

Thirty-Seventh
Conference



Analytical Chemistry
in
Energy Technology

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MASTER



Gatlinburg, Tennessee
October 7-9, 1997

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ABSTRACTS OF PAPERS

THIRTY-SEVENTH ORNL/DOE CONFERENCE ON
ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

Park Vista Hotel
Gatlinburg, Tennessee
October 7-9, 1997

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Tuesday, October 7

8:25 WELCOME, M. L. POUTSMA, DIRECTOR, CHEMICAL AND ANALYTICAL SCIENCES DIVISION, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

TUESDAY AM, OPPORTUNITIES FOR COLLABORATION: INDUSTRY, ACADEMIC, NATIONAL LABORATORIES

CHAIRMAN: MARVIN L. POUTSMA, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

8:30 DOE OFFICE OF INDUSTRIAL TECHNOLOGIES. Daniel E. Wiley, Department of Energy, Office of Industrial Technologies, Washington, DC 20585.

The DOE Office of Industrial Technologies (OIT) has as its mission improved resource efficiency of energy- and waste-intensive U.S. industries to: - reduce raw material and depletable energy use per unit output, - reduce generation of wastes and pollutants, and - provide advanced science and technology options that dramatically increase the productivity of U.S. industry. Continuous process manufacturers such as aluminum, chemicals, forest products, glass, metalcasting, oil refining, and steel consume two-thirds of the energy used in the manufacturing sector and generate over 80% of both air and water born pollutants. As overview of the OIT program which focuses its research and develop agenda on the development of new, precompetitive process technologies, as well as technologies which result in more efficient and cost-effective ways of acquiring raw materials, recycling materials, minimizing impact on the environment, and developing new products or innovative uses for existing products will be presented.

9:00 THE U.S. DOE LABORATORY TECHNOLOGY RESEARCH PROGRAM. S. J. Barish, Department of Energy, Advanced Energy Projects and Technology Research Division, Germantown, MD 20874-1290.

The Laboratory Technology Research (LTR) program supports high-risk, multidisciplinary research partnerships to investigate challenging scientific problems whose solutions have promising commercial potential. A distinguishing feature of the DOE Energy Research (ER) multi-program laboratories is their ability to integrate broad areas of science and engineering in support of national research and development goals. The LTR program leverages this strength for the Nations benefit by fostering partnerships with US industry. The program funds the national laboratory research while the industrial partner funds its research and often contributes funds, equipment, or supplies to the laboratory. Industry is thus able to explore scientific and technical approaches that would be too risky to undertake alone. Projects supported by the LTR program are conducted by the five ER multi-program laboratories: Argonne, Brookhaven, Lawrence Berkeley, Oak Ridge, and Pacific Northwest National Laboratories. These projects explore the applications of basic research advances relevant to DOE's mission over a full range of scientific disciplines. The program currently emphasizes three areas of mission-related research: advanced materials, intelligent processing/manufacturing, and sustainable environments. Measurements technology is an important enabling technology. Since its inception in 1992, the LTR program's technologies have won 12 R&D-100 awards, 15 Federal Laboratory Consortium awards, and 7 other awards including those from the popular press.

9:30 TECHNOLOGY VISION 2020: THE U.S. CHEMICAL INDUSTRY. Donald E. Jost, Executive Director, Council for Chemical Research, Washington, DC 20036.

Leaders in the U.S. chemical industry began a study in 1994 on the factors affecting competitiveness in the rapidly changing business environment and set out to develop a vision for its future. The work focused on needs in research and development capabilities which are directly linked to growth and competitive advantage. The product, "Technology Vision 2020", 1996, available from the American Chemical Society (ACS) Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, DC 20036 is the joint effort of the ACS, American Institute of Chemical Engineers, Chemical Manufacturers Association, Council for Chemical Research, and Synthetic Organic Chemical Manufacturers Association. Four disciplines identified as crucial to progress in the chemical industry are a) new chemical science and engineering technology, b) supply chain management, c) information systems, and d) manufacturing and operations. The Council for Chemical Research has played a lead role in developing more detailed road maps for research and development leading to the New Chemical Science and Engineering Technology vision. Priority areas identified are Chemical Synthesis, Bioprocesses and Biotechnology, and Materials Technology. Chemical Measurement is identified as a critical enabling technology. The Vision and the more detailed roadmaps being developed serve to identify specific topics for which the Chemical Industry encourages collaborative Industry-Academia-Government programs.

10:00 **BREAK**

10:30 INDUSTRY-GOVERNMENT PROGRAMS WITH THE FORMER SOVIET UNION. Michael E. Ehinger, National Security Program Office, Lockheed Martin Energy Systems, Inc., Oak Ridge, TN 37831-8257.

The end of the cold war and subsequent opening of the Former Soviet Union has provided a window into the vast military complex that was the heart of the Soviet system. Under the Soviet system, the very best and brightest were recruited and educated to serve the military complex. The manufacturing complexes were often located in closed and secret cities across the entire country. Most of these cities remain closed today, inaccessible to average Russian citizens without need to visit. The enterprises and institutes of the former Soviet military complex remain as concentrations of the very best scientists and manufacturing capabilities of the country.

The U.S. Government now recognizes that proliferation of weapons of mass destruction, including nuclear, chemical and biological, remains as probably the greatest threat to our national security and world stability. Like the entire soviet society, the scientists and enterprises of the Former Soviet Union's weapons complex are attempting to make the transition to a western, market driven economy. The success of this transition is extremely important to national security, especially in the weapons complex where materials and scientific talent could be diverted to clandestine manufacture of weapons. The U.S. Government has a number of programs aimed at stabilization to deter proliferation. Different programs target stabilization of nuclear materials, engagement of the scientists, and stabilization of the institutes and enterprises. The ultimate success in non-proliferation is transition to a market economy that involves the weapons complex. The programs offer opportunities for U.S. laboratories and industry, and the long term success indeed requires active, successful participation of U.S. industry. This paper describes U.S. non-proliferation U.S., their focus and inter-relationships, and the opportunities for industry participation.

11:00 COLLABORATION IN COMMERCIALIZATION OF SPECIAL TECHNOLOGIES. Vivian M. Baylor, Acting Manager, Special Projects Office, National Security Program Office, Lockheed Martin Energy Systems, Inc., Oak Ridge, TN 37831-8206.

The Oak Ridge National Security Program Office develops and manages projects for the Department of Energy and other federal agency sponsors to support national mission needs in intelligence, special operations, security and law enforcement. The goal of virtually all these projects is to develop prototype hardware within 2-3 years that can be manufactured by the private sector and sold in quantity to the government. Despite the fact that many of these projects are classified, there are numerous ways that private sector companies can collaborate with Oak Ridge on all stages of the technology development process. Specific examples of these collaborations will be detailed, including Work For Others contracts with the private sector, joint R&D through the Small Business Innovation Research (SBIR) program, licensing innovative technologies, Cooperative Research and Development Agreements (CRADAs), and other types of collaborations. Several currently-funded projects will be described as potential candidates for industry collaboration.

11:30 LUNCH

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TUESDAY PM, DEVELOPMENTS IN SENSOR TECHNOLOGY

CHAIRMAN: TIMOTHY J. McINTYRE, OAK RIDGE NATIONAL
LABORATORY, Oak Ridge, TN 37831

1:10 SURFACE-ENHANCED RAMAN DOSIMETERS AND
SENSORS. T. Vo-Dinh, Life Sciences Research Division,
Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge,
TN 37831-6101.

NO ABSTRACT RECEIVED

1:30 NEW SPECTROELECTROCHEMICAL SENSOR. C. J. Seliskar, W. R. Heineman, Y. Shi, A. F. Slaterbeck, S. Aryal, T. H. Ridgway, and J. H. Nevin, Departments of Chemistry and Electrical and Computer Engineering, University of Cincinnati, Cincinnati, OH 45221-0172.

A new type of spectroelectrochemical sensor that embodies two modes of instrumental selectivity (electrochemical and spectroscopic), in addition to selective partitioning through an applied film barrier, is described. The sensor consists of a planar optical substrate/electrode coated with a sol-gel-derived or polymeric selective film. Sensing is based on the change in the attenuation of light passing through the guided wave substrate which accompanies a chemical reaction of an analyte induced by electromodulation. Thus, for an analyte to be sensed, it must partition into the selective coating, be electrolyzed at the potential applied to the electrode, and either the analyte or its electrolysis product absorb light at the wavelength chosen for operation of the waveguide. Threefold selectivity for a chosen analyte relative to other environmental components is obtained by the choice of coating material, the electrolysis potential, and the wavelength for optical monitoring. The sensor concept is demonstrated with an indium tin oxide coated glass waveguide that has been over-coated with a sol-gel derived charge-selective thin film. One such selective coating used was a charge-selective sol-gel derived PDMDAAC-SiO₂ composite film, where PDMDAAC = poly(dimethyldiallylammonium chloride). Fe(CN)₆⁴⁻ was used as the model analyte to demonstrate that the change in the transmittance of the waveguide resulting from electrochemical oxidation of Fe(CN)₆⁴⁻ to transmittance of the waveguide resulting from electrochemical oxidation of Fe(CN)₆⁴⁻ to Fe(CN)₆³⁻ can be used to quantify an analyte. Micromachining this sensor concept into more fully integrated devices and testing of this sensor in a variety of environments will be described.

1:50 LAB-ON-A-CHIP DEVICES FOR CHEMICAL DETECTION AND IDENTIFICATION. Stephen C. Jacobson, Jörg P. Kutter, Christopher T. Culbertson, Andrew G. Hadd, Robert S. Foote, and J. Michael Ramsey, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6142.

Chemical and biological analysis will benefit from the ability to perform automated, rapid, and precise procedures. One approach to this end is to microfabricate components to be integrated into a single instrument to execute a complete procedure. Because microfabrication techniques are employed, advantages include low cost, compact devices with high speed processing while providing operational simplicity and reliability. Moreover, integration of chemical processing and analysis functions allows automated manipulation of samples and reagents at volumes orders of magnitude smaller than is feasible manually or robotically reducing reagent consumption and minimizing waste output. Miniaturized devices that have been fabricated recently by our group perform high speed electrophoretic separations, continuous flow homogeneous enzyme assays, gradient elution micellar electrokinetic chromatography, and cross-correlation chromatography. In addition, monolithic devices that integrated PCR with electrophoretic analysis have been demonstrated. These devices have exhibited the features mentioned above, and their design, fabrication, and operation will be discussed.

2:10 MICROCANTILEVER SENSORS. Thomas G. Thundat, Life Sciences Research Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6123.

Micromachined, mass produced cantilevers, such as those used in atomic force microscopes, are excellent micromechanical sensors. Microcantilever sensors operate by detecting changes in resonance response or deflection caused by mass loading, surface stress variation or changes in damping conditions. When molecules adsorb on surfaces they can also produce a surface stress due to forces involved in adsorption process. This surface stress can be observed as variation in microcantilever deflection or resonance frequency. We have developed a number of extremely sensitive physical, chemical, and biological sensors based on microcantilevers. Microcantilevers that are metal coated on one side (bimetallic microcantilevers) undergo bending with a thermal sensitivity of 10^{-5} K when exposed to thermal radiation. Using this concept we have developed sensitive thermal imaging devices. Because of its small thermal mass they can be heated to few hundred degrees and cooled down to room temperature in a fraction of a second making it an ideal tool for scanning calorimetry. Using conventional techniques these cantilevers can be mass produced from silicon, silicon nitride, and other materials. We have developed microcantilever array sensors consisting of 648 microcantilever on a single chip. Advantages of these extremely sensitive devices include miniature size, simplicity, low power consumption, low manufacturing cost, as well as their ability to operate in air or liquid. They can be the basis for a universal platform for real-time, in-situ measurement of many physical, chemical, and biochemical properties.

2:30 SIGNAL ACQUISITION TECHNIQUES IN SPECTRO-ELECTROCHEMICAL SENSING. A. F. Slaterbeck, T. H. Ridgway, C. J. Seliskar, and W. R. Heineman, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

A new type of spectroelectrochemical sensor employing three modes of selectivity (electrochemistry, spectroscopy and selective partitioning) has been described. The sensor consists of a planar optical light guide/electrode coated with a sol-gel derived selective thin film. For an analyte to be sensed by this device, it must partition into the selective coating, be electroactive at the potential applied to the electrode, and have a change in its absorbance at the wavelength of light propagated within the light guide. In general, the spectroelectrochemical signal acquisition will be achieved under the conditions of modulating the electrochemical potential and recording the light intensity changes which occur with wavelength. Modulating the electrochemical potential provides two significant benefits. First, the changes in absorbance of the analyte resulting from the repetitive potential waveform being applied to the electrode become time dependent. Therefore selectivity for the analyte can be achieved by temporal discrimination between the modulating absorbance of the analyte and a constant interference signal resulting from compounds which can also penetrate the sensing film, but are electroinactive in the applied potential range. Second, the repetitive nature of the absorbance signal provides the opportunity to use signal averaging techniques which can reduce noise and lower the detection limit of the sensor. An early prototype of the acquisition system has been developed. Its construction and operating will be discussed and demonstrated with a model chemical system that emphasizes the advantages obtainable from the new sensor.

2:50 **BREAK**

3:10 SPECTROELECTROCHEMICAL SENSING: THREE-MODE SELECTIVITY ACHIEVED SIMULTANEOUSLY IN A SINGLE DEVICE. Y. Shi, C. J. Seliskar, and W. R. Heineman, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

Three modes of selectivity based on charge-selective partitioning, electrolysis potential and spectral absorption wavelength were demonstrated simultaneously in a new type of spectroelectrochemical sensor. Operation and performance of the three modes of selectivity for detection of analytes in the presence of direct interferents were investigated using binary mixture systems. These binary mixtures consisted of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{bpy})_3^{2+}$ and of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{CN})_6^{4-}$ in aqueous solutions. Results on the $\text{Fe}(\text{CN})_6^{3-}/\text{Ru}(\text{bpy})_3^{2+}$ binary mixture showed that an anion-exchange coating consisting of PDMDAAC-SiO₂ [where PDMDAAC = poly(dimethyldiallylammonium chloride)] and a cation-exchange coating consisting of Nafion-SiO₂ can trap and preconcentrate analytes with charge selection. At the same time such coatings exclude interferents carrying the same type of charge as that of the exchange sites in the sensor coating. Using the $\text{Fe}(\text{CN})_6^{4-}/\text{Ru}(\text{CN})_6^{4-}$ binary mixture, the $\text{Fe}(\text{CN})_6^{4-}$ component can be selectively detected by restricting the modulation potential cycled to a range specific to the redox active $\text{Fe}(\text{CN})_6^{4-}$ component and simultaneously monitoring the optical response at the overlapping wavelength of 420 nm. It was also shown that when the wavelength for optical monitoring was chosen as 500 nm, which is specific to the $\text{Ru}(\text{CN})_6^{4-}$ component, interference from the $\text{Fe}(\text{CN})_6^{4-}$ component for spectroelectrochemical detection of $\text{Ru}(\text{CN})_6^{4-}$ was significantly suppressed even though the cyclic modulation potential encompassed the redox range for the $\text{Fe}(\text{CN})_6^{4-}$ component.

3:30 NON-INTRUSIVE PRESSURE SENSING IN CLOSED DRUMS. Mark Henderson and R. Daniel Costley, Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, Mississippi State, MS 39762.

At most waste sites, transuranic (TRU), low-level, and mixed wastes are stored in 55-gallon drums. Many of these drums contain hazardous, organic wastes as well. Radiolysis or other physical or chemical processes may result in gaseous emissions inside these drums. When this happens the pressure within the drum will increase, sometimes to unacceptable levels. In more drastic cases, these emissions may produce flammable or explosive atmospheres (e.g., hydrogen from radiolysis). Currently regulatory procedures require that each drum be individually opened and inspected for the presence of hazardous organic waste. This situation will be dangerous for workers if either of the conditions described above exist (high pressure or flammable atmosphere).

Researchers at DIAL are developing a non-intrusive technique that can detect whether the pressure inside the drum is above ambient. The natural frequencies of vibration of the drum change as the pressure inside the drum is increased. In experiments conducted at DIAL, pressures as small as 1 psi have been detected on a 10 gallon drum. These changes are audibly perceptible. More importantly to this application, these changes can be detected by simple, standard signal processing techniques. We believe that these results could be the basis for a simple, hand-held instrument that could detect whether the pressure inside the drum was at or above ambient. Such a system would alert workers of potential danger and greatly increase safety. Conversely, it would allow the segregation of suspect drums, and more rapid treatment of safe drums.

3:50 A PROTOTYPE QUARTZ RESONATOR DENSITY-VISCOSITY SENSOR SYSTEM FOR SLURRY MONITORING. R. W. Cernosek and A. N. Rumpf,* Sandia National Laboratories, Microsensor Research and Development Dept., P.O. Box 5800, MS 1425, Albuquerque, NM 87185-1425.

Sandia National Laboratories has developed fluid monitors based on thickness-shear-mode (TSM) quartz resonators. The TSM resonator consists of a thin AT-cut quartz crystal with metal electrodes deposited on opposing faces. Application of an RF voltage to the electrodes introduces a shear strain in the crystal producing maximum surface displacement at mechanical resonance. Materials in contact with the crystal surface perturb the resonant frequency and resonance magnitude proportional to the material mass, density-viscosity, or viscoelastic properties. The TSM quartz resonators are the primary component in a prototype slurry monitoring system. This system consists of two sensor probes, one for *in situ* tank monitoring and one for in-line pipe flow monitoring; a data acquisition interface module for measuring sensor frequencies and voltages; and a notebook computer for control, graphic display, and data storage. Each probe contains a quartz resonator sensor with oscillator electronics, a temperature sensor, and a gamma radiation monitor. The sensors have a density-viscosity measurement range of 0-500 g/cm³-cP and can operate in environments up to 100 °C and 200 kRad of total gamma dose. Performance of the prototype system was recently evaluated in comparative field trials at Oak Ridge National Laboratory. Details of sensor theory and operation along with construction, calibration, and evaluation of the prototype will be presented.

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

*on contract from Ktech Corporation Albuquerque, NM

4:10 DETECTING ^{137}Cs BREAKTHROUGH IN AN ION EXCHANGE PROCESS. R. L. Brodzinski, W. K. Hensley, E. A. Lepel, and M. R. Smith, Battelle, Pacific Northwest National Laboratory, P. O. Box 999, Richland, WA 99352.

