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Thirty-Fourth
Conference

ORNL DOE

Analytical Chemistry in Energy Technology

Gatlinburg, Tennessee
October 5–7, 1993

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ABSTRACTS OF PAPERS

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

Park Vista Hotel
Gatlinburg, Tennessee
October 5-7, 1993

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Prepared by the Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

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Tuesday, October 5, 1993

9:00 WELCOME: W. D. SHULTS, DIRECTOR, Analytical Chemistry Division, ORNL

TUESDAY AM: MANAGEMENT OF ENVIRONMENTAL RESTORATION PROGRAMS

CHAIRMAN: M. H. CARTER, U.S. DEPARTMENT OF ENERGY, Germantown, MD 20874

9:05 UPDATE ON THE ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT ANALYTICAL SERVICES PROGRAM. M. H. Carter, U.S. Department of Energy, Germantown, MD 20874.

(NO ABSTRACT RECEIVED.)

9:30 THE DEVELOPMENT AND APPLICATION OF PLANNING PROCESSES TO MEET ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT DATA NEEDS. David W. Bottrell and W. Robert Newberry, Office of Environmental Restoration and Waste Management, U.S. Department of Energy, Germantown, MD 20874.

The Department of Energy is faced with a huge and highly publicized environmental challenge. Large volumes of radioactive and hazardous waste have been accumulating at DOE weapons facilities over the last 45 years. Conservative estimates suggest that $200 billion will be spent on cleaning up this environmental contamination. In any decision-making process establishing when, where, and how to clean up contamination, environmental data are essential. In addition, the definition and determination of project completion rely on environmental data. Recognizing that environmental data are both essential and costly, the US EPA developed the Data Quality Objective (DQO) Process. This process focusses on the necessity of planning and tying data collection with a specific decision. Elements of a second decision support tool, the Observational Approach, also contribute to the planning process. The Observational Approach recognizes the inevitability of decision error and emphasizes monitoring and management of this residual error, i.e., uncertainty. The common theme of these approaches is that data are relevant only to the extent that they effect an action or a decision, e.g., which of two engineering alternatives is technically acceptable and cost-effective. DOE's need to enhance environmental restoration and waste management processes results from the complexity of site problems. This presentation describes key enhancements DOE has made to the DQO Process and efforts to integrate and streamline planning processes for environmental programs.

9:50 DOE'S QUALITY ASSESSMENT PROGRAM FOR ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT (EM) SAMPLING AND ANALYSIS ACTIVITIES. W. Robert Newberry and David W. Bottrell, Office of Environmental Restoration and Waste Management, U.S. Department of Energy, Germantown, MD 20874.

DOE Order 5700.6C, Quality Assurance (QA), defines policy and requirements to establish QA programs ensuring that risks and environmental impacts are minimized and that safety, reliability and performance are maximized. This is accomplished through the application of effective management systems commensurate with the risks imposed by the facility and the project. Every organization surrounding EM's environmental sampling and analysis activities must develop and document a QA program. Management of each organization is responsible for the appropriate QA program implementation, assessment, and improvement. The collection of credible and cost-effective environmental data is critical to the long-term success of remedial and waste management actions performed at DOE facilities. Only well-established and management-supported assessment programs within each EM support organization will enable DOE to demonstrate that the right amount of the right data is collected to support the right decision. EM's Laboratory Management Division has developed such an assessment program, consisting of a series of guidance documents and assessment plates for management, laboratory and field assessments. The assessment program and two pilot assessments will be described.

10:10 BREAK

NOTES

TUESDAY AM: RECOGNITION OF THE 50th ANNIVERSARY OF THE MANHATTAN PROJECT

CHAIRMAN: W. D. SHULTS, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831

10:40 FIFTY YEARS OF CONTINUOUS IMPROVEMENT. (WHAT HAS DOE DONE FOR ANALYTICAL CHEMISTRY?) W. D. Shults, Director, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6129.

Several DOE installations began to celebrate golden anniversaries last year, and others will soon follow. Such times breed healthy reflection. Over the past five decades, analytical scientists within the AEC/ERDA/DOE complex have had tremendous impact on the field of analytical chemistry. This paper suggests several "high impact" research and development areas that either originated within or were brought to maturity within the DOE laboratories. "High impact" means they resulted in new subdisciplines and/or new ways of doing business. The progress has been remarkable.

11:00 **TITRIMETRY AND SPECTROPHOTOMETRY: FROM COLORS TO COMPUTERS.** Carlton D. Bingham, Director, New Brunswick Laboratory, U.S. Department of Energy, Argonne, IL 60439.

In keeping with the Conference theme -- *Historical Aspects of Nuclear Material Measurements* -- the author traces progress and improvements, both in sensitivity and precision, in titrimetric and spectrophotometric measurement technology applied to nuclear materials.

11:20 EVOLUTION OF PLUTONIUM MEASUREMENTS AT LANL. Darryl D. Jackson, Analytical Chemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545.

For 50 years analytical chemistry and the nuclear industry have been entwined, each influencing the development of the other. The stringent requirements imposed upon chemical measurements and the unique nature of the materials used in the nuclear industry have made the analytical chemistry both fascinating and challenging. The measurement of plutonium provides a good example of these challenges and how we have met them. From the very beginning, product certification and accountability required accurate measurements of plutonium in various matrices and chemical forms. Accurate measurements of impurities in plutonium oxide and metal have also been needed. I will briefly describe some of the history of plutonium measurements at LANL, contrasting some of the older methods for plutonium assay and impurity measurements with our modern methods.

The challenges keep coming. In the past, the primary emphasis was on improved precision and accuracy; now the emphasis has shifted to minimizing waste and reducing or eliminating hazardous materials. I will describe some of the ways we are redirecting our efforts to meet these goals.

11:40 **FROM HEVESY TO THE ADVANCED NEUTRON SOURCE--THE PAST AND FINAL FRONTIER OF NEUTRON ACTIVATION ANALYSIS.** F. F. Dyer, Analytical Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831-6128.

Neutron activation analysis (NAA) was born at the University of Copenhagen in 1936 when Hevesy and Levi using neutrons produced by alpha particle bombardment of beryllium, measured dysprosium in yttrium. In 1934 Fermi activated uranium with neutrons and produced a set of radionuclides that confused science for five years. Finally in 1939, the radiochemists of Germany announced that the uranium had fissioned. This new reaction led to the creation of the Oak Ridge Graphite Reactor (now a national shrine) which began operation in November, 1943. Constructed to make test quantities of Pu-239, the reactor was soon being used for NAA. The neutron flux, some ten million times that of α,n sources, enabled measurement of trace amounts of more than 60 elements and resulted in the formation of a group devoted to NAA. This group was for many years the world focus in the development of methods, equipment, and training in NAA. From its early years of radiochemistry and beta counting, NAA has evolved into a computer-based analytical discipline that successfully competes in costs and quality of measurement with all other methods of elemental analysis. Soon, if the Advanced Neutron Source (ANS) is built, the neutron flux for NAA will evolve in another dramatic way. For the first time, large uniform thermal neutron fluxes will be available without fast neutrons or significant gamma heating. This "kinder, gentler" neutron flux will permit unique irradiