ge crystal. Both source and detector are collimated to define a narrow (<1mm dia.) beam used to probe the sample. Unlike other assay techniques, the K-edge method is not sensitive to sample geometry. The K-edge inspection system was successfully field demonstrated at several sites. During a large-scale demonstration at the Savannah River Site a series of exhaust ducts containing uranium deposits were inspected, and the results were compared with conventional passive gamma NDA measurements. Good agreement between the two techniques was observed, with the K-edge method providing greater precision and much better spatial mapping of the deposits. Other demonstrations of the technology have included detection of mercury, thorium, and uranium in drain pipes, and measurement of uranium deposits ranging from 10 mg/cm² to 6000 mg/cm² in 1/8 inch wall monel pipes. In another application, measurement of uranium concentration in spent nuclear fuel plate assemblies (up to 3000 mg/cm² for 18 fuel plates) was demonstrated with better than 5% precision within five minutes measurement time.

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