High-level liquid radioactive wastes can be transformed to low-level wastes by removing the major radioactivity, ^{137}Cs , to reduce the radiation level sufficiently to meet low-level disposal requirements: thus saving high-level repository space while reducing the costs of disposal. This process requires a highly reliable, near real time monitoring system for the specific detection of ^{137}Cs in the eluent from an ion exchange column which is likely to upset the normal equilibrium between the ^{137}Cs and its daughter and may preferentially allow the $^{137\text{m}}\text{Ba}$ daughter to pass through. Since the 662-keV gamma ray normally attributed to ^{137}Cs is actually produced in the decay of the equilibrium daughter activity, $^{137\text{m}}\text{Ba}$, detection of the 662-keV gamma ray won't directly indicate cesium breakthrough. A matched pair of radiation detectors will be used to monitor the $^{137\text{m}}\text{Ba}$ activity in the effluent stream at two locations separated by a short span of time, or on separate fixed volumes of effluent, each for short periods of time. The deviation of the two measured activities from the ratio expected based on the decay of pure $^{137\text{m}}\text{Ba}$ represents the concentration of ^{137}Cs in the effluent. Different types of detectors have been evaluated based on the projected operational parameters of the actual production system. Actual spectra have been obtained with each type of detector on each of the radionuclides possibly present in any of the process streams which may pass through this ion exchange process. These spectra can be combined in any proportions to represent a composite spectra for any given feed stream, and the acquisition times, separation times, confidence levels, sensitivities, etc. can be estimated for any chosen process. These spectra can also be mimicked by a PNNL developed computer code, SYNTH, to extrapolate to different physical parameters in any process environment. Software must be capable of providing the necessary data, at a minimum the net 662-keV gamma ray count rate, but preferably the activity levels of all other isotopes present in the process stream as well, including ^{90}Sr , in extremely short periods of time, - perhaps no more than one second. The software will also have to work with the resolution available from the chosen detectors, which could be relatively poor if NaI(Tl) detectors are deemed to provide adequate information. Additional software will

evaluate the data with respect to the ^{137}Cs concentration in the process stream, display and archival of this information for operator information, historical and predictive capability to anticipate column loading and capacity, and process control output as, and if, desired. Byproduct information, such as the actual concentration of all other radionuclides present in the process stream will also be compiled and archived for use in waste inventory control. If the radionuclide concentrations can be measured on the input side of the waste form fabrication process, it will eliminate the need to sample and characterize the finished waste forms prior to disposal.

4:30 THE ACOUSTIC PLATE MODE TRACE ION CONTAMINANT SENSOR. J. Andle, M. Schweyer, J. Munson, R. Roderick and D. McAllister, BIODÉ, Bangor, ME 04401, L. French, and J. Vetelino, ECE Dept. & LaSST, University of Maine, Orono, ME 04469, C. Watson, J. Foley, A. Bruce and M. Bruce, Dept. of Chemistry, University of Maine, Orono, ME 04469.

Industrial processes, such as fossil fuel combustion and nuclear materials processing, have resulted in heavy metal contamination of soils and potentially of the surrounding groundwater. In particular, mercury contamination of groundwater is a serious threat to the ecosystem, cumulating in serious health problems for humans as well as wildlife. Monitoring of mercury contamination in groundwater requires a method of long-term verification. Sensors with lifetimes of months to years of operation without operator intervention are required. One sensor geometry, which is capable of detecting relevant concentrations of aqueous ionic contaminants, such as mercury, while withstanding typical environmental conditions, is the acoustic plate mode (APM) sensor. This piezoelectric sensor protects the electronics from the potentially corrosive aqueous fluid environment while providing a significant interaction with the fluid. Gold films are employed to accumulate the mercury via surface amalgamation. The added mass is measured as a change in the resonant frequency of the piezoelectric element. Electrochemical techniques are employed to impart selectivity, reversibility and to accelerate response kinetics. Preliminary mercury sensor results are presented. Potential applications in the detection of halogenated hydrocarbons and monitoring bacteria in bioremediation are introduced.

Supported by US Department of Energy under contract DE-FG02-94ER81717.

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TUESDAY PM, ANALYSIS IN CONTAINMENT FACILITIES

CHAIRMAN: JOHN H. MARLOW, WEST VALLEY
DEMONSTRATION PROJECT, West Valley, NY 14171

1:30 ICP ANALYSES OF VITRIFICATION PROCESS SAMPLES
USING GLOVEBOX ASSEMBLIES. J. Z. Christopher, J. H.
Marlow, K. M. McCarthy, and N. R. Tamul, West Valley
Demonstration Project, 10282 Rock Springs Road, P.O. Box
191, West Valley, NY 14171-0191.

An inductively coupled plasma-atomic emission spectrometer (ICP) coupled to a glovebox assembly is being used to analyze high-level waste (HLW) vitrification samples at the West Valley Demonstration Project (WVDP). There are two ICP glove box assemblies to provide continuous process support. The WVDP vitrification process started in July 1996 with a goal of processing the HLW in the tank in batches producing continuous feed to melter. Each batch results in desirable solified HLW of glass contained in stainless steel canisters. The glass is processed through various steps in which glass forming chemicals and other reagents are added to the HLW. Selected parameters are analyzed to monitor the process during the HLW initial (WI), the cold chemicals or glass formers (GF), the waste plus glass formers (WGF), and sugared feed (SF) stages. In addition, a random 10% of the canisters are sampled and analyzed for any metal oxide greater than 0.5% weight oxide in the glass composition. A typical analysis involves proper slurry aliquoting from the sample vials and dissolution and dilution in the shielded analytical cells followed by ICP and radiochemical analyses. The ICP glovebox assemblies support 80% of the total analytical requests for the vitrification samples. The chemical analysis is required to ensure each batch falls within the target range of the final HLW glass formulation. Based upon the results as of July 1997, the reported ICP data are in agreement with the process control values.

1:50 EVALUATION OF THE COMBUSTION SYSTEMS OF THE PLASMA HEARTH PROCESS USING FTIR SPECTROSCOPY. K. C. Carney, M. Powers, O. Tolstikhine, Argonne National Laboratory-West, P.O. Box 2528, Idaho Falls, ID 83403, J. Demirgian, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439, P. R. Lang and J. S. Lindner, Diagnostic Instrumentation and Analysis Laboratory, P.O. Drawer MM, Mississippi State, MS 39762.

The Plasma Hearth Process (PHP) has been developed to evaluate the use of plasma torch technology on surrogate, radionuclide spiked, and real mixed wastes. The system consists of a 150Kw torch operated on nitrogen. The torch furnace or plasma chamber is equipped with a propane burner that is used for preheating and is followed by a propane secondary combustor, an evaporative cooler, HEPA filters, a packed-bed scrubber, an induced draft fan, and an exhaust stack. All of the components with the exception of the fan and stack are located within secondary confinement. The facility is operated under radiological controls even when the feed to the furnace is a surrogate composition. Evaluation of burner performance is critical for minimizing environmental impact and for controlling facility economics. Organics in the feed may not completely oxidize to CO₂ given the gas composition within the furnace. Thus, the ability of the secondary combustor to destroy organics is of interest. Gas stream compositions have been determined using both a process monitor FTIR and an extractive unit. Concentrations of CO₂, CO, and H₂O have been determined for individual burner operation and while processing a surrogate (combustible debris) mixed-waste. Results indicate that each of the burners operates at stoichiometries (air/fuel) near a value of one. Processing of the feed, however, indicated that the secondary combustor was unable to accommodate the increased organic loading. Options to remedy this situation include the use of air as the torch working gas, or the incorporation of additional controls on the secondary burner. Details of the measurements including on-line calibrations, correlation between the two systems, and comparisons to calculations based on burner input and feed composition will be discussed.

2:10 ICP/MS ANALYSIS OF HANFORD'S HIGH-LEVEL
RADIOACTIVE WASTE. Jon W. Ball and William I.
Winters, Numatec Hanford Corporation, Richland, WA 99352.

The 222-S Laboratory on the Hanford Site is a full service analytical laboratory equipped to analyze Hanford's high-level radioactive waste. Within the past year, two custom inductively coupled plasma mass spectrometer (ICP/MS) systems have been installed and evaluated for use at 222-S. The first system is a unique Laser Ablation ICP/MS (LA-ICP/MS) designed and developed by Pacific Northwest National Laboratory (PNNL). This system is installed inside of an analytical hot cell for the analysis of direct radioactive sludges. Analyzing direct sludges inside of the hot cell provides significant benefits in the areas of cost reduction, waste minimization, and radiological exposure reduction. The second instrument system is a Thermo Jarrell Ash (TJA) Plasma Optical Emission Mass Spectrometer (POEMS) that has been built inside a radiological fume hood. The POEMS is a dedicated ICP/MS for the solution analysis of digested sludges and direct liquids. This presentation will focus on these installations and recent applications that have been developed or are under evaluation using these two instrument systems.

2:30 ACCELERATED SOLVENT EXTRACTION FOR ANALYSIS OF VOLATILE AND SEMI-VOLATILE ORGANIC COMPOUNDS IN HOMOGENEOUS TRANSURANIC WASTE. Chris P. Leibman and David V. Martinez, Los Alamos National Laboratory, Chemical Science and Technology, Los Alamos, NM 87545.

Characterization of transuranic (TRU) waste is required to meet the waste acceptance criteria of the Waste Isolation Pilot Plant (WIPP). This includes the characterization of TRU waste for hazardous organic compounds regulated under the Resource Conservation and Recovery Act (RCRA). Two analytical methods are typically employed to characterize the suite of hazardous organic compounds potentially present in TRU waste: one method for volatile organic compounds (VOCs) and one for semi-volatile organic compounds (SVOCs). As an alternative to these two methods, we have developed an automated procedure for the extraction and analysis of VOCs and SVOCs in homogeneous solidified TRU waste. This procedure is based on US EPA SW-846 Method 3545, accelerated solvent extraction (ASE), coupled with on-line GC and GC/MS analysis. Portland or envirostone gypsum cement stabilized TRU waste is placed in a gas tight milling vessel and ground using a ball mill. After grinding, the milling vessel is connected to an accelerated solvent extractor designed and built at LANL. Extraction is accomplished with 20 mLs of isopropanol at elevated temperature and pressure in approximately 20 minutes. The sample extract is then transferred via closed loop to a sample collection vessel, which can be removed to archive the sample. VOC and SVOC analyses are performed on-line using gas chromatography with photoionization, flame ionization, electrolytic conductivity and mass spectral detection. An electronic balance, ball mill, and extraction cell with heater are mounted in a glovebox for sample processing. Ancillary hardware, control systems and GC/MS instrumentation are mounted outside of the glovebox. The complete instrument is computer controlled. A graphical user interface facilitates instrument operation. Work to date has shown comparable or improved recoveries for target analytes using the ASE method compared to existing methods. ASE offers the distinct advantages of waste minimization, reduction of analytical time, and reduced worker radiation exposure compared to currently employed analytical methods.

2:50 **BREAK**

3:10 ORGANIC ANALYSES OF HIGHLY RADIOACTIVE SOLUTIONS REQUIRING PRETREATMENT BY Cs-137 REMOVAL. Chia-Lin W. Hsu, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, SC 29808.

The gamma-emitting radionuclide Cs-137 is removed from the Savannah River Site (SRS) high-level waste by adding sodium tetraphenylborate (TPB). The concentrated and washed precipitate slurry containing CsTPB is transferred to Defense Waste Processing Facility (DWPF) Salt Processing Cell and hydrolyzed to yield an aqueous product (PHA) free of benzene. The PHA is highly radioactive ($10E+11$ dpm) and contains some organic compounds that need to be analyzed for process control and process history. The major organic components are water soluble. One of the minor components, phenylboronic acid (PBA) must be analyzed quickly to verify that the hydrolysis reaction is complete. High performance liquid chromatography (HPLC) methods were developed to analyze these compounds with instruments contained in unshielded fume hoods. Removing Cs-137 from PHA prior to HPLC analyses is essential to minimize personnel radiation exposure.

The most important criteria for the sample preparation procedure were consistent and good recovery of the organic compounds, a minimum decontamination factor of 300, and convenience for use in the shielded cell. In this study ammoniummolybdate-phosphate (Bio-Rad AMP-1) was used for removing Cs-137 in PHA (pH 3.8), because it is effective in an acidic solution. With a two-step application of AMP slurry, a DF of $1E+4$ was achieved for Cs removal. Two separate HPLC methods were used to analyze PBA and three other organic compounds. The recovery of all the organic compounds were above 80%. In this paper we will discuss the sample preparation techniques and HPLC methods that were used to achieve an effective method.

3:30 MOBILE EMISSION SPECTROGRAPH USING A FIBER OPTIC CABLE FOR REMOTE SIGNAL ACQUISITION. W. A. Spencer, C. J. Coleman, J. E. McCarty, and R. S. Beck, Westinghouse Savannah River Company, Aiken, SC 29808.

The Defense Waste Processing Facility (DWPF) at the Savannah River Site analyzes radioactive waste sludges and vitrified waste in a small process support laboratory located inside the processing facility. The lab desired a second ICP system to relieve its analyses load and asked the Savannah River Technology Center to evaluate the use of a fiber optic coupled emission spectrometer to provide additional ICP analyses. The request asked for a design that would fit into a 24 wide x 36 long x 40 high box to be located at locations 4 and 10 meters from the plasma source. The request asked for the stability at 2 and 6 hours intervals and background detection limits for 5 days. Basic characteristics of the optical pick-up as a function of distance from the torch and height above the plasma coils were requested. In response to the request, SRTC successfully modified an existing Thermo Jarrel Ash Iris ICP system and characterized it to demonstrate the technology.

The modified fiber optic system covers a 190-850 nm range with better than 0.03 nm resolution. The system was made mobile and can fit the size requirement. Average relative standard deviation for 2 hours was 2% and for 6 hours was 4%. Both 4 and 10 meter fiber optic cables have detection limits comparable to those of the current DWPF instrument. 10 meter fiber had increasing loss of signal in the UV range and shorter fiber is preferred for measurements below 300 nm. Solarization of the fiber occurred while viewing an emission plasma for extended periods. New type "non-solarizing" fiber did not prevent the UV transmission losses. The solarization of the fiber caused a severe loss of signal below 235 nm making measurement of Ni 231.6 and Zn 213.8 lines difficult because of drifting calibration curves. Alternative lines are available for those elements. The system was insensitive to the collection height above the coil. Similar signals strength were obtained between 13 and 18 mm above the coil. An optimum occurred at approximately 16 mm above the coil. Measurements were made from distances as great as 40 cm from the torch with adequate signal. Signal improved with the expected square of the distance relationship. Best signal was obtained approximately 4 cm from the torch.

3:50 TOTAL ANION CONTENT OF DOE RADIOACTIVE WASTE TANK SLUDGES USING A PEROXIDE/HYDROXIDE FUSION PREPARATION METHOD. J. M. Giaquinto, D. L. Denton, J. M. Keller, and T. P. Mills, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6043.

The conventional preparation method used to determine anions in soils and sludges by ion chromatography is a simple water leach of the material. A typical anion analysis for radioactive waste tank sludges characterized by the Radioactive Materials Analytical Laboratory (RMAL) involves leaching up to one gram of material in a total volume of ten milliliters with type II water. The leachate is then analyzed for inorganic anions by ion chromatography using conductivity detection. This method, although quick and simple, will only yield accurate results for those anions which are present as components of water soluble compounds or are already in the interstitial liquid of the sludges. For waste stabilization processes however, an accurate determination of the total anion content is needed with emphasis on total phosphorous as phosphate and total sulfur as sulfate. As an example, tributyl phosphate which is commonly used as an extractant in nuclear processing, may make up a large fraction of the phosphorous present in the sludges. Tributyl phosphate has low solubility in water and is not detected using a water leach. The RMAL performed a study to determine the feasibility of combining a classical high temperature peroxide/hydroxide fusion preparation method with quantitation using modern analytical instruments to determine the total anion content of the sludges. Data from this study will be presented as well as the problems which had to be resolved to obtain accurate analytical results. Future challenges and remaining questions will also be discussed.

Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract DE-AC05-90OR22464.

6:00 WESTERN BUFFET

--NOTES--

Wednesday, October 8

WEDNESDAY AM, IMPROVING THE QUALITY OF ENVIRONMENTAL DATA

CHAIRMAN: PETE C. LINDAHL, ARGONNE NATIONAL LABORATORY, Argonne, IL 60439

8:00 RESULTS OF PILOT IMPLEMENTATION STUDIES OF DOE'S INTEGRATED PERFORMANCE EVALUATION PROGRAM (IPEP).* P. C. Lindahl, W. E. Streets, J. J. Marr, K. J. Parish, A. E. Scandora, Jr., and G. A. Anast, Argonne National Laboratory, Argonne, IL 60439; W. R. Newberry, U.S. Department of Energy, Washington, DC 20585; J. R. Dahlgran, U.S. Department of Energy, Idaho Falls, ID 83415; C. Watkins and J. Connolly, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415; and J. Fisk, U.S. Environmental Protection Agency, Washington, DC 20460.

The Department of Energy's (DOE's) Office of Environmental Management (EM) has developed the Integrated Performance Evaluation Program (IPEP) to collate and assess analytical results from the laboratories participating in national performance evaluation (PE) programs. Reports of the assessments will be provided to the participating analytical laboratories, sample management organizations, and EM Program Managers at DOE Operations Offices, and Headquarters. In addition, IPEP will provide guidance to these various audiences on the need for corrective actions regarding unacceptable performance by the laboratories. The goal is to have in place an integrated, consistent system for assessment and continuous improvement of laboratory performance throughout the DOE Complex.

During this past year, IPEP conducted two pilot implementation studies, one with the Idaho National Engineering and Environmental Laboratory (INEEL), and the other with Los Alamos National Laboratory (LANL). The IPEP reports prepared for these pilot studies included laboratory PE program data for the various commercial analytical laboratories contracted to support the EM programs at these two DOE sites. The following PE programs were used as data sources: the U.S.

Environmental Protection Agency's Water Pollution (WP) and Water Supply (WS) programs, and the DOE's Quality Assessment Program (QAP). These pilot studies provided an opportunity for the IPEP developers and the users to collaborate on the format and technical content of the IPEP reports during the developmental stage and to ensure that the reports meet the users' needs.

*Work supported by the U.S. Department of Energy under Contract W-31-109-ENG-38.

8:20 QUALITY ASSURANCE TASK FORCE - 1996 PERFORMANCE EVALUATION STUDY. Richard E. Jacquish, Washington Department of Health, Radiation Protection Division, 1906 Peachtree Lane, Richland, WA 99352.

There are approximately 12 organizations in the Pacific Northwest that are involved in environmental radiation monitoring and they have formed a group called the Environmental Radiation Quality Assurance Task Force for the Pacific Northwest (QATF). One activity the QATF has used to evaluate and improve environmental radiation data is to conduct quality assurance exercises that involve joint sampling, co-located TLDs, and intercomparison studies using split samples. These exercises are conducted about every other year.

In 1996, the QATF conducted an Intercomparison Study that involved the analysis of a reference sample prepared by the Washington Department of Health. The environmental reference sample consisted of soil collected from the 100 Area on the Hanford site. The soil had been contaminated with liquid effluents from the single-pass reactors which had been shut down since the early 1970's. This type of sample was selected because these facilities are now being characterized, cleaned up and closed.

A large sample was collected, sieved, dried, homogenized, packaged and distributed to the participants. All samples were analyzed by gamma spectroscopy prior to distribution. The participants were asked to analyze the sample in triplicate by gamma spectroscopy and they were told that the sample contained less than 200 pCi/g of gamma emitting radionuclides.

Analytical results were received from 12 participating organizations. The primary radionuclides identified in the study were ^{40}K , ^{60}Co , ^{137}Cs , ^{152}Eu , and ^{154}Eu , and ^{155}Eu .

This paper will discuss the results obtained by the participants, statistical analysis of results, and the details of the sample preparation.

8:40 OVERVIEW OF DOE'S ENVIRONMENTAL MEASUREMENTS LABORATORY. Mitchell D. Erickson, Director, US Department of Energy, Environmental Measurements Laboratory (EML), 201 Varick Street, New York, NY 10014.

The Environmental Measurements Laboratory (EML), located in New York City, is a federal resource for environmental measurements and for ensuring data quality. The Laboratory's staff of 70 is dedicated to serving DOE's technical community by conducting environmental measurements of radioactivity or other environmental contaminants on site or through laboratory-based analyses of collected samples. A number of EML's activities focus on data quality, for example, the development of manuals, the assessment of laboratory practices, participation in working groups, and response to DOE needs/crises. EML is celebrating its 50th anniversary this year.

9:00 THE LONGEVITY STUDY OF WATER SUSPENSION STANDARDS OF HIGH EXPLOSIVES. Gracy Elias, Steven D. Hartenstein, and William J. Carmack, Lockheed Martin Idaho Technologies Company, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415.

The work presented here expands upon a method developed by the Federal Aviation Administration (FAA) for the preparation of standard suspension of high explosives. These suspensions are necessary to produce the simulated fingerprints used to evaluate trace explosive detection systems. The simulated fingerprints provide a safer and more reproducible and accurate means of applying explosives to testing surfaces. To enhance the use of these standard suspensions, work at the Idaho National Engineering and Environmental Laboratory (INEEL) has involved the study of the changes in the concentrations of suspensions during storage.

Water suspension standards of Composition C-4, Semtex H, and Detasheet were prepared and then analyzed using High Performance Liquid Chromatography (HPLC). The standards were stored both in a freezer and a refrigerator. The concentrations of these standards were checked periodically. The FAA recommended freezing for the long term storage of water suspensions. But the period of long term storage recorded was only up to three days. At the INEEL, the results of long term storage of the water suspensions of the high explosive standards of C-4 and Semtex H show that these standards can be kept in the freezer and refrigerator for longer period of time. The Relative Standard Deviation (RSD) for RDX and PETN did not change considerably for over two months in the Semtex H suspensions both in refrigerator and freezer. The RDX concentration of C-4 in the freezer was also acceptable after two months. The RDX concentration in C-4 which was kept in the refrigerator did not change considerably for one month. Detasheet suspension concentration changed considerably both in freezer and refrigerator samples. In addition to HPLC analysis, the suspensions were analyzed for particle size characteristics, both in suspension/solution and following drying of the suspension media. The particle analysis was completed using a volumetric particle analyzer and using a microscope with NIH-Image particle analysis software. The observations and results of this study as well as the particle analyses of these suspensions will be discussed in detail.

- 9 ⁹⁹Tc BIOASSAY: A DIRECT COMPARISON OF LIQUID SCINTILLATION RADIATION DETECTION AND ICP-MS MASS DETECTION OF THE ⁹⁹Tc ISOTOPE. Linda A. Lewis, Analytical Services Organization, Lockheed Martin Energy Systems, 113C Union Valley Road, Oak Ridge, TN 37831.

Historically, ⁹⁹Tc analysis has been based on the radiometric detection of the 293 keV beta decay product by liquid scintillation or gas flow proportional counting. In a urine matrix, the detection of ⁹⁹Tc has been plagued with many difficulties using conventional radiation detection methods. Difficulties may originate during chemical separation due to the volatile nature of Tc₂O₃, and/or during radiation detection due to color/chemical quenching. A separation scheme for ⁹⁹Tc in urine has been developed to prepare samples for analysis using ICP-MS. The analysis of ⁹⁹Tc using ICP-MS has proven to be a sensitive and robust analytical alternative. A comparison of methods using radiometric and mass quantitation of ⁹⁹Tc from a urine matrix has been conducted, and an evaluation of results and radiometric vs. mass detection sensitivities (λ vs. k) will be presented.

9:40 **BREAK**

10:10 OPTIMIZING ULTRA-HIGH PRESSURE AND TEMPERATURE CONDITIONS FOR MICROWAVE PREPARATION OF HIGH MOLECULAR WEIGHT ORGANICS FOR AA AND ICP ANALYSIS. Bob Fidler, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200.

Microwave digestion techniques are well-accepted as a means of preparing samples prior to AA and ICP analysis. Pressurization of sample vessels accelerates the dissolution process by permitting acids to attain higher temperatures than under ambient conditions. However, it has been historically difficult to control the microwave digestion process under ultra-high temperature and pressure conditions. This paper will demonstrate new approaches for optimization of ultra-high pressure and temperature conditions for microwave preparation of high molecular weight organics for AA and ICP analysis.

10:30 APPLICATION OF MULTIVARIATE METHODS TO QUANTITATIVE ICP/AES ANALYSES. David M. Haaland, William B. Chambers, Michael Keenan, David Melgaard, and Howland D. T. Jones, Sandia National Laboratories, Albuquerque, NM 87185-0342.

The advent of inductively coupled plasma atomic emission spectrometers (ICP-AES) with CCD detectors allows the application of multivariate methods to the quantitative analysis of the spectral data. These methods provide distinct advantages for the determination of trace elements in materials with high concentrations of spectral-rich elements. The disposition of excess DOE weapon components requires the determination of trace amounts of precious and RCRA hazardous metals in a complex mixture of aluminum and ferrous alloys. We have applied classical least squares (CLS) methods to the ICP-AES analysis of a set of samples containing 12 elements typically found in recycled electronic scrap. The elements included in the study were Ag, Al, As, Au, Cd, Cr, Cu, Fe, Ni, Pb, Pd, and Se. By performing the CLS analysis separately in each of 46 spectral windows and by pooling the CLS concentration results for each element in all windows in a statistically efficient manner, we have been able to significantly improve the accuracy and precision of the ICP-AES analyses relative to univariate and single window multivariate methods that are supplied with the spectrometer. This new approach simplifies the analyses by providing a single determination from all spectral windows simultaneously. We have compared the results for the univariate and single window multivariate methods provided by the instrument software to those results provided by the new CLS method. The new method's detection limits tend to be better than 10 ppb for each element in the presence of multiple interferences. Detailed improvements in detection limits, precision, and accuracy will be presented.

10:50 CHEMOMETRIC DATA ANALYSIS FOR GAS CHROMATOGRAPHIC DATA. Steven M. Thornberg and M. R. Keenan, Analytical Chemistry Department, P.O. Box 5800, Sandia National Laboratories,* Albuquerque, NM 87185-0343 and L. J. Woods, Mason & Hanger Corporation, P.O. Box 30020, Amarillo, TX 79120-0020.

Often sample analyses using gas chromatography yield many peaks in the chromatogram but not the identities or quantities of compounds (a formidable task for samples containing many unknowns). A need exists to be able to extract useful information from chromatograms without having to identify and quantitate all peaks. Examples of useful information include: 1) In which population does this chromatogram belong? 2) Is this chromatogram "normal" for the population or an outlier? and 3) What are the similarities or differences of this chromatogram to the population?

Chemometric data analysis tools applied to chromatograms can answer these questions and provide qualitative information through pattern matching. In contrast to typical data analyses which use only selected peaks, chemometric analyses use all meaningful data in the chromatogram.

In this talk, results from applying these tools to over 100 chromatograms obtained from weapon gas samples will be presented. Considerations when applying chemometric tools to chromatograms along with data preprocessing techniques will be discussed. Special attention will be given to finding outliers in a population since these outliers are most interesting when trying to find anomalies.

*Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:10 INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY. Zoe Grosser, Sarah Howden, and Ken Fredeen, The Perkin-Elmer Corporation, 50 Danbury Road, Wilton, CT 06897-0219.

Inductively coupled plasma emission spectrometry provides a convenient and speedy analysis of a variety of environmental matrices for trace metals. The accuracy of the method can be affected by spectral interferences and the quality and ruggedness of compensation techniques are critical. Laing, et al. point out that conventional interfering element correction factors (IECs) can often yield incorrect results without warning. Modern spectrometers, which capture spectral shape in their measurements, rather than sparsely sampled points, can use the additional information for more sophisticated interference correction routines. We will describe a multicomponent spectral fitting algorithm (MSF) for interference correction and compare it with other types of correction for environmental samples.

11:30 SUBSURFACE QUANTITATIVE SITE CHARACTERIZATION EMPLOYING AN IMPLANTED SAMPLING MODULE. Ralph H. Ilgner, Rob R. Smith, Roger A. Jenkins, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory,* P.O. Box 2008, Oak Ridge, TN 37831-6120, and Daniel P. Lucero, Consulting Thermodynamicist, 18421 Cedar Drive, Triangle, VA 22172.

An analytical system employing a diffusion limited sampling module and a direct sampling ion trap for quantitative assessment of subsurface fluids was developed and field tested. The sampling module is deployable with a cone penetrometer. It can be retrieved or remain as an implant for an indefinite time period. The device geometry, consists of two planar membranes enclosing a diffusion cell, provides good implant ruggedness and reliable service in the field. Also, the sampling module is protected within a push pipe housing to extend implant service life. Subsurface volatile organic compound (VOC) vapors, in nanoliter amounts, diffuse through the sampler membrane wall by a diffusion-limited process that is independent of the soil permeability. The soil gas sample extraction rates or volume are in the nanoliter/min. or microliter range. By design, the membrane soil gas diffusion impedance is set at a much higher level than the impedance offered by the permeability of dense clays, on the order of 0.1 millidarcy (md); consequently, gas flow in the sampler is a membrane diffusion limited process that is independent of the surrounding soil permeability. Of equal importance, this design feature renders the sampler unpluggable with soil, which is a severe operational limitation with certain other samplers. Sample vapors are transported to the surface for analysis by ion trap, or other analytical devices. Metered pressurized or reduced pressure carrier gas is utilized for sample transport to the surface. The vapors obtained are a function only of the fluid partial pressure and the vapor conductance of the sampler. Thus, quantitative analytical data is obtained regardless of soil conditions. The sampling module was deployed in the field at Dover Air Force Base at depths of 5 to 8.5 feet by

*Research sponsored by the U.S. Army Environmental Center (USAEC), DOE No 1769-F054-A1, U.S. Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

the US Army Site Characterization and Analysis Penetrometer System (SCAPS). Relatively small 1.75 inch diameter push pipe and the small vapor samples extracted cause minimal soil disturbance which preserves the integrity of the sampler subsurface surroundings. Analytical results were obtained for the system sampler operating in real time and as an implant where equilibrium was obtained between sampler interior and the external surroundings. Results in the real time and implant mode correlated to within 10%. The utility of the entire analytical system, deployed with a US Army cone penetrometer, was satisfactorily demonstrated. No plugging of the membranes, calibration gas ports, or transport gas ports was noted during field implantations. More field applications are needed to more conclusively demonstrate implant utility for more widespread applications including ground water analysis.

11:50 LUNCH

WEDNESDAY AM, PROCESS ANALYSIS

CHAIRMAN: R. DANIEL COSTLEY, DIAGNOSTIC INSTRUMENTATION AND ANALYSIS LABORATORY, Mississippi State, MS 39762

8:20 ANALYSIS OF COMPOSITES BY SCANNING TUNNELING MICROSCOPY. Catherine E. Vallet, Chemical and Analytical Sciences Division, and R. A. Zuhr, Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN-37831-6197.

Thin films of {RuO₂, TiO₂} mixed oxide on Ti substrates were analyzed by Scanning Tunneling Microscopy (STM) operating in the constant height mode. Large local differences in the tunneling current, through a tip maintained at a constant distance from the sample surface, reflected the difference in electrical conductivity of metallic RuO₂ and semiconducting TiO₂.

A digital processing of the 3D images of current gave the composition of conductive RuO₂ at the sample surface. The results of analysis for three samples are quantitatively compared with analyses by Scanning Electron Microscopy/Energy Dispersive X-ray imaging (SEM/EDX) and Rutherford Backscattering Spectroscopy (RBS).

STM shows promises for giving a quantitative analysis with high spatial resolution of nanometer composite materials of technologic relevance to catalysis, non linear optics, sensors and electronic devices.

The RBS measurements were done at the Surface Modification and Characterization (SMAC) user facility at ORNL.

Research sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-94OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

8:40 AIR MICROWAVE PLASMA CALIBRATION FOR REAL-TIME MONITORING OF METALS EMISSION. P. P. Woskov, K. Hadidi, B. R. Pollack, K. M. Green, G. J. Flores, P. Thomas, and D. R. Cohn, Plasma Science and Fusion Center, Massachusetts Institute of Technology, Cambridge, MA 02139.

Microwave-plasma atomic-emission spectroscopy (AES) in undiluted furnace exhaust gases is under development as a continuous-emissions-monitoring technology for hazardous metals. Such monitors are needed to insure that thermal waste treatment processes do not produce a secondary pollution stream of hazardous metals into the atmosphere. It has been shown that a large (~ 25 mm dia. X > 100 mm), continuous plasma sustained by microwaves in a shorted waveguide can be flange mounted into or onto a furnace exhaust duct with a short exhaust sample line, and that it can be a robust excitation mechanism for sensitive, AES measurements in a furnace environment [1]. The current challenge is to develop a real-time calibration method to quantify the metal light emission signals under all furnace exhaust matrix conditions. Our approach is to periodically add to the furnace off-gas sample a known mass of one or more of the metals being monitored. This is accomplished by a concentric pneumatic nebulizer with spray chamber attached to a branch line of the exhaust sample line. The nebulizer adds approximately 0.5 L/min continuous flow to the 20-30 L/min sample exhaust flow into the plasma. The mass transport efficiency of the nebulizer system is established under actual operating conditions by a comparison with direct sample insertion of a known sample mass on an alumina rod. Results of these calibration experiments will be presented.

[1] P. P. Woskov et al., *Rev. Sci. Instrum.* **67**(10), 3700 (1996).

9:00 CONTINUOUS EMISSION MONITORING OF HAZARDOUS AIR POLLUTANT METALS IN INCINERATOR STACK GASES. Gerhard A. Meyer, Thermo Jarrell Ash Corporation, 27 Forge Parkway, Franklin, MA 02038, Jim Dunn, East Tennessee Technology Park, Oak Ridge, TN 37831, and Michael D. Seltzer, Naval Air Warfare Center - Weapons Division, China Lake, CA 93555.

Thermo Jarrel Ash (TJA) has recently manufactured a commercial automatic continuous emissions monitor (CEM) for stack gas metals from burners and industrial furnaces. The instrument was developed and tested by the US Naval Air Warfare Center Weapons Division under a contract by the US Army Armaments Research Development and Engineering Center for their explosive ordnance deactivation project. The CEM employs automated extraction of the sample air from a stack under isokinetic conditions, periodic introduction of aliquots of sample air into an argon based inductively coupled plasma (ICP) optical emission spectrometer, and simultaneous multielement analysis of all hazardous air pollutant (HAP) metals, in addition to other process related elements. The entire sample is analyzed by the CEM, complete with particulate matter and moisture, i.e. no pretreatment or filtration of the stack sample is performed prior to making the measurement. Detection limits lower than 1 microgram per dry standard cubic meter have been achieved for most of the HAP metals. Among several prototype technologies presently being considered for metals emissions monitoring, the ICP based system has been the most successful to date in meeting many of the performance specifications drafted by the US EPA Office of Solid Waste.

This system was recently tested at East Tennessee Technology Park at the TSCA incinerator. The unit consisted of an inductively coupled plasma atomic emission spectrometer detector and associated electronics housed inside a climate controlled enclosure, comes complete with stack sampling system, sampling interface, and software for unattended and automatic operation of the CEM from a remote location. Results from the recent field demonstration will be presented.

9:20 CONTINUOUS EMISSION MONITORS BASED ON ION TRAP TECHNOLOGY: PRELIMINARY EXPERIMENTS AND FUTURE PROMISE. Kevin J. Hart, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6120.

The commercialization of ion trap mass spectrometers for the benchtop GC/MS market has spurred many new developments to improve the performance of this analytical instrument. Indeed, detection limits for some organic species have been reported in the part-per-trillion to part-per-quadrillion range. However, the success of the ion trap on the benchtop has also, to some extent, overshadowed the true versatility of this remarkable device. For example, experiments have been performed not only on positively charged organic ions using conventional electron ionization but also negative charged organic ions, inorganic species and even suspended particles. This presentation will review initial work aimed at developing the ion trap for continuous emission monitoring applications (e.g., monitoring volatile organic chemicals in flue gas) and the future promise of ion trap-based continuous emission monitors.

9:40 **BREAK**

10:10 FIBER OPTIC RAMAN SPECTROSCOPY FOR IN SITU WASTE TANK CHARACTERIZATION. Kevin R. Kyle and Steven B. Brown, R Division, Lawrence Livermore National Laboratory, Livermore, CA 94550.

The Hanford underground storage tanks provide a challenging environment for chemical characterization, with respect to the chemical complexity and reactivity of the heterogeneous waste matrix. A radiation and chemically hardened fiber optic Raman probe has been developed for the tank environment for cone penetrometer (CPT) deployment. Deployed in situ, the Raman probe provides a depth profile of both inorganic and organic chemical constituents. Ex situ deployment allows for tank leak detection utilizing sodium nitrate as a marker. Chemical constituents are identified on(c)line by a neural network hardware package that extracts signal from high background noise. The design of the Raman probe and the results of hotcell testing using archived tank waste samples will be presented.

10:30 LIQUID LEVEL AND DENSITY SENSOR FOR LIQUID SLURRIES. R. Daniel Costley, W. M. Ingham, and Jason A. Simpson, Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, Mississippi State, MS 39762.

It is extremely important for operators of vitrification facilities to know the properties of the liquid slurries they are processing. Currently a bubbler device (Hollidge gauge) is used to determine slurry level and slurry density in process vessels at some facilities. These gauges have performed their intended functions well, but require frequent and costly maintenance. The primary problem has involved either wear or plugging of this bubbler device by the viscous slurries.

A versatile new technology has been developed which provides slurry level and density in a single package which is more reliable than the instrument currently used. The instrument is simply a specially constructed rod, one end of which is inserted into the liquid slurry. Torsional waves are generated in the rod, via a magnetostrictive mechanism, by passing current through a coil which fits over the dry end of the rod. Slurry properties are measured by sensing the torsional waves which travel down the rod and reflect off the end inserted into the liquid. Different properties of the slurry can be determined using rods (waveguides) of different cross-section. Noncircular cross-sectional rods are used to measure density. Viscosity of the slurry can be measured with circular rods. Other properties that can be measured are liquid level and temperature. An intriguing aspect of the sensor is that it can provide information about the slurry as a function of depth, rather than at just a fixed point.

10:50 APPLICATION OF FTIR SPECTROSCOPY TO PROCESS CONTROL. J. M. Hamilton,¹ H. Toghiani,² and J. S. Lindner, Diagnostic Instrumentation and Analysis Laboratory, P.O. Drawer MM, Mississippi State, MS 39762.

The use of FTIR spectroscopy as a continuous emission or process monitors has augmented traditional facility characterization methods. A number of applications exist in the pharmaceutical industry and for combustion processes. Another possible application for FTIR spectroscopy is as an element in conventional process control of a facility. Most process control strategies currently used rely on standard sensors such as gas analyzers which do not provide speciation and quantitation of gas phase molecules. Correlation of process emissions to crucial control and operating variables can provide a means to assess the environmental impact and economics of a process.

FTIR spectroscopy implemented within a suitable control platform can provide a more detailed analysis and correlation of process performance with principle operating variables and can facilitate the control of the process through compositional analysis. Experiments focusing on this implementation are currently in progress. Extractive experiments are being investigated using a 10 m gas cell. Studies on spectral processing and interferometer operation have indicated that 2 cm^{-1} resolution provides sufficient discrimination for interferents and that measurement and analysis requires about 15 seconds (dependent on the number of molecules). Thus, the FTIR measurement can provide a rapid, on-line determination of gas phase composition for select species which could then be used as a control variable for process operation. Experiments on the DIAL 150 kW torch are in progress. Details of the implementation issues associated with using diagnostic instrumentation in control schemes will be discussed.

¹MS Student Department of Chemical Engineering

²Joint Appointment Department of Chemical Engineering

11:10 APPLICATION OF RAMAN SPECTRAL INSTRUMENTATION OF A CONFOCAL OPTICAL DESIGN TO MEASUREMENTS IN HARSH ENVIRONMENTS. Sheng Dai, J. P. Young, and Haiming Xiao, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6142.

It is difficult to spectrally access samples located in harsh environments. The various optical spectroscopies, however, yield qualitative and quantitative analytical information that is of value. In the past, so-called windowless cells were devised to carry out absorption, fluorimetric, and Raman spectral studies of corrosive samples such as molten salts. We have developed a new concept of windowless spectral measurement suitable for Raman or fluorometric spectral measurement. Instead of windowless openings into a sample container, this technique uses a confocal optical arrangement that can excite and gather optical signals from a distance through the top surface of the sample. With this device, we have obtained Raman spectral information in samples of molten alkali carbonates at 650°C and molten NaF-AlF₃ up to 1050°C. A description of the optical set-up plus an evaluation of its usefulness will be given.

Research sponsored by the Office of Industrial Technology and Office of Energy Research Laboratory Technology Research Program, U.S. Department of Energy, under CRADA 95-0362. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation under contract DE-AC05-96OR22464 with the U.S. Department of Energy.

11:30 LUNCH

WEDNESDAY PM, FIELD ANALYSIS

CHAIRMAN: DIANNE A. BLAKE, TULANE UNIVERSITY, New Orleans, LA 70112

- 1:30 TEAMING UNIVERSITIES AND NATIONAL LABORATORIES FOR SUCCESSFUL ANALYTICAL TECHNOLOGY DEVELOPMENT. Dianna S. Blair, Environmental Characterization and Monitoring Department Sandia National Laboratories, Albuquerque, NM 87185-0755 and Leslie Moore, Center for Process Analytical Chemistry, University of Washington, Seattle, WA 98195-0005.

A three year joint development effort involving Sandia National Laboratories (SNL), the Center for Process Analytical Chemistry (CPAC), and the CPAC industrial Sponsors was undertaken to transfer a new and innovative technology to the commercial sector. This technology, the FlowProbe™, is a generic platform for performing chemical analysis using reagent based chemistry in the field. The concept was originally researched at CPAC. However, they lacked the facilities, engineering expertise, and funding to further the design. SNL, with the skills set required to fulfill its basic weapons mission, was an ideal engineering partner for CPAC to team with. Jointly, the partners pursued, and obtained funding for the project from DOE.

Design of the FlowProbe™ was undertaken with input from DOE, the CPAC Sponsors, and other potential end users. The technology transfer mechanism chosen for this project was to develop a prototype FlowProbe™ instrument, conduct field testing of the prototype at DOE and CPAC Sponsor industrial sites, and aid commercialization of the FlowProbe™ technology based on the prototype design and field

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

test results. The three stages of the project (prototype development, field testing, and commercialization) address the gap that frequently exists between the proof-of-concept results from typical academic research and the successful commercialization of that technology. The FlowProbe™ technology and the transfer process will be discussed.

1:50 EVALUATION OF FIELD TECHNOLOGIES FOR THE MEASUREMENT OF PCBs.*Amy B. Dindal,¹ Charles K. Bayne,² Roger A. Jenkins,¹ ¹Chemical and Analytical Sciences Division, ²Computer Science and Mathematics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6120, David M. Carden, U.S. Department of Energy, Oak Ridge Operations Office, Three Main Street, Oak Ridge, TN 37830, and Stephen Billets, U.S. Environmental Protection Agency, National Exposure Research Laboratory, P.O. Box 9378, Las Vegas, NV 9193-3478.

The collaborative effort between the U.S. Environmental Protection Agency (EPA), U.S. Department of Energy (DOE), and the Oak Ridge National Laboratory (ORNL) represents a viable team to administer, plan, execute, and report on demonstrations of commercially available field characterization and monitoring technologies. This effort is part of the EPA's Environmental Technology Verification (ETV) Program. One of the overriding goals of this effort is to develop regulatory-accepted and cost effective alternatives to conventional fixed laboratory analyses through the identification and evaluation of innovative, field technologies.

A technology demonstration of polychlorinated biphenyl (PCB) field analytical techniques was conducted during July 22 through 30, 1997. The demonstration was conducted at a DOE site (ORNL) where there is a substantial repository of PCB-contaminated materials from

*Research sponsored by the Environmental Protection Agency, National Exposure Research Laboratory, Las Vegas, Nevada, under interagency agreement 1824-JO93-C1 and the Environmental Management Program, U. S. Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

multiple DOE sites. Technology developers with PCB monitoring instrumentation were evaluated. These instruments included field portable gas chromatographs with surface acoustic wave and electron capture detectors, and field analysis kits, including immunoassay and ion specific electrode kits. These instruments are suitable for the quantification of PCBs in a variety of matrices. Soil and surface samples were evaluated during the demonstration. The demonstration focused on the current DOE-Oak Ridge analytical needs to support Toxic Substance Control Act (TSCA) decisions, while allowing developers to showcase the features of their technologies. Results from the demonstration will be published as environmental technology verification reports.

2:10 ANALYSIS OF SEMI-VOLATILE NITROAROMATIC COMPOUNDS BY HEADSPACE SPME. William B. Chambers, Susan F.A. Bender, and Phillip J. Rodacy, Sandia National Laboratories, Albuquerque, NM 87185-0342.

The quantitative determination of nitroaromatic compounds such as trinitrotoluene (TNT) and dinitrotoluene (DNT) in water and soil have applications to environmental remediation programs and potentially to the detection of buried, unexploded ordnance (UXO). Recent advances in the development of solid phase micro-extraction (SPME) methods have enabled the determination of part-per-billion and lower quantities of these compounds in environmental samples by gas chromatography (GC) without the need for solvent extractions. SPME headspace analysis has been shown to offer advantages in the determination of many volatile organic compounds (VOC's) in soil samples. A method has been developed at Sandia Laboratories for the SPME-GC headspace determination of semi-volatile nitroaromatics in soil and sediment samples, based on water extraction and partitioning of these compounds into the vapor state. The sensitivity is comparable to GC analysis by organic solvent extraction and allows for the rapid determination of these compounds in complex environmental matrices. Additional improvements in sensitivity can be obtained by utilizing ion-mobility spectrometry (IMS) in conjunction with SPME headspace concentration. The results of GC and IMS analysis of laboratory standards and field samples will be discussed along with the potential for field applications of these techniques.

2:30 ASSAY OF HEAVY METALS USING ANTIBODIES TO METAL CHELATE COMPLEXES. D. A. Blake,¹ M. Khosraviani,¹ A. R. Pavlov,¹ H. Yu,¹ G. C. Flowers,² and R. C. Blake, II,³ ¹Department of Ophthalmology, Tulane University School of Medicine, ²Department of Geology, Tulane University, and ³Department of Basic Pharmaceutical Sciences, Xavier University of Louisiana, New Orleans, LA 70112.

Immunoassays are becoming increasingly accepted for environmental applications because they are quick, inexpensive, simple to perform, and sufficiently portable to be used at the site where the sample is collected. An antibody-based assay for ionic cadmium has been developed using a previously described monoclonal antibody that binds to Cd(II)-EDTA complexes with high affinity (Blake, D.A. et al. [1996] *J. Biol. Chem.* 44:27677). The competitive immunoassay reliably measured ionic cadmium at concentrations from 7 to 500 ppb in aqueous samples. Ca(II), Na(I), and K(I), cations commonly encountered in ambient water samples, did not interfere with the cadmium immunoassay at concentrations approaching their limit of solubility. The assay compared favorably with atomic absorption spectroscopy in its ability to measure cadmium in spiked water samples taken from a Louisiana bayou. A second antibody has been developed which recognizes chelated complexes of Pb(II). This antibody has been used to construct prototype immunoassays that measure ionic lead at concentrations from 0.2 ppb to 200 ppm. A prototype immunoassay for chelated complexes of Hg(II) has also been constructed. This assay measured ionic mercury at concentrations from 5 to 100 ppb but did not recognize metallic mercury.

Supported by the U.S. EPA Grant R-824029 (to D.A.B.) and U.S. DOE Grant DE-FG01-93EW53023 (to the Tulane/Xavier Center for Bioenvironmental Research).

2:50 ENVIRONMENTAL APPLICATION OF AN AUTOMATED GAS CHROMATOGRAPHIC SYSTEM. Gary S. Brown, Dennis J. Morrison and Dianna S. Blair Environmental Characterization and Monitoring Systems Department, Sandia National Laboratories, Albuquerque, NM 87185-0755.

The Pinellas Plant, located in Largo, Florida, is site of the Innovative Treatment Remediation Demonstration, ITRD, Program, funded out of DOE Office of Environmental Restoration, EM-40. It is an advisory group composed of representatives from DOE, EPA, industry and state and federal regulatory agencies assembled for the cooperative evaluation of innovative remediation technologies. As part of the ITRD project, a BioRemediation Project was undertaken on the Pinellas Northeast Site in early 1997. An automated purge-and-trap gas chromatograph, the AQUASCAN, manufactured by Sentex Systems Inc., Ridgefield, NJ, was purchased and plumbed so that the contaminated ground water pumped from the Pinellas Northeast Site could be monitored for chemicals of concern during the project. The AQUASCAN purge-and-trap gas chromatograph is designed to be a complete system that can perform an entire water analysis without the need for additional equipment. It is designed to automatically perform calibration or analysis at predefined frequencies, collect calibration or process sample, purge-and-trap sample, thermally desorb and subsequently inject sample trapped on sorbent, perform chromatographic separation and identification, identify and integrate chromatographic peaks, and display chromatograms, retention times, concentration levels and operating conditions. Automated routine calibrations in the field required access to a stable calibrant. To fulfill this requirement, a facility for refrigeration, storage, and delivery of a calibration solution was designed, built, and

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

implemented on site. During an initial 3 week on-site evaluation of the system was determined to be reliable and accurate. The AQUASCAN reported concentration values for methylene chloride, trichloroethylene, and toluene in the Pinellas ground water were within 20% of reference laboratory values. These results and the instrument's performance during the BioRemediation project will be presented.

3:10 DEVELOPMENT OF SYNCHRONOUS LUMINESCENCE ...,
T. Vo-Dinh, Life Sciences Division, P.O. Box 2008, Oak Ridge
National Laboratory, Oak Ridge, TN 37831-6101.

NO ABSTRACT RECEIVED

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WEDNESDAY PM, RADIOLOGICAL SEPARATIONS

CHAIRMAN: JAMES R. STOKELY, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

1:30 DETERMINATION OF Pu AND Am IN CORAL SAMPLES AND SOIL SAMPLES WITH VERY HIGH CALCIUM CONTENT. Dr. Anna Berne, Environmental Measurements Laboratory, U.S. Department of Energy, 376 Hudson Street, New York, NY 10014.

Coral and soils with unusually high calcium content represent a unique set of problems when an analyst needs to analyze them for Pu and Am. At Environmental Measurements Laboratory (EML) the standard approach would be to treat these samples as soils and follow the sequence of: 1. acid digestion and leach, 2. Pu valence adjustment and anion exchange column to remove Pu, 3. purification of the Am fraction using calcium oxalate coprecipitation, followed by iron hydroxide coprecipitation, and ending with several different schemes, all designed to remove iron, remains of Pu and Th, and lanthanides, 4. preparation of both Pu and Am for alpha spectrometry by coprecipitation with neodymium fluoride. However, with 10 gram aliquots there is as much as 4 grams of calcium present and the calcium oxalate coprecipitation requires increased volumes and becomes much more labor intensive. In addition, some of the schemes referred to in step 3 cannot be used, and only the classical, labor-intensive and waste-generating methods are possible.

Because of time constraints, a method had to be proposed and used, which could eliminate or at least minimize some of these problems. For most of the samples that had to be analyzed, the following approach was taken: 1. acid digestion and leach, 2. Pu valence adjustment and anion exchange column to remove Pu, 3. iron hydroxide coprecipitation to remove calcium, 4. 200 mg calcium added and calcium oxalate coprecipitation to remove iron, 5. TRU Resin column to remove remains of Pu and Th, 6. TEVA Resin column to remove lanthanides, 7. preparation for alpha spectrometry.

There was a significant decrease in the time required for the analysis, as well as reduction in waste generated. Data will be presented for recoveries, reproducibility, and the quality of the spectra.

1:50 Tc-99 SEPARATION FOR ANALYSIS IN HIGH ACTIVITY WASTE TANK SAMPLES AT SRS. Matthew R. Nelson, Westinghouse Savannah River Company, Aiken, SC 29808.

A new high speed separation method for the analysis of Technetium-99 (Tc-99) in high activity waste tank samples has been developed at the Savannah River Site (SRS) Central Laboratory. The ratio of Cesium-137 (Cs-137) to Tc-99 produced in SRS reactor assemblies is a minimum of 4430 to a maximum of 8420. To eliminate the Cs-137 interference in samples prior to Liquid Scintillation Counting, a multi-stage column technique was developed using Ammonium Phosphomolybdate (PMA) and TEVA Resin® in series. Ammonium Phosphomolybdate, from Atomergic Chemetals, is a cesium specific ion exchange resin in low molarity nitric acid and TEVA Resin®, from Eichrom Industries, is a tetravalent actinide column extraction resin that is used for technetium separation in low molarity nitric acid. This method, in conjunction with an applied vacuum system, allows for rapid separation of Tc-99 from high activity waste tank samples and maximizes Cs-137 removal prior to the TEVA Resin® cartridge. Decontamination factors for Cs-137 are approximately 1,000,000 prior to Liquid Scintillation Counting. Tc-99 spike recoveries are 92 to 94 percent.

2:10 RAPID ACTINIDE SEPARATION METHODS. Sherrod L. Maxwell, III, Westinghouse Savannah River Company, Aiken, SC 29808.

New high speed actinide separation methods have been developed by the Savannah River Site Central Laboratory that can be applied to nuclear material process samples, waste solutions and environmental samples. As part of a reengineering effort to improve efficiencies and reduce operating costs, solvent extraction methods (TTA, Hexone, TBP and TIOA) used for over thirty years in the SRS Central Laboratory were replaced with new rapid extraction column methods able to handle a variety of difficult sample matrices and actinide levels. Significant costs savings were realized and costly mixed waste controls were avoided by using applied vacuum and 50-100 micron particle size resins from Eichrom Industries. TEVA Resin, UTEVA Resin, and TRU Resin columns are used with flow rates of approximately 2 to 3 milliliters per minute to minimize sample turnaround times. Single column, dual column and multistage cartridge methods for plutonium, uranium, neptunium, americium and curium were developed that enable rapid, cost-effective separations prior to alpha counting, thermal ionization and inductively couple plasma mass spectrometry, and laser phosphorescence measurements.

2:30 AUTOMATED SEPARATION OF RADIONUCLIDES IN ENVIRONMENTAL AND WASTE SAMPLES. D. K. Mann, E. L. Jordan, A. M. Likens, S. P. Webb. Lockheed Martin Energy Systems, Inc.,* Analytical Services Organization, Oak Ridge, TN 37831-7458.

A commercially available system for the full automation of Solid Phase Extraction (SPE) to clean up and preconcentrate samples for radiochemical analysis is described. A Gilson ASPEC TM XL System has been modified for use with common radiochemical separation procedures using EIChroM resins. The system, primarily designed to handle organic separations, was modified to withstand the corrosive reagents used in radiochemical analysis. Uranium was determined using EIChroM UTEVA resin. The sample was loaded in 2 M nitric acid onto 0.7 grams of UTEVA resin packed in a syringe barrel SPE cartridge. The column was then washed with a 2M nitric acid/0.5 M oxalic acid mixture to remove any interfering isotopes. Finally, the uranium was eluted with a dilute nitric acid solution. All steps, including column conditioning, sample addition, elution and collection, are performed by the ASPEC TM XL System. The accuracy and precision of the system was compared to that of traditional manual methods. Laboratory standards, EMSL Performance samples, and both groundwater and liquid waste samples were analyzed using both methods. Sample transfer efficiency and cross contamination was measured. Other methods, such as the determination of Tc-99 using EIChroM TEVA resin, have been modified for automation using this system and will be discussed.

*The Oak Ridge Site is managed by Lockheed Martin Energy Systems, Inc. for the US Department of Energy under Contract DE-AC05-84OR221400.

2:50 ANALYSIS OF Pb-210 IN WATER AND SOIL SAMPLES,
USING EICHRHROM'S LEAD RESIN. Anil Thakkar and
Dr. James Harvey, Eichrom Industries, Inc., 8205 S. Cass
Avenue, Ste. 107, Darien, IL 60561.

A procedure has been developed by Eichrom Industries for
Pb-210 in water and soil matrices using specific extraction
chromatography resin which was designed for Lead analysis.

After preconcentration of Lead in water samples or leaching of
lead from a soil sample, it is separated using Eichrom's Pb resin column.
A stable Pb carrier is used as a tracer, which is monitored gravimetrically
and Pb-210 is measured as Bi-210 using a Gas-flow proportional counter.
This presentation will discuss the development of the procedure, test
sample results and trace recoveries.

3:10 GROSS ALPHA DETERMINATIONS ON SAVANNAH RIVER SITE HIGH ACTIVITY WASTE SOLUTIONS USING EICHROM'S ACTINIDE RESIN AND LIQUID SCINTILLATION ANALYSIS. D. P. DiPrete, S. F. Peterson, and R. A. Sigg, Westinghouse Savannah River Company, Aiken, SC 29808.

As a consequence of waste vitrification efforts underway at the Savannah River Site, a need has arisen to obtain gross alpha values in samples having high salt contents and high beta activities. Current waste treatment processes result in sample matrices with 6 to 7 orders of magnitude greater beta than alpha activity. Traditional methods for determining gross alpha activities at SRS were based primarily on gas flow proportional counter analyses of samples flame mounted on planchets. Sample pre-treatment to reduce the beta was necessary before an alpha analysis could be carried out. Plate mounting losses from volatile solids, as well as varying self-attenuation factors, made quantification difficult. A less time consuming method was desired to analyze these samples to provide a more rapid turn-around to the customer.

Liquid scintillation counting is a well established technique for screening samples for radioactivity. Relatively recent advances in liquid scintillation counters have made it possible to use pulse shape discrimination to simultaneously discern alpha and beta components for large quantities of samples. For samples of similar composition and radionuclide distributions, these instruments can be adjusted to give excellent gross alpha and beta results. However, SRS waste samples span a number of combinations of materials and radionuclide distributions. A constant discriminator setting, with fixed alpha and beta efficiencies, invariably leads to erroneous results. Packard Instruments Model 2550/AB Tri-Carb Liquid Scintillation Analyzer has been used to investigate the potential for a high turn-around low-cost method of obtaining quantitative gross alpha and gross beta values from samples of varying matrices. It was found spill-over from the beta to alpha channels could be reduced to levels of approximately 0.1%

A method has been explored to measure the alpha activity in this sample type using Eichrom's Actinide Resin in conjunction with liquid scintillation analysis with pulse shape discrimination. As has been previously demonstrated by Eichrom, the DIPEX extractant will disperse in liquid scintillation cocktail, allowing for a quantitative liquid scintillation analysis of environmental samples. Results of these experiments to extend the method to analyses of higher activity samples will be discussed.

WEDNESDAY PM, INTERACTIVE ANALYTICAL SEMINARS

CHAIRMAN: LINDA K. PLEMONS, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

3:30-5:00 POSTER SESSION

DEVELOPMENT OF EVALUATION PROTOCOLS FOR DOE'S INTEGRATED PERFORMANCE EVALUATION PROGRAM (IPEP).* W. E. Streets, P. C. Lindahl, J. J. Marr, K. J. Parish, A. E. Scandora, Jr., G. A. Anast, Argonne National Laboratory, Argonne, IL 60439; and W. R. Newberry, U.S. Department of Energy, Office of Environmental Management, Analytical Services Division, Washington, DC 20585.

The Department of Energy's (DOE's) Office of Environmental Management (EM) has developed the Integrated Performance Evaluation Program (IPEP) in response to the Inspector General's request for consistent oversight of laboratories providing analytical services to EM. The program is designed to collate and evaluate results from existing national performance evaluation (PE) programs and to provide reports of the evaluations to the participating analytical laboratories, sample management organizations, and program managers from DOE EM Operations Offices and Headquarters. In addition, IPEP will provide guidance to these various audiences on the need for corrective actions for unacceptable performance by the laboratories, thus providing an integrated, consistent system for evaluation and continuous improvement of laboratory performance throughout the DOE Complex.

The IPEP will use results from existing PE programs administered by U.S. Environmental Protection Agency (EPA) and DOE when these are available and appropriate for the matrix/analytes being

*Work supported by the U. S. Department of Energy under Contract W-31-109-ENG-38.

determined for DOE's environmental restoration and waste management programs. These PE programs provide a spectrum of matrices and analytes covering the various inorganic, organic and low-level radiologic species found in routine environmental and waste samples. These PE programs already provide some evaluation of laboratory performance; IPEP will expand these evaluations by incorporating historical performance, as well as results from multiple PE programs, thereby providing an enhanced usage of the PE program information.

The use of information from multiple PE programs will allow a more global evaluation of an individual laboratory's performance, as well as providing a means of more fairly comparing laboratories' performance in a given analytical area. Areas where corrective action might be needed will be identified. The IPEP will provide reports of PE performance to the laboratories to assist them in self-evaluation and improvement. Evaluation reports are being designed to facilitate consistent and fair laboratory oversight. This paper presents the proposed IPEP evaluation protocols.

THE EUROPEAN PROJECT ON DESTRUCTIVE
RADWASTE CONTROL. H. J. Steinmetz, H. Heimbach, and
R. Odoj, Research Centre Jülich, Forschungszentrum, Jülich,
GmbH ISR/PKS, GERMANY.

Present destructive measurements in quality control of radioactive waste are based on traditional analytical methods including many and often rather complicated radiochemical and radioanalytical procedures. According to increasing analytical tasks, routine controls of radioactive waste require new fast methods which allow the processing of many samples per week with high accuracy. In order to minimize time, manpower and other costs, sample characterization should be performed by making use of automated analytical systems with as few steps as possible.

The European Project on Evaluation and Standardization of Fast Analytical Techniques for Destructive Radwaste Control (short title: Destructive Radwaste Control) is carried out in the frame of the Nuclear Fission Safety research and training programme of the European Commission and is coordinated by the Institute of Safety Research and Reactor Technology (ISR) of the German Research Centre Jülich. Besides the ISR, the Central Institute for Chemical Analysis of the Research Centre Jülich (ZCH), the National Laboratory for Radioactive Waste Characterization, belonging to the Italian research organization ENEA and located in the Sallugia Research Centre (ENEA-ERG-RAD-LAB), the University of Antwerp, Belgium, Micro and Trace Analysis Centre (MITAC), the University of Innsbruck, Institute for Analytical Chemistry and Radiochemistry (UIBK), as well as the Institute for Reference Materials and Measurements of the European Joint Research Centre (JRC-IRMM) in Geel, Belgium, participate in this project.

The „Destructive Radwaste Control“ project aims at evaluating fast wet chemical laboratory techniques as well as isotope mass spectrometry for routine analysis in comparative tests on standards and genuine radioactive waste (LLW) of various compositions. In detail the project comprises evaluation of fast pretreatment techniques of samples and fast separation of radionuclides by High Performance Ion

Chromatography (HPIC), Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) and Ion extraction chromatography (IEC) as well as the detection of radionuclides either in solutions by Liquid Scintillation Counting (LSC) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or in solids by Laser Ablation ICP-MS (LA-ICP-MS) and Glow Discharge Mass Spectrometry (GDMS).

COMPARISON OF COMMERCIAL NEBULIZATION SYSTEMS FOR THE ANALYSIS OF FIRST ROW TRANSITION ELEMENTS BY ICP-MS. Shelby J. Morton, David H. Smith, and Douglas C. Duckworth, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375.

Inductively coupled plasma mass spectrometry is a powerful technique for trace (sub-ng/g) multi-element analyses. The technique is limited primarily by the formation of polyatomic interferences (e.g., ArO^+ , NaAr^+) and the presence of high levels of dissolved solids, which can result in signal suppression and drift. These problems are very evident in the analysis of the first row transition elements (e.g., Cr, Fe, Cu, Zn). In this work a standard Meinhard glass concentric nebulizer is compared to an ultrasonic nebulizer and the ultrasonic nebulizer with an additional membrane desolvation unit. These were evaluated in terms of sensitivity and the reduction of polyatomic interferences.

Research sponsored by the Laboratory Directed Research and Development Program of ORNL and the Office of Basic Energy Sciences, U.S. Department of Energy, under contract number DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

A MICROMACHINED FULLY-INTEGRATED
SPECTROELECTROCHEMICAL SENSOR. S. K. Aryal,¹

J. H. Nevin,¹ Y. Shi,² C. J. Seliskar,² and W. R. Heineman,²

¹Department of Chemical Electrical and Computer Engineering
and Computer Science, ²Department of Chemistry, University
of Cincinnati, Cincinnati, OH 45221-0172.

This paper describes a micromachined fully-integrated spectroelectrochemical sensor. A channel waveguide fabricated by diffusion of K^+ or Ag^+ ion in soda-lime glass substrate is discussed. An aluminum mask is used to make the channel. An electrode is made by depositing a thin layer of gold (for better conductivity) on top of aluminum, which also prevents aluminum from coming into contact with the analyte. The fabricated waveguide is polished and aligned with optical fiber on both ends. A V-groove and a pit are etched anisotropically on a silicon substrate using KOH solution for the alignment of the optical fiber with the waveguide. This device is capped with a silicon slab, which has an opening over the waveguide portion for interaction with the analyte. The channel waveguide is coated with a sol-gel derived charge-selective thin film, for example, PDMDAAC-SiO₂ composite film. The output optical attenuation is monitored. The absorbance is proportional to the concentration of the chemical species present in the sample. In this micromachined channel waveguide sensor the signal loss would be less; therefore, the sensitivity would be better than that of an ITO/SiO₂-coated sensor. The permanent alignment of the waveguide with the optical fiber makes this sensor more versatile to use.

DETECTION OF METHYL VIOLOGEN UTILIZING A NOVEL SOL-GEL/NAFION BLEND IN A NEW SPECTROELECTROCHEMICAL ATTENUATED TOTAL REFLECTANCE CONFIGURATION. Michael R. Clager, Carl J. Seliskar, and William R. Heineman, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

Methyl viologen is a dicationic organic compound developed in the 1960's as an herbicide. It has the characteristics of being hydrophobic as well as electrochemically active (i.e., undergoes reduction at a negative potential) and absorbs light in the visible region of the electromagnetic spectrum. These characteristics make methyl viologen ideal as a model organic compound for a new spectroelectrochemical sensor configuration developed in our laboratory. This new sensor platform utilizes attenuated total reflectance in a planar waveguide and an optically transparent working electrode that works in conjunction with a novel sol-gel/Nafion blend sensing layer. This sensing layer has the benefits of being optically transparent into the UV range as well as having chemical selectivity through two factors: the pore size of the sol-gel matrix and the ionic exchange of hydrophobic cations with the Nafion "islands" throughout the sensing layer. Results to be presented include signal strength based on composition of sol-gel/polymer sensing layer, a detection limit for the most optimized configuration, leaching of analyte from sol-gel/polymer matrix, and affinity for reduced methyl viologen in the presence of potential interferents.

GAMMA-IRRADIATED PDMDAAC/GRAPHITE
ELECTRODES WITH ENHANCED RESPONSE TO
FERRI/FERROCYANIDE COUPLE. M. Maizels, W. R.
Heineman and C. J. Seliskar, Department of Chemistry,
University of Cincinnati, Cincinnati, OH 45221.

The suitability of polydimethyldiallylammonium chloride (PDMDAAC) as a potential coating component for a ferrocyanide sensor is explored. Spectroscopic graphite electrodes were used as substrates for polymer immobilization. Gamma-irradiation was used to immobilize the polymer on the graphite surface. The ferri/ferrocyanide couple served as the model analyte to demonstrate electrochemical properties of the polymer film. Voltammograms of ferri/ferrocyanide at PDMDAAC modified electrodes exhibit significant partitioning of the analyte into the polymer film with current enhancements up to 200-fold. Immobilization of PDMDAAC onto graphite enables $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ to be present at the electrode at very high concentration, hence increasing the magnitude of the sensor response. Chronocoulometry was used to determine an apparent diffusion coefficient in the polymer network. The results of ion-exchange reactions of $\text{Fe}(\text{CN})_6^{3-}$ with PDMDAAC/graphite film were used to determine distribution coefficients between the polymer film and the bulk solution of the analyte. Variation in radiation dose does not seem to change the cross-link density of PDMDAAC on the graphite surface since voltammograms on electrodes exposed to dosages from 0.48 to 5.5 Mrad were almost identical. The PDMDAAC/graphite electrodes are reusable over an extended period of time. The feasibility of anchoring the polymer to the ITO glass is discussed.

NEW TRANSPARENT AND ION-EXCHANGEABLE
POLYMER BLENDS FOR OPTICAL SENSING. Letian Gao
and Carl J. Seliskar, Department of Chemistry, University of
Cincinnati, Cincinnati, OH 45221-0172.

Polymer membranes are an important part of many chemical sensors. To develop new planar spectroelectrochemical sensors, the selective layers on the top of sensor substrates are necessary. The materials for the layers must be clear, chemically stable and robust. Several new polymer blends have been formulated for the purpose of selectively incorporating solution-phase anions and cations of environmental interest. In all of the blends, poly(vinyl alcohol) was used as the host matrix and cross-linked with glutaraldehyde in the presence of HCl. Ionomers such as poly(acrylic acid) (PAA), Nafion, poly(diallyldimethylammonium chloride) (PDMDAAC), poly(vinylbenzyltrimethylammonium chloride) (PVTAC) and poly(styrenesulfonic acid) (PSSA) were physically entrapped inside the PVA-matrix to form the ion-exchangeable and clear materials. $[\text{Ru}(\text{BiPy})_3]^{2+}$, ferrocyanide and Cu(II) were used as the prototype analytes to study the new blends' ion-exchangeability. Two silane coupling agents, 3-glycidoxypropyltrimethoxysilane (GPTS) and 3-aminopropyltriethoxysilane (APTS), were used to covalently attach the new polymer blends to glass substrates which had been etched with 2 M NaOH, washed with 1 M HCl and rinsed with water. The silane reagent provides sites for the covalent attachment of the polymer membrane to the sensor surface. The thickness of spin-coated films was determined by an optical interference method. The coatings of Nafion and PAA blends exhibit better adhesion, that is they can stay on glass for days in solutions pH from 8 to 0. The prism-coupling method was used to make prototype wave-guide sensors with polymer blend coated slides to detect $[\text{Ru}(\text{BiPy})_3]^{2+}$ and ferrocyanide. Sample working curves for the analytes will be provided.

ELECTROCHEMICAL BEHAVIOR OF Re-DMPE COMPLEX ON POLYMER-MODIFIED ELECTRODES. Zhongmin Hu, William R. Heineman, and Carl J. Seliskar, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

To evaluate the performance of several coating films which are the candidates for the on-going development of a new spectroelectrochemical sensor, the electrochemical behavior of $[\text{Re(I)}(\text{DMPE})_3]^+ / [\text{Re(II)}(\text{DMPE})_3]^{2+}$ couple, where DMPE is 1,2-bis(dimethylphosphino)ethane, has been investigated at graphite electrodes coated with Nafion®- or Poly(styrenesulfonic acid) (PSSA)-doped poly(vinyl alcohol) (PVA) and sol-gel films. $[\text{Re}(\text{DMPE})_3]\text{CF}_3\text{SO}_3$ is the nonradioactive analog of $[\text{Tc}(\text{DMPE})_3]\text{CF}_3\text{SO}_3$. By investigating the rhenium compound, information directly applicable to the technetium compound may be derived while avoiding the use of radioactive material. The colorless $[\text{Re(I)}(\text{DMPE})_3]^+$ undergoes electrochemical oxidation, forming $[\text{Re(II)}(\text{DMPE})_3]^{2+}$ which is pink in aqueous solution. Thus, the redox reaction can be investigated electrochemically or spectroelectrochemically.

The incorporation of the cation exchangers, especially PSSA, promotes the partition of the rhenium complex ions into the coating, giving a significant enhancement in voltammetric signal. In PVA matrix, PSSA gave 3 times greater enhancement in voltammetric signal. In PVA matrix, PSSA gave 3 times greater enhancement than Nafion® did. Moreover, compared with an unmodified electrode, both the oxidation peak of $[\text{Re(I)}(\text{DMPE})_3]^+$ and the reduction peak of $[\text{Re(II)}(\text{DMPE})_3]^{2+}$ shifted to more negative potentials, indicating that the dopants interact stronger with $[\text{Re(II)}(\text{DMPE})_3]^{2+}$ than with $[\text{Re(I)}(\text{DMPE})_3]^+$. The merits of the dopants in sol-gel film will also be presented.

CAPILLARY ELECTROPHORESIS SEPARATIONS OF AMINOPOLYCARBOXYLATE HEXADENTATE LIGANDS INVOLVING THE FORMATION OF FLUORESCENT TERNARY COMPLEXES. Jason E. Dickens and Michael J. Sepaniak, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

A capillary electrophoresis (CE) separation of negatively charged hexadentate-based ternary complexes is described. Fluorescent ternary complexes are formed on-column when 8-hydroxyquinoline-5-sulfonic acid (HQS) is chelated to hexadentate ligand - lanthanide metal (lutetium) binary complexes. The effective electrophoretic mobility and separation efficiency of these ternary complexes are dependent on CE running buffer parameters which influence the complexation reaction (e.g., pH and HQS concentration). The fluorescence intensities of the ternary complexes are also dependent on these running buffer characteristics. Limits of detection using laser induced fluorescence detection are approximately 10^{-7} M. Three common hexadentate ligands are resolved in less than 4 minutes with efficiencies of approximately 10^5 plates/m. The ability to measure hexadentate ligands in waste water without interference from calcium or magnesium is also demonstrated.

DEVELOPMENT OF A SEPARATION-BASED FIBEROPTIC SENSOR FOR REMOTE MEASUREMENTS OF ENVIRONMENTAL POLLUTANTS. Victoria Tropina, David L. Stokes, Michael J. Sepaniak, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Tuan Vo-Dinh, Life Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6101.

Reported is the development and evaluation of an integrated separation-based fiber optic sensor (SBFOS) for remote analyses, that incorporates capillary electrophoresis (CE) directly at the fiber sensing terminus. The potential for high sensitivity is provided by laser-induced fluorescence detection while selectivity is afforded by the separation power of CE. Fluorescence-based sensors that utilize a chemical reagent phase to achieve selectivity are not readily adaptable to the detection of different species and tend to be one-measurement-only sensors. Conversely, the SBFOS described in this poster is both versatile and reusable. The design and construction of the sensor is illustrated. Additionally, the results of an evaluation of the SBFOS are presented which include observed separation efficiencies of 10^3 - 10^4 plates (8-cm separation capillary), migration time and bandfront height reproducibilities of less than 10% nanomolar limits of detection, and a linear response over two orders of magnitude in concentration. The performance of the sensor and the potential for remote control are shown in a micellar electrokinetic capillary chromatography mode with separations involving neutral fluorescent compounds including aflatoxin environmental pollutants

POST-COLUMN DERIVATIZATION FOR CAPILLARY ELECTROPHORESIS UTILIZING LASER INDUCED FLUORESCENCE DETECTION WITH A SHEATH FLOW CELL. William F. Nirode, Jason E. Dickens, Tracy D. Staller, and Michael J. Sepaniak, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

Many researchers have demonstrated ultra-sensitive laser induced fluorescence (LIF) detection using sheath flow cells. In some cases this mode of detection has been employed with separation techniques such as capillary electrophoresis (CE). Derivatization by pre-column, on-column, and post-column techniques are often performed to exploit the benefits of LIF for non-fluorescent solutes. With reduced dimension separation techniques such as CE, solute band volumes are extremely small and the reaction chambers associated with post-column derivatization often produce an unacceptable degree of band dispersion. We describe herein the use of a sheath flow cell as both an LIF flow cell and a reaction chamber to non-covalently derivatize DNA fragments separated by CE. It has been shown that ethidium bromide (EB) can be used as an intercalating dye in the separation of DNA fragments. It has been demonstrated that transition and rare earth metals can be separated by CE and in some cases detected via a post-column chemiluminescence reactor. Experimental details will be described and analytical figures of merit including sensitivity and dynamic range will be presented. The effects of experimental parameters such as position of the detection zone on the performance of the detector and sheathing and electrophoretic flow rates will be demonstrated. Preliminary experiments involving post-column chemiluminescence detection of various metals and hexadentate ligands using the sheath flow cell will be described.

ANALYSIS OF POLYCHLORINATED BIPHENYLS IN RADIOACTIVELY CONTAMINATED MATERIALS BY MASS SPECTROMETRY WITH SELECTED ION MONITORING. Stephen L. Crump and John E. Young, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, SC 29808.

The analysis of polychlorinated biphenyls (PCB's) in environmental/process waste samples is complicated by two primary factors. First, PCB's as commercially produced, are a mixture of congeners present in varying proportions. Second, PCB analysis, as prescribed by the regulatory methods, is carried out using gas chromatography with electron capture detection (GC-ECD) for low concentration analyses. GC-ECD requires extensive preparative work prior to sample analysis, and is further complicated by false positives arising from the extreme sensitivity and modest selectivity of the ECD. Part of the work being carried out at the Savannah River Site is further complicated by the presence of radionuclides in the sample matrix. The goal of this work was to analyze PCB's without extensive preparative measures, to both expedite sample analysis times and reduce preparative materials needed in handling the radioactive matrix samples.

Gas chromatography/mass spectrometry with selected ion monitoring (GC/MS-SIM) was chosen as the analytical tool for PCB analysis. As a GC/MS method, it provides retention time information on the analyte, but where scan mode GC/MS can only offer instrument detection limits of one to ten ppm, operating in SIM mode can offer at least a three order of magnitude increase in sensitivity. GC/MS-SIM does not afford the sensitivity found in using GC-ECD, however for PCB analysis the method allows for simple preparative procedures, and offers detection limits well below the regulatory action levels.

Recent experience using the GC/MS-SIM analytical technique to make PCB determinations in a variety of sample matrices will be presented, highlighting advantages of this useful methodology.

DETERMINATION OF HYDROGEN ISOTOPIC CONTENT
IN WASTEWATERS CONTAINING RECOVERABLE
DEUTERIUM OXIDE. John E. Young, Westinghouse
Savannah River Company, Savannah River Technology Center,
Aiken, SC 29802.

Summary. Gas Chromatography-Mass Spectrometry using a purge and trap inlet device has been applied to the analysis of hydrogen/deuterium ratios in Savannah River process wastewaters. The method provides advantages over the previous analysis methods, including freedom from interference and increased safety when handling radioactive samples.

Background. Deuterium, a natural non-radioactive isotope of hydrogen, is present in nature at a concentration of 0.0125%. Water that has been enriched in the deuterium isotope has been extensively studied, and is commonly referred to as "Heavy Water". Because of the nuclear properties of deuterium oxide, it has been extracted from water and used as a moderator/coolant in many nuclear production reactors, including those at the Savannah River Site. The value of the D₂O in off-specification/low grade D₂O material may contain common anionic, cationic soluble neutral, and radioactive impurities. These impurities interfere with conventional methodology for measurement of hydrogen/deuterium isotope ratio in water by increasing the density or infrared opacity of the sample. Preparation of the sample by distillation increases processing time, cost, and the possibility of sample contamination. Most importantly, extended handling of radioactive samples can result in increased direct occupational exposure to the radiation/radioactivity in the sample.

Experimental. Approximately 10 mg of water is evaporated from a sample of wastewater (100 to 500 μ L sample volume) by passing dry helium over the sample at a rate of 20 mL/minute at ambient temperature. The helium is passed through an adsorbent trap designed for the capture of volatile organic compounds. A portion of the water is adsorbed onto the trap from the helium stream, and is subsequently thermally desorbed into the inlet of a gas chromatograph. Thermal

desorption temperature is selected to be mild enough (150°C) to slowly release the trapped water over a 4 minute period.

The desorbed sample is transferred to a 60 m x 0.75 mm glass capillary column where minimal chemical interaction and/or separation takes place. After passing through the column, the gas stream passes through a glass molecular jet separator for enrichment of the analyte (water) from the helium stream prior to introduction into the mass spectrometer.

Mass spectrometric conditions are set up for scanning the 15 to 25 AMU range at a rate of 3 scans per second. Prior to analysis the mass spectrometer is tuned for optimum performance at this low mass range. In this measurement, water from the sample is slowly bled into the mass spectrometer over a four minute period. During the maximum signal strength, 100 mass spectra are averaged for the data analysis. Mass spectral ion ratios are measured and compared against standards obtained using identical conditions. A simple chemometric model is used to model the standards and calculate the concentration of unknown samples.

Conclusion. GC/MS has been demonstrated to be a rapid, cost effective, and safe method for the determination of hydrogen isotopic distribution in low grade deuterated wastewaters. Data obtained in the development of the method, and from actual process wastewater sample results will be presented along with a descriptive comparison of the advantages realized by this new method.

VOLATILE METALS RECOVERY USING A
TEMPERATURE CONTROLLED OPEN VESSEL
MICROWAVE SYSTEM. Jim Price, CEM Corp., P.O. Box
200, Matthews, NC 28106-0200.

With the growing popularity of open vessel microwave digestion has come questions concerning the retention of volatile metal elements during sample digestion. The importance of correct reagents, temperature control, automatic reagent addition, and the various open vessel accessories are shown to greatly influence the analyte recovery for samples digested by this technique. The relatively new technique has proven to be a efficient, accurate, and a reliable process by which volatile metal elements have been recovered with good precision.

Versatility of individual temperature control has been shown through the simultaneous digestion of different sample types at various programmed instrument parameters. Retention of volatile metal elements has been proven through ICP analysis of numerous standard reference materials. Correct digestion chemistry has been shown to effect volatile element recoveries by digestions of organic samples using various reagents, temperatures, and order of automatic reagent addition. Also included are studies of analytical results obtained for samples of various sizes and matrix.

CONTAINMENT OF A HEWLETT PACKARD 4500 ICP-MS
WITH LASER ABLATION SAMPLING FOR THE FUTURE
SUPPORT OF THE STABILIZATION OF SCRAP NUCLEAR
MATERIALS. V. D. Jones, Westinghouse Savannah River
Company, Technical Services Division, Building 772-F, Aiken,
SC 29802.

The stabilization of scrap nuclear materials is a continuing concern for Westinghouse Savannah River Co., and the DOE Complex. The WSRC 772-F Laboratory is currently undergoing building renovations and equipment upgrades to enable analytical support of stabilization initiatives outlined by the Defense Nuclear Facility Safety Board (DNFSB 94-1). Some of the analytical capabilities required will include actinides and impurities on both the dissolved material and any solid residues remaining after rigorous dissolution. A Hewlett Packard 4500 ICP-MS and CETAC LSX-100 Laser Ablation System were purchased as part of the instrumentation upgrade package. Plans for containment of the ICP-MS and Laser in a hood enclosure will be discussed along with expected obstacles to be overcome.

APPLICATION OF LOW-ENERGY ELECTRON
IONIZATION MASS SPECTROMETRY TO THE
MEASUREMENT OF NITRIC OXIDE IN EXHAUST GAS.
Gerald L. DeVault, Q. C. Grindstaff, Sam A. Lewis, Robert W.
Smithwick , III, and John M. Storey, Oak Ridge National
Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-8189.

The oxides of nitrogen (NO_x), from combustion sources such as diesel engines and coal-fired boilers, contribute to the formation of tropospheric ozone and smog. Nitrogen oxides have also been implicated in the formation of "acid rain". Mass spectroscopy offers the possibility of selective and rapid detection of NO.

The primary problem in the use of mass spectroscopy to measure NO(+) at $m/z = 30$ is the presence of interfering ions. One example of an interfering ion is CH₂O(+), which has the same nominal mass as the NO(+) ion. A second example of an interfering ion is the NO(+) ion produced from the fragmentation of nitrous oxide (N₂O). Abundance sensitivity between nitrogen (N₂) at $m/z = 28$ and NO at $m/z = 30$ is another potential problem. Ordinarily, the strategies used to overcome these interferences are separation of the analytes by gas chromatography or the use of a high resolution mass spectrometer. In the present work, the strategy investigated involves taking advantage of the relatively low ionization energy of NO gas (9.3 eV) with respect to other common gases found in exhaust. As the ionization energy of the electrons is lowered, the contribution of potential interfering ion species at $m/z = 30$ is minimized relative to the amount of NO(+) observed. Consequently, NO in exhaust can be directly measured without separation or the use of a high resolution instrument.

The purpose of this work is to measure NO by mass spectrometry using low-energy electron ionization. This work involves calibration of the response to known concentrations of NO, evaluation of the NO measurement in the presence of gases which may interfere, and the analyses of real samples of internal combustion engine exhaust.

GAS CHROMATOGRAPHY DATA CALCULATION AND REPORT GENERATION USING MICROSOFT ACCESS DATABASE PROGRAMMING. Rick Zingg, John McCall, and Elizabeth Justice, Analytical Services Organization, Lockheed Martin Energy Systems, Inc., Oak Ridge, TN 37831-8081.

The increased customer desire to see full "CLP like" data packages necessitated the development of computer generated reports summarizing the gas chromatography data. Since the data would generate hundreds of records due to multiple individual peaks per run, a database software was chosen over a spreadsheet format. Microsoft ACCESS was the easiest to understand and the programming could be done by the chemist instead of a programmer combining an understanding of the mechanics of the gas chromatography instrumentation and analysis methods with computer efficiency.

Data from Aroclor, Pesticide, Herbicide, Congener, Diesel Range Organics, and Industrial Hygiene methods can all be calculated using this software. The data is no longer hand entered eliminating typing errors. The raw data is transferred directly from the Hewlett Packard Chemstation into an ACCESS database. In each individual method database, a menu with command buttons (consisting of a series of macros) allows the user to import a specific run of data, update calibration data, calculate the data, and then generate custom reports summarizing all the necessary quality control information and sample calculations.

MAPPING THE BRAIN WITH SECONDARY ION MASS SPECTROMETRY. Carl A. McCandlish, J. M. McMahon, and Peter J. Todd, Chemical & Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6365.

We have developed a secondary ion microprobe to detect, identify and map the distribution of targeted compounds in biologic tissue. At present the term "targeted" means compounds which emit abundant secondary ions. For example, phosphatidylcholine is ubiquitous in biologic tissue, mainly because it is a principal component of cell membrane. It is thus not surprising that secondary ion emission of m/z 184 from tissue is similarly common, since it arises from the head group of phosphatidylcholine. Emission of m/z 184 is however heterogeneous, being more intense from regions where there is a high density of cells. We have used this feature to map secondary m/z 184 emission in brain tissue samples. With images thus created, we can readily identify anatomical features, such as corpus callosum, cerebral cortex, etc. Moreover, we can also observe the development of mammalian brain, from undifferentiated cells, to the adult brain organization.

SIGNIFICANT ASPECTS OF ALPHA/BETA LSC - A FOCUS
ON ENVIRONMENTAL APPLICATIONS. Charles J. Passo,
Jr., Packard Instrument Company, 800 Research Parkway,
Meriden, CT 06450.

The ability to discriminate alpha and beta activity in LSC (alpha/beta LSC) by pulse shape discrimination is gaining in popularity as an important analytical tool for gross alpha/beta screening and individual radionuclide analysis. In order to use this analytical tool properly, one must be aware of the theory and practical aspects of employing alpha/beta discrimination techniques. Cocktail chemistry, quenching, vial types and volumes all influence the ability to accurately separate alpha events from beta events in liquid scintillation analyzers employing some form of pulse shape analysis. Time-Resolved Pulse Decay Analysis (TR-PDA) is the pulse shaping technique used in Tri-Carb alpha/beta LS analyzers. This paper will discuss the practical aspects of alpha/beta analysis by LSC and discuss both limitations of the technique and methods to optimize alpha/beta separation. Several environmental application examples are presented.

COCKTAIL SELECTION FOR ENVIRONMENTAL
SAMPLES. Jock Thomson, Packard Instrument Company, 800
Research Parkway, Meriden, CT 06450.

The components present in Liquid Scintillation Cocktails are discussed to show how their presence affects both the performance and the safety of the cocktail. Components discussed include the solvents (traditional and new safer), surfactants (type and functionality) and scintillators (primary and secondary). By explaining how and why these base components are selected it is hoped to show that cocktail performance can be tailored to suit specific application areas. The specific problems likely to be encountered in environmental sample preparation are discussed, and methods of overcoming these problems by either correct cocktail selection or by modifying sample preparation are presented.

Particular problems that may be found include acidity, solubility, extraction, chemical and colour quench, and matrix effects. In general correct cocktail selection can overcome most of these problems but occasionally, depending on the radionuclide, some compromises may be necessary. Finally, safety and environmental concerns will be considered to show how the new 'safer' liquid scintillation cocktails offer a less hazardous solution for the environmental researcher.

RECLAMATION AND REUSE OF RADIOACTIVE
CONTAMINATED FREON IN TOTAL PETROLEUM
HYDROCARBON ANALYSES. Amy A. Ekechukwu,
Westinghouse, Savannah River Technology Center, Bldg.
773-A, Aiken, SC 29808.

At the Savannah River Technology Center (SRTC), we have developed a method to reclaim the spent Freon solvent used in total petroleum hydrocarbon (TPH) analyses of radioactive samples. A wide variety of sample types including ground water, organics, laboratory waste, process control, sludge, soils, and others are received by our lab for total petroleum hydrocarbon analyses. The standard analysis method for determining total petroleum hydrocarbons involves solvent extraction of the hydrocarbons using Freon followed by quantitation using infrared detection. This has been the method of choice because it is simple, rugged, inexpensive, and applicable to solid and liquid samples and radioactive samples. However, due to its deleterious effect on the ozone layer, the use of Freon and other chloro-fluorocarbons (CFCs) has been greatly restricted.

Several methods have been proposed to replace the Freon extraction method. These methods include solid-phase extraction, solvent extraction, and supercritical fluid extraction all of which use gravimetric determination or infrared analysis of the extracted hydrocarbons. For reasons of cost, sensitivity, precision, or simplicity, none of the replacement methods are feasible for analysis of radioactive samples at our facility. We therefore opted to keep the standard Freon extraction method and reclaim the spent solvent. The method we developed involves two steps: radioactive decontamination of the spent solvent by liquid/liquid extraction of the radionuclides present followed by removal of the hydrocarbons by passage through a commercially available carbon bed. Using this method, we have been able to successfully recover 95-98% of the radioactive contaminated Freon.

INORGANIC AND ORGANOMETALLIC SPECIATION IN ENVIRONMENTALLY RELEVANT MEDIA. C. M. Barshick, S. A. Barshick, and P. F. Britt, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6375.

Conventional solid sampling techniques (e.g., x-ray fluorescence, glow discharge mass spectrometry, and inductively coupled plasma mass spectrometry) provide only a limited amount of information about the types of species in a sample aliquot. Although gas chromatography/mass spectrometry (GC/MS) may never be the analyst's first choice for elemental analysis, in our laboratory it has proven useful when information about both the organometallic and inorganic constituents is needed. As a first step in our technique, a solid phase microextraction (SPME) fiber is used as a sampling medium for organometallic compounds. Once the organometallic analytes are quantified, quantification of the inorganic species is performed using the same sample; this is facilitated by a chemical alkylation step that produces an organometallic compound not found in the original sample. Subsequently, this solution is analyzed by GC/MS.

As a test case, we have been reacting mercury with a series of organic compounds of cobalt (III). Two such compounds, methylpentacyanocobaltate and methylpyridinocobaloxime are effective at alkylating mercury to MeHgX. Both these reagents have shown a strong pH dependence (increasing with increasing pH) and a dependence on the counter ion in solution (e.g., Cl, I, etc.). We have demonstrated an effective scheme for quantification that possesses good accuracy (better than 10% relative error) and a relatively short sampling time (< 5 minutes), as well as the ability to speciate a wide range of organometallic compounds. Detection limits are 2 ppb for organomercury compounds in water and 10 ppb in soil. LOD's for inorganic mercury compounds are 100 times poorer in both media.

Research was sponsored by the Laboratory Directed Research and Development Program, under Contract DE-AC05-96-OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

SOL-GEL DERIVED SORBENTS FOR SAMPLING AND ANALYSIS OF VOLATILE AND SEMIVOLATILE ORGANICS IN AIR. M. E. Sigman, A. B. Dindal, R. H. Ilgner, S. M. Smith, R. A. Jenkins, M. R. Guerin and A. C. Buchanan, III, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6100.

High surface area, high thermal stability and a wide analyte range are characteristics of sol-gel derived sorbents developed at Oak Ridge National Laboratory for use in air sampling of organic analytes. A family of related materials have been synthesized wherein the composition of the sorbent and the associated air sampling properties can be controlled. The thermal stability of the materials, 600°C, exceeds that of carbon sorbents by nearly 200°C. The surface area of the materials generally range from 700 - 1000 m² g⁻¹ (N₂ BET). The sorbents have been found to exceed the performance of some commercial sorbents for sampling volatile and semivolatile organics (comparison with carbon sorbents) and CW simulant DIMP (comparison with Chromosorb 106). The structure of the new sorbents, physical characteristics and sampling performance will be discussed.

THE SYNCHRONOUS SCANNING LUMINOSCOPE. Dr. George J. Hyfantis, Jr. and Timothy P. Finnegan, International Waste Management Systems, An Environmental Systems Corporation Division, Knoxville, TN 37912.

In the past several years, there has been an increased demand for cost-effective, field-portable analytical instrumentation in the environmental industry. While many qualitative methods have been introduced, few reliable quantitative instruments are available. To meet this demand, the Synchronous Scanning Luminoscope (SSL), a suitcase-sized spectrofluorometer operated by a laptop computer, was developed at Oak Ridge National Laboratory under EPA sponsorship. The SSL is based on luminescence principles and the characteristics of fluorescent high molecular weight organic compounds. The SSL has been used on over 30 sites by the EPA and International Waste Management Systems (IWMS).

The SSL uses the synchronous scan which simplifies the spectra of conventional excitation and emission scans, allowing for greater selectivity. The resulting synchronous spectrum is useful in two ways; first, the area under the spectrum is directly proportional to the concentration of analyte within the sample and, second, an analyte can be distinguished by its spectral characteristics. The synchronous spectrum enables the SSL to perform quantitative, qualitative, and fingerprinting analyses of poly aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs), phenols, and creosotes in soil and water in the low ppb range. Samples can be analyzed in less than 15 minutes at a 75 % savings over conventional laboratory analysis. Based on the speed of analysis and quantitative ability of the instrument, on-site decisions can be made, eliminating laboratory costs and remobilizations due to waiting for laboratory results. For instance, the SSL can be used to find either non-detect samples or samples at an established regulatory limit in order to define a plume of contamination in one mobilization.

Recently, IWMS, in conjunction with International Technology Corporation, used the SSL on a Department of Defense site contaminated

with the jet fuel, JP4. During the first task of this project, the SSL was used to fingerprint samples. The assignment was to identify and define other potential sources of contamination besides JP4 such as gasoline, diesel fuel, or hydraulic fluid. The results showed that of 45 samples found to have contamination, 35 contained JP4, three showed some gasoline characteristics, four showed some diesel characteristics, and three were likely hydraulic fluid. During the second task of this project, 83 monitoring well samples were split with an approved laboratory and analyzed for total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene, xylene (BTEX), and naphthalene. There was an excellent correlation to laboratory analysis with correlation coefficients of 0.93 (TPH), 0.96 (Naphthalene), and 0.90 (BTEX). During the next sampling event, the SSL will be used exclusively to determine TPH, BTEX, and naphthalene concentrations. The results will be obtained in the field thus saving the client 75 % by avoiding conventional laboratory costs. Prior to IWMS's use, the EPA used the SSL for quantifying PAHs and creosote concentrations in soil on sites such as Winter Quarters Bay adjacent to McMurdo Station in Antarctica and American Creosote Works, a National Priorities List Superfund Site, in Tennessee. The SSL fills the niche within the environmental industry for a cost and time-effective, field-portable, quantitative, analytical instrument.

APPLICATION OF FLASH GC TOF/MS TO ENVIRONMENTAL ANALYSIS. George B. Jarvis and Michael Sweeney, Thermedics Detection Inc., 220 Mill Road, Chelmsford, MA 01824.

Applications include real-time analytical determinations for environmental analyses. The key to FLASH GC TOF/MS is the micro-oven heating technology used to heat and cool only the GC column. The FLASH micro-oven heating technology is compatible with all conventional GC column types with the exception of 0.53mm ID columns. Typical column heating rates are between 10 - 30°C/second to a maximum of 350°C. Cool down from 350°C takes approximately 1 minute making instrument cycle times approximately 2 minutes. A 40 cm linear TOF/MS is interfaced to the FLASH GC through a short transfer line and a differentially pumped chamber. To acquire and process the data in real-time a high-speed transient recorder, a high-speed data bus and a digital signal processor are used. Electron impact ionization allows chemical identification from existing mass spectral libraries such as NIST/EPA/NIH. Real-time data processing converts the ion currents into mass chromatograms, deconvolves GC peaks, identifies and selects spectra for library identification of the sample constituents and performs quantitation. Typical analysis time for determinations such as PCBs, SVOCs, explosives, diesel fuels and VOCs is 60 seconds. This paper will discuss FLASH GC TOF/MS design and application to environmental analysis.

A NEW APPROACH FOR THE SEPARATION OF RADIOACTIVE ELEMENTS BY REVERSED-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (RP-HPLC). S. Seekamp,^{1,2} H-J. Steinmetz,¹ A. Seubert,²
¹Forschungszentrum Jülich, Institute for Safety Research and Reactor Technology, 52425 Jülich, Germany, ²University of Hannover, Institute of Inorganic Chemistry, Callinstraße 9, 30167 Hannover.

Low- and intermediate-level radioactive waste is frequently supercompacted or solidified in cement for final disposal. In waste characterisation matrix problems arise in analysing the drum content by chromatographic methods.

The coupling of ion chromatographic methods with liquid scintillation counting is not always favourable. Often the more organic and ion free or ion poor solvents used in RP-HPLC offer better options. Therefore the evaluation of RP-HPLC separations will be extended. The cations from the cement occupy the capacity of the column and no separation of the analytes takes place. By a selective complexation the analytes get separated from the matrix. They are bound by sodium diethyldithiocarbamate (NaDDTC) as complexes on a precolumn and subsequently separated on a silica based C-18 reversed-phase column. Experiments shows the robustness of the system against high ion strength. Recovery rates of 60 % can be reached. Detection is performed by a UV/VIS spectral range detector and a liquid scintillation detector (Pb-210, Se-79, Ni-63, Co-60) in series. This allows to get the total amount and the amount of mass and of radioactivity in one measurement.

The complexation and enrichment technique offers the possibility of a fully automatic chromatography without handling of open radioactive samples and chloroform.

DEVELOPMENT OF DISPOSABLE PLASTIC SYRINGES
AS EFFECTIVE DEVICES FOR SAMPLING
HETEROGENEOUS RADIOACTIVE SLURRIES. C. J.
Coleman and J. W. Clymire, Savannah River Technology
Center, Westinghouse Savannah River Site, Aiken, SC 29808.

One of the most persistent pitfalls in analyzing heterogeneous slurry samples is corrupting the sample before beginning the analyses. Sampling the melter feed slurry in the Defense Waste Processing Facility (DWPF) at the Savannah River Site is particularly prone to errors because the borosilicate frit particles settle at a much higher rate than the relatively small radioactive sludge particles. An approach was recently developed that avoids sub-sampling errors by taking samples in 3 mL Teflon, plastic, or zirconium sample vial inserts. The entire sample is analyzed by dropping the insert into the digestion vessel. The only drawback to this approach is that for very high temperature procedures, such as vitrifying the feed at 1100°C, the insert materials are incompatible with this temperature.

Disposable plastic syringes can be fashioned into simple, inexpensive, and yet highly effectively process sample containers that are compatible with the DWPF sampling slurry samples from the process line to platinum crucibles for vitrification of the feed. The quantitative transfer of slurry samples into crucibles without need for rinse water means that melter feed samples can be conveniently vitrified in 2-3 hours, versus over 12 hours when a larger vial must be rinsed with several volumes of water to ensure quantitative transfer. The vitrified samples can then be dissolved without crushing by several alkali salt fusion methods for elemental and radionuclide analyses. The combination of syringe sampling and dissolution of glass chunks would result in a dramatic improvement in analytical turnaround times for the DWPF. Development of a near-foolproof system for remote handling of slurries taken in syringe samplers will be described and demonstrated. The advantages of the syringe sample containers for heterogeneous samples will be discussed.

TEQ MEASUREMENTS OF VOCS, DIOXINS, PCBS, AND DIBENZOFURANS IN 10 SECONDS TO PICOGRAM LEVELS. George A. Pappas, Edward J. Staples, David McGuire, and Gary Watson, Electronic Sensor Technology, 1077 Business Center Drive Circle, Newbury Park, CA 91320.

This poster describes the research and commercialization of a gas chromatograph using a surface acoustic wave (SAW) detector to characterize volatile and semi-volatile compounds in 10 seconds from air, water, and soil matrices. The project is sponsored by the Department of Energy, EM-50 with the goal of applying innovative technologies to meet environmental restoration objectives.

The ability to obtain TEQ measurements to detect picogram and parts per billion levels of environmentally significant compounds has been previously demonstrated. However, the capability of analyzing these compounds in 10 seconds is novel and unique, thus allowing personnel to use the instrument for site investigation, plume chasing, contamination mapping, and post-closure monitoring. The technology allows for the speciation of semi-volatiles and volatile compounds in PCBs, dioxins, and VOCs. It is also useful in determining dilution levels for GC/MS analysis.

The design and theory of operation will be presented as well as test results obtained from the field demonstrations conducted at several Super Fund/DOE sites. Field screening protocols will be discussed as they relate to the California Environmental Protection (CAEPA) certification and data acceptance. Various rapid screening molds will be discussed related to field work. The related deployment strategies, cost/benefits, and maintainability issues will be noted.

UNIVERSAL QUALITY APPROACH IN THE ANALYTICAL CHEMISTRY LABORATORY. Jo Ann Boyd and J. P. Hsu, Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78228-0510.

Analytical chemistry utilizes many applications. These applications can be routine environmental analysis, mixed waste analysis, analyses for nuclear power plants, chemical assay and impurities analysis, pesticide registration, food analysis, pharmacokinetic studies, and other areas of concern. In addition to these applications, problem solving and method development are also a crucial function for an analytical chemistry laboratory. However, different applications require various types of quality assurance/quality control programs. How does a laboratory implement all QA/QC requirements without physical separation of the laboratory by each application? How do chemists perform different applications using different QA/QC systems without any confusion?

Southwest Research Institute (SwRI) has developed several methods for EPA, such as Methods 1 to 9 for stack gas sampling, SwRI refined the TO14 air sampling method, air analysis using polyurethane foam plugs, and EPA Methods 606, 607 and 608. SwRI has developed a quality system for method development and problem solving. In 1985, SwRI entered EPA contract laboratory program (CLP) and special analytical service (SAS). For this program, a QA/QC system was developed to train the chemists to follow a strict chain of custody documentation control, rigid analytical methods and criteria. Since criteria is at times difficult to meet, analytical techniques are modified and analysis is performed using new and improved instrumentation. Due to laborious chain of custody, quality control, and documentation requirements; automated procedures and the laboratory information management system (LIMS) have been developed by SwRI in several areas to expedite the reporting operation and reduce human error. Around 1991, Southwest Research Institute performed mixed waste analysis following DOE NQA1 criteria for nuclear waste. This program, in addition to the requirements for CLP, required chemists to be trained in writing standard operation procedures (SOPs) for new and modified

procedures developed as they were performed in the laboratory. This developed a large number of procedures in the laboratory. The procedures were placed in the LIMS for easy access to laboratory personnel and modifications were performed only by QA personnel. Due to the liability involving radioactive nuclei, the radiation safety and radioactive waste disposal became crucial. All chemists were routinely trained for nuclear safety and waste disposal. In addition to routine analysis, there were problems incurred in the mixed waste analysis, such as ultra low detection limits, different matrices, and unusual analytes. Therefore, the method development required implementation be expedited and criteria development to simulate the those used in routine analyses. The methods developed were treated as routine analysis for all quality and safety requirements. For analysis of the samples from nuclear plants, surveillance by a trained quality technician required for each analysis as well as the mixed waste requirements.

SwRI also performed pesticide registration, food analysis for FDA and pharmacokinetic analyses, which required Good Laboratory Practices (GLP). This program is very similar to the NQA1 requirements for nuclear facilities without the mixed waste requirements.

However, a Study Director is assigned to direct the study and critical phase inspections are performed on each critical phase of the analyses. SOP's must be established and study deviations are required for any deviation to the SOP. Corrective actions are documented and immediately evaluated as they affect on the study and any further procedures needed for documentation and correction.

In conclusion, CLP, NQA1, GLP, and analysis for nuclear power plants have a great deal of overlapping. In addition to applying their analytical knowledge and experience on chemical analysis, chemists must know the additional requirements for each application to avoid confusion.

DEVELOPMENT OF A PORTABLE HIGH RESOLUTION
FOURIER TRANSFORM ION CYCLOTRON RESONANCE
MASS SPECTROMETER. Gregory Miller, Mathias Koch,
J. P. Hsu, and Frank Ozuna, Southwest Research Institute,
6220 Culebra Road, San Antonio, TX 78228-0150.

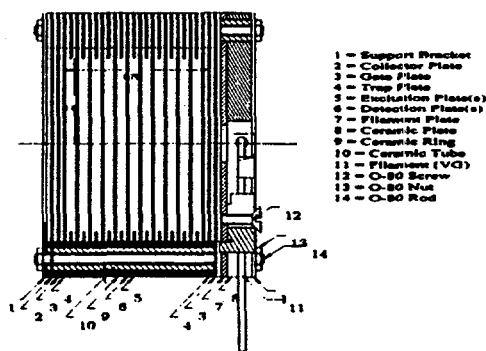
The need for small, compact, portable, high-resolution mass spectrometers for on-line, real-time monitoring of compounds of interest to the semiconductor industry and for environmental monitoring has prompted us to design a field-portable bench top instrument based on the principle of Fourier transform ion cyclotron resonance (FTICR). The high resolution capabilities inherent in FTICR allow us to more accurately ascertain the identification of chemical species based on their exact mass. The mechanical simplicity of this instrument and the lack of complex ion-optical components allowed the construction of a very rugged device ideally suited for harsh environments.

By limiting the mass range to $M/Z = 15 - 300$ g/mol, a low field $B = 0.5$ T rare-earth neodymium-iron permanent magnet was chosen which decreased the size and weight of the instrument with the added advantage of no power consumption due to the permanent magnet. Since the primary anticipated use of this instrument is for continuous on-line monitoring, a high conductance ICR cell (*fig. 1*) was designed with good accessibility for gas sample introduction. By maintaining the physical size of the vacuum system to a minimum (*fig. 2*), and by the use of Summa passivation of the vacuum chamber, high vacuum requirements needed for high resolutions up to $M/\Delta M = 7500$ were able to be achieved with a constant flow of gas into the cell.

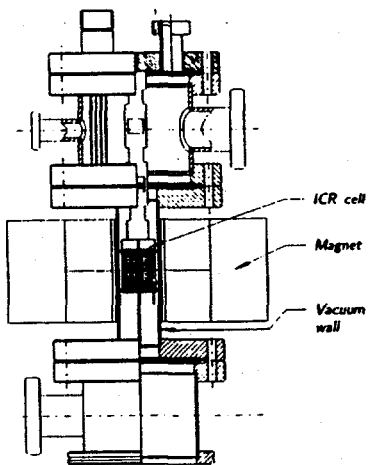
The ion cyclotron cell chosen is a screened cell of cubic geometry made up of alternating layers of beryllium-copper shims separated by ceramic insulators and assembled on ceramic posts to make up four faces of the cube. The two additional faces of the cubic cell comprise of trap plates, gating electrodes filament support, collector and the screen plates. The alternating layers of shims isolate electrically the two sides used for the excitation electrodes and the two sides for the detection electrodes. The gap left between the alternating beryllium-

copper shims allows for high cell conductance and provides for accessibility for sample introduction.

All instrument control, from SWIFT waveform generation through mass spectral data acquisition was achieved using Virtual Instruments (VI's) written using LabVIEW graphical programming language running on an Intel Pentium-90 with 32 Mb of main memory. The interface consisted of National Instruments NI-DAQ data acquisition board with a total of six separate channel inputs and outputs, and a general purpose interface bus board (GPIB). The time-domain digital SWIFT waveform was generated in LabVIEW and sent to an Analogic 2040 arbitrary polynomial waveform generator via the GPIB interface card for analog waveform generation. The RF-waveform was clocked out to the excitation electrodes of the ICR cell from a time pulsed sequence. The detected transient waveform was amplified and captured on a LeCroy digital storage oscilloscope (DSO) which sends the digitized waveform to the PC for post signal processing and display. A single time-domain transient and its Fourier transform mass spectra are shown in (fig. 3) below for room air from a constant leak.



(fig.1)



(fig.2)



(fig.3)

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Thursday, October 9

THURSDAY AM, MEASUREMENTS AND CHEMICAL INDUSTRY
INITIATIVES

CHAIRMAN: STEVEN C. WEINER, BATTELLE PACIFIC
NORTHWEST NATIONAL LABORATORY, Washington, DC 20024

8:40 THE OFFICE OF INDUSTRIAL TECHNOLOGIES:
PARTNERING WITH THE CHEMICAL INDUSTRY. Steven
C. Weiner, Pacific Northwest National Laboratory, 901 D Street
SW, Suite 900, Washington, DC 20024-2115.

The Chemicals Team in the U.S. Department of Energy's Office of Industrial Technologies is charged with effectively managing research, development, deployment, and commercialization in partnership with industry, national laboratories, academia and other organizations to maximize economic, energy and environmental benefits. The team has been actively engaged with the industry during the development of *Technology Vision 202: The U.S. Chemistry Industry*, which is becoming the key focus of its initiatives. This talk will provide an overview of Chemicals Team activities, highlighting key initiatives and reinforcing its commitment to continuing its focus on the chemical industry of the future.

9:10 CHEMICAL INDUSTRY MEASUREMENTS NEEDS
ROADMAP. Arlene A. Garrison, University of Tennessee,
Measurement and Control Engineering Center (MCEC),
Knoxville, TN 37996-2350.

The major technical societies associated with chemical manufacturing are leading an effort to define "Technology Vision 2020 - The U.S. Chemical Industry." Industry, government and academic leaders are participating in the project. In December 1996 a report was published summarizing the technical and business issues that are most critical to the continued success of the chemical industry.

Six major areas have been identified as significant for New Chemical science and engineering technology: Chemical synthesis, bioprocesses and biotechnology, materials technology, process science and engineering technology, chemical measurement and computational technologies. The vision process is designed to provide direction to government agencies to encourage the allocation of research funds into key areas of importance to the future of the industry.

All the technical areas are now further refining the needs and challenges listed in the published report. Progress reports are presented regularly at Council for Chemical Research meetings. The current status of the Chemical Measurements Needs Roadmap will be presented. Under the direction of Hrach Semerjian of NIST, the Chemical Measurements Task Force has identified six key sub-topics within measurement and have a working list of strategies for meeting the challenges. Various workshops, including a discussion at the 1997 IFPAC meeting, have provided forums for input to the report.

9:30 **SENSORS AND CONTROLS CROSSCUT INITIATIVE.**
 Timothy J. McIntyre, Instrument and Controls Division -
 Services, Oak Ridge National Laboratory, P. O. Box 2008, Oak
 Ridge, TN 37831-6004.

The DOE Office of Industrial Technologies (OIT) has as its mission improved resource efficiency of the energy- and waste-intensive U.S. manufacturing sector. A critical element of the program is the development and deployment of new sensors and controls technologies which result in increased energy efficiency, minimized waste generation, and increased productivity through enhanced process understanding and closed-loop process control. An overview of this planned activity and a perspective on the sensors and controls technology needs for the aluminum, chemicals, forests products, glass, metalcasting, oil refining, and steel industries will be presented.

9:50 **BREAK**

10:10 LEVERAGING RESOURCES THROUGH INDUSTRIAL COLLABORATION WITH UNIVERSITIES AND GOVERNMENT LABORATORIES. Mel Koch, Associate Faculty Director, Center for Process Analytical Chemistry (CPAC), University of Washington, Box 351700, Seattle, WA 98195-1700.

Industry continues to move towards globalization of its businesses. The main drivers are productivity and quality, which lead to value added products or low cost producer status. However, these goals are being pursued with constricted resources. As a result, partnering and leveraging is needed. One of the successful consortia to emerge has been the Center for Process Analytical Chemistry (CPAC), at the University of Washington. CPAC conducts research on novel sensors, data analysis methods, and instrumentation for real-time process monitoring and control. CPAC has been the base for a recent initiative to develop an Interactive Program. This Interactive Program, its status, and its ties to other National initiatives will be described.

10:30 THE WILLIAM R. WILEY ENVIRONMENTAL MOLECULAR SCIENCES LABORATORY: A NEW DOE NATIONAL SCIENTIFIC USER FACILITY. S. A. Rawson, Wm. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, K8-84, Richland, WA 99352.

The Department of Energy's Office of Energy Research/Office of Biological and Environmental Research, is opening a major national scientific user facility, the William R. Wiley Environmental Molecular Sciences Laboratory, in Richland, WA, in October, 1997. The fundamental environmental molecular science conducted within the facility provides a knowledge base for addressing DOE's serious environmental issues. The mission of the user facility is to develop a molecular-level understanding of the physical, chemical, and biological processes that underlie environmental remediation, waste processing and storage, human health effects, and atmospheric chemistry.

The analytical and computational capabilities of the Laboratory are available at no cost, by application, to scientists from universities and national laboratories; proprietary use by the private sector requires full-cost reimbursement. Available research equipment and general laboratory infrastructure include a High Field Magnetic Resonance Facility, a High Field Mass Spectrometry Facility, a Molecular Sciences Computing Facility, and several Research Environments dedicated to nanostructural materials, interfacial structures and compositions, reactions at interfaces, and gas-phase monitoring and detection. Case studies of contaminant migration in the subsurface and tank waste processing are used to illustrate some of the available analytical capabilities.

10:50 MEASUREMENT AND CONTROL ENGINEERING CENTER (MCEC). Arlene A. Garrison, University of Tennessee, Measurement and Control Engineering Center (MCEC), Knoxville, TN 37996-2350.

The Measurement and Control Engineering Center is an interdisciplinary research and educational institution directed toward the development of new sensors and control systems. The Center, founded in 1985, is a cooperative venture between the University of Tennessee College of Engineering and the Instrumentation and Controls Division of the Oak Ridge National Laboratory. MCEC became a National Science Foundation I/UCRC in 1986.

Several research projects which have been completed will be summarized, including the Raman sensor for distillation column control. Current capabilities in on-line sensing and control will be discussed. The research agenda for the 97-98 year will be summarized. Future plans include increased partnering with other universities and interaction with a broader cross-section of ORNL, including the Engineering Technology and Chemical and Analytical Sciences Divisions.

THURSDAY AM, ISOTOPIC MEASUREMENTS AND MASS SPECTROMETRY

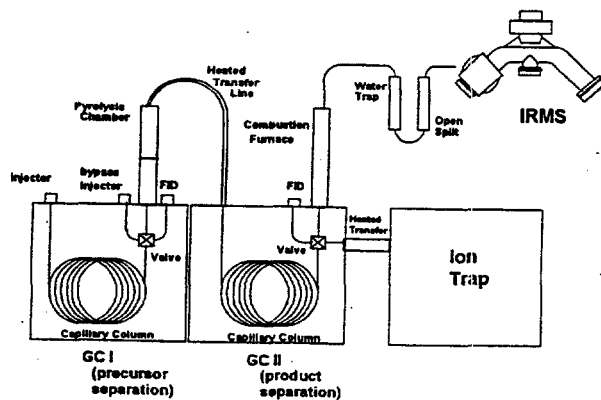
CHAIRMAN: PETER J. TODD, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

8:00 HIGH PRECISION POSITION-SPECIFIC ISOTOPE ANALYSIS. J. Thomas Brenna and Thomas N. Corso, Cornell University, Division of Nutritional Sciences, Ithaca, NY 14850.

Intramolecular carbon distributions are normally determined at low precision requiring high levels of labeling to enable analysis by conventional organic mass spectrometry or NMR. Studies targeted at determination of intramolecular carbon isotope concentrations due to *natural* processes have been undertaken to reveal the origin of organic compounds and provide insight on the status of complex systems, such as environmental or physiological state. Such studies require very high precision to detect small changes and have always required laborious chemical degradation and separation steps prior to isotope ratio mass spectrometry (IRMS) analysis. A strategy is reported here for online continuous-flow (CF) high-precision determination of $^{13}\text{C}/^{12}\text{C}$ ratios at specific positions in organic compounds separated from complex mixtures which can be applied to very high sensitivity measurement of artificially labeled compounds.

The system shown in the figure. A GC is interfaced to a CF variable temperature microreactor which fragments the analyte admitted as a heart-cut from the GC. At appropriate temperatures and analyte concentrations, analyte is pyrolyzed by free-radical breaking of a single C-C bond with stabilization once the fragment leaves the hot pyrolysis chamber. A second GC separates fragments and directs them to either a combustion system coupled to a isotope ratio mass spectrometer (IRMS) for high-precision isotope ratio measurements or an ion trap MS for structure identification. Methyl palmitate (Me16:0) was used as a test molecule. Two series of fragments identified as either a) ω -unsaturated methyl esters from losses from the methyl end of the parent, or b) α -

olefins from losses of the methyl ester end, are observed. Average precisions for the fragments are ($\delta^{13}\text{C}$) < 0.4‰. Isotope labeling in the carboxyl, terminal, and methyl positions demonstrates the absence of rearrangement during activation and fragmentation. Experiments to determine pyrolysis temperature effect on fragment isotope ratio revealed a very subtle relationship dependence on degree of fragmentation. [1- ^{13}C]-methyl palmitate with overall $\delta^{13}\text{C}$ = 4.06‰, yielded values of +457‰ for the carboxyl position, in agreement with expectations from the dilution, and an average of -27.95‰ for the rest of the molecule, corresponding to -27.46‰ for the olefin series. These data demonstrate that online pyrolysis 1) can produce highly reproducible carbon isotope ratios, 2) rearrangement induced by pyrolysis is negligible, 3) fractionation during pyrolysis is minor, and 4) facilitates calculations of isotope ratios of individual positions at precisions required for enriched tracer experiments and some natural abundance applications.



8:20 SPATIAL AND TEMPORAL PB ISOTOPE VARIATIONS IN BAYOU TREPAGNIER, LOUISIANA: FINGERPRINTS OF POLLUTION. Franco Marcantonio,¹ George Flowers,¹ Leonard Thien,² and Erik Ellgaard,² ¹Department of Geology, ²Department of Cell & Molecular Biology, Tulane University, New Orleans, LA 70118.

Pb has four naturally-occurring isotopes, only one of which is stable, ²⁰⁴Pb. ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb are the radiogenic daughter products of ²³⁸U, ²³⁵U, and ²³²Th, respectively. Natural lead in soils and sediments is isotopically distinct from pollution Pb which is, ultimately, derived from natural ore bodies. We have measured the Pb isotopic composition of tree rings from five trees and surficial sediments in both highly-contaminated and relatively non-contaminated regions of Bayou Trepagnier, a stream that has had oil refinery effluent discharged into it over the past 70 years. The tree ring record affords the opportunity to assess the Pb isotope variations through time, while the surficial sediment analysis allows a mapping of the different Pb sources in space.

When tree ring and sediment ²⁰⁶Pb/²⁰⁸Pb and ²⁰⁶Pb/²⁰⁷Pb isotope ratios are plotted against one another, a straight line is defined with a correlation coefficient (R^2) of 0.995. We interpret the line as an indication of mixing between two sources of Pb. One of the sources is derived from the highly polluted dredge spoils on the banks of the bayou and the other from the natural environment. The nature of the contaminant Pb is unique in that it is relatively homogenous and extremely radiogenic, similar to ores of the Mississippi Valley. The Pb isotope data for contaminated trees are identical to those for bayou sediments and show the same mixing relationships. A discussion of how the isotope data may be used to yield information on the fate and transport of Pb in the environment will be presented at the meeting.

8:40 A SECONDARY ION MICROPROBE FOR ISOTOPE RATIO MEASUREMENT. P. J. Todd, R. T. Short, M. Wiedenbeck, and J. M. McMahon, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6365.

Isotope ratio mass spectrometers used for gaseous samples have two important features that permit accurate measurement of isotope ratios. First, ion beams of two isotopes are measured simultaneously. Secondly, measurement is continuously switched between sample and reference compound. These features, introduced by Nier in the '50's, improved the precision of isotope ratio measurements by an order of magnitude.

Gas phase analysis of isotope ratios requires that the sample be volatile, and cannot provide information about the spatial distribution of elements. Secondary ion mass spectrometry (SIMS) is more appropriate for determining spatial resolution of involatile elements, but shows far less precision in isotope ratio measurement. To remedy this situation, we have constructed a secondary ion microprobe, incorporating the features of gas phase isotope ratio instruments into the design of the microprobe. A large field of view is employed so that the ratio from a reference can be measured and compared with a sample. Secondly, measurement of two isotopes from a sample can be measured simultaneously. Results of our initial evaluation of this instrument will be addressed.

9:10 OPTIMUM TRACER TO SAMPLE RATIO FOR MEASURING URANIUM BY ISOTOPIC DILUTION MASS SPECTROMETRY. David H. Smith¹ and Charles K. Bayne²,
¹Chemical and Analytical Sciences Division, ²Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365.

Measurements of isotope ratios by thermal mass spectrometry must account for isotopic fractionation during evaporation. A bias correction factor for fractionation can be estimated by external calibration using standard reference materials. Sample-to-sample variation of the estimated isotopic ratios can be large due to different analytical conditions for sample and external calibration measurements. Some of the factors difficult or impossible to control are temperature, sample matrix, and filament geometry.

Internal calibration can be used to improve measurement of $^{235}\text{U}/^{238}\text{U}$ ratios by calculating internal bias factors for the analysis in question. This method requires addition of a uranium spike to the sample; the spike has a well-known $^{233}\text{U}/^{236}\text{U}$ ratio that is used to calculate the bias correction necessary to apply to the data set associated with it. The isotopes are ^{233}U and ^{236}U because they are either absent or present at very low abundance in the samples of interest. Analysis using internal calibration is complicated by the fact there is ^{235}U in the spike, which affects the estimate of $^{235}\text{U}/^{238}\text{U}$. This report describes a theoretical analysis to determine the optimum amount of tracer to add to the sample. It was determined that a 1:6 tracer to sample ratio balanced the advantages and disadvantages of the internal calibration method. Out analysis used a Poisson regression model to represent the count measurements as a sum of source components. A series of experiments using NIST standard uranium reference material determined a tracer to sample ratio close to the theoretical value.

9:30 THE USE OF ICP-MC-MS FOR THE HIGHEST PRECISION ISOTOPE RATIO ANALYSIS OF URANIUM. Ian Bowen, Andrew J. Walder, Andrew Entwistle and Andrew Burrows, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, UK, and Tom Hodgson, Urenco (Capenhurst) Ltd., Capenhurst, NR Chester, CH1 6ER, UK.

High precision and high accuracy isotope ratio measurements of both the major and minor isotopes of uranium have traditionally been performed by Thermal Ionization Mass Spectrometry (TIMS). Recent instrumental developments have seen the introduction of Inductively Coupled Plasma-Multiple Collector-Mass Spectrometers (ICP-MC-MS). These instruments are now established as a routine methodology for uranium isotopic ratio measurement. The performance of these instruments offers greater analytical flexibility, faster sample throughput, simplified sample preparation and improved precision and accuracy of measurements.

Previous studies with ICP-MC-MS have discussed the isotopic ratio measurement of uranium using an initial calibration material to correct for mass bias. The analysis of subsequent samples are corrected for mass bias using this correction value. While impressive isotopic data has been produced with this technique, the precision of the data is limited by the stability of mass bias with time.

This study will discuss a new methodology for determining the isotopic composition of uranium. This technique uses an initial calibration to produce a mass bias parameter that is corrected by an internal reference. This parameter is imported into subsequent sample measurement procedures where an internal reference is used to produce a mass bias factor. This technique has led to unprecedented levels of analytical precision. The technique, methodologies and isotopic results will be presented and opportunities for future work discussed.

9:50 BREAK

10:10 NOVEL ON-LINE ELECTROCHEMICAL PRETREATMENT FOR URANIUM ANALYSIS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Jack R. Pretty, Douglas C. Duckworth, and Gary J. Van Berkel, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6375.

The application of a variety of electrochemical stripping methodologies on-line with inductively coupled mass spectrometry is a promising approach for matrix elimination and analyte preconcentration. An electrochemical cell is employed in a flow injection configuration. Analyte(s) are accumulated on the working electrode from the sample matrix, which is often troublesome due to high levels of dissolved solids or interfering concomitant species. The accumulated analyte can then be stripped into a clean mobile phase (e.g., nitric acid) with preconcentration resulting from differences in the sampling-to-stripping volumes. A novel and elegant method for uranium accumulation and stripping will be presented which involves the electrochemical pretreatment of a glassy carbon electrode to form a reactive surface for uranium accumulation at relatively low negative potentials. A positive potential strips the uranium into nitric acid for ICP-MS analysis. Preconcentration and matrix elimination (up to 2% Na) were effected. Sub-ppt levels of U have been measured. Quantification of trace uranium in undiluted seawater will be presented, demonstrating the success of this hybrid approach.

Research sponsored by the Laboratory Directed Research and Development Program of ORNL and the Office of Basic Energy Sciences, U.S. Department of Energy, under contract number DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

10:30 THE DEVELOPMENT OF ANALYTICAL PARAMETERS FOR IMPLEMENTATION OF RCRA SW-846 METHOD 6020. Marc Paustian, Ruth Wolf, and Zoe A. Grosser, The Perkin-Elmer Corporation, 50 Danbury Road, Wilton, CT 06897-0219.

Since its introduction as a commercial technique in 1983, Inductively coupled plasma mass spectrometry (ICP-MS) has developed from a research instrument to a routine environmental production tool. Increasing numbers of laboratories have invested in the technology for environmental analyses with much success. However, many laboratories are still concerned about implementation of a performance-based method and the choices that must be made in optimizing method performance.

In this talk we will describe the development of analytical parameters for implementation of RCRA SW-846 Method 6020. The thought processes used in decision making will be outlined to give the user guidance in general method development and in judicious choice of operating parameters for the most rugged performance.

10:50 DIRECT ANALYSIS OF DIFFICULT MATRICES WITH HR-ICPMS. C. B. Douthitt¹, M. Schmidt², M. Hamester³, and D. Wiederin³, ¹Finnigan MAT, 9412 Rocky Branch Drive, Dallas, TX 75201, ²Finnigan MAT, San Jose, CA 95101, ³Finnigan MAT, Bremen, Germany.

One of the goals of analytical chemistry is "direct analysis", analysis of a substrate without sample pretreatment or prior knowledge of sample composition. There are many reasons to pursue the goal of direct analysis, including but not limited to eliminating the potential for contamination during sample handling, speeding up the analysis by eliminating chemical pretreatment steps, and improving detection limits by eliminating excessive dilutions. While Q-ICPMS has emerged as a powerful tool for elemental and isotopic analysis, there are many polyatomic interferences which cannot be resolved on a quadrupole mass analyzer. Identification and avoidance- or at least mitigation- of interferences that arise during analysis of complex matrices of nuclear, biological and environmental interest pose an extraordinary challenge to the analyst, which has led to the widespread adoption of nitric acid as the matrix of choice, which often requires extensive chemical processing of a sample prior to analysis. The use of a double focusing magnetic sector analyzer, often referred to as "high resolution ICP-MS", allows the analyst to choose a mass resolution sufficient to identify and remove most polyatomic and doubly charged interferences, thus opening the door to direct analysis of many substrates that are either difficult or impossible with Q-ICPMS, a category which could be dubbed "difficult matrices".

Liquids that are difficult to analyze include mineral acids (e.g., phosphoric acid and sulfuric acid), natural brines (e.g., sea water, formation waters, bitterns), biological fluids (e.g., whole blood, serum, urine), organics liquids (e.g., tributylphosphate, photoresist, photostrip). Successful direct analysis of all of these matrices, with specific attention to ppb and sub-ppb levels of metals in TBT and photoresist, using a high resolution ICP-MS (Finnigan MAT model **ELEMENT**) will be documented, along with identification and characterization of the interferences which compromise Q-ICPMS analysis.

Direct analysis of *all* solid materials is desirable, particularly for the refractory ceramic materials of interest to the nuclear industry, unless all that is required is a bulk analysis. Production of aerosols using UV laser ablation followed by high resolution ICP-MS analysis has been demonstrated to be very effective in this regard. Compared to analyses of liquid matrices, but the need for high resolution is somewhat mitigated, although not eliminated, but the need for the highest possible sensitivity and the lowest background is more important. The use of laser ablation-high resolution ICPMS for chemical analyses of ZrC, silicate inclusions in diamonds, and high precision lead isotopic analyses of zircon ($ZrSiO_4$), galena (PbS) and pottery glaze will be presented

11:10 ENVIRONMENTAL SIGNATURES AND IAEA SAFEGUARDS PROGRESS IN CLEAN CHEMISTRY TECHNIQUES. P. F. Zahradnik, M. E. Agarande, and D. L. Donohue, International Atomic Energy Agency, Safeguards Analytical Laboratory, A-2444 Seibersdorf, AUSTRIA.

The traditional role of IAEA Safeguards is to detect and confirm that no significant quantities of safeguarded nuclear materials have been diverted from nuclear plants for non-peaceful purposes. In recent years, however, these traditional measures have been complemented by techniques designed to confirm the absence of undeclared nuclear activities in countries covered by comprehensive safeguards agreements. Environmental sampling in enrichment plants and hot cell facilities, using the method of swipe sampling, is not being used to detect chemical and isotopic signatures of undeclared nuclear activities. Recently, a class 100 Clean Laboratory for Safeguards designed to handle environmental samples has entered into operation. The chemical activities under progress are mainly: 1) Validation of the cleanness of the working areas in order to minimize cross contamination of samples that contain elements like U and Pu in the sub nanogram range. 2) Blanking of the reagents, the glassware and sampling material. 3) Preparation of environmental sampling kits for the IAEA safeguards inspectorate. 4) Preparation of reference material for distribution to the analytical laboratory network, and 5) Performance of the chemical treatment and separation of samples prior to the measurement by Thermal Ionization Mass Spectrometry.

This paper describes the progress achieved by the laboratory in some of the above mentioned activities, the difficulties encountered and how they are being solved. It also gives information on the level of cleanliness achieved in the working surfaces, labware, etc., and the analytical sensitivity expected on inspection samples.

11:30 METHOD FOR MEASURING DEUTERIUM IN ERBIUM HYDRIDE FILMS. James R. Brangan and Steven M. Thornberg, Analytical Chemistry Department, P.O. Box 5800, Sandia National Laboratories*, Albuquerque, NM 87185-0343.

Determining the quantity of deuterium in an erbium hydride (ErD₂) film is essential for assessing the quality of the hydriding process but is a challenging measurement to make. First, the ideal gas law cannot be applied directly due to high temperature (950°C) and low temperature (25°C) regions in the same manifold. Additionally, the metal hydride does not release all of the deuterium upon heating. Therefore, the method developed must provide a means to compensate for the temperature inhomogeneities as well as the retained deuterium. This paper presents two thermal desorption methods evaluated for measuring not only the amount of deuterium evolved at high temperatures (950°C) but also the quantity of deuterium remaining in these films at the high temperature. One of these methods, a multiple volume expansion technique, presented significant difficulty due to rapid temperature changes that were hard to quantify. Another technique, using a repeated pump-down approach, yielded data that indicates approximately 10% of the deuterium is retained in the metal film at 950°C and a pressure of approximately 1 Torr. When the corrected values for moles of deuterium were divided by the moles of erbium (determined by ICP/AES), a nearly stoichiometric value of 2:1 was obtained. Although this work presents data for erbium and deuterium, the method is applicable to other metal hydrides as well.

*Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:50 ADJOURN

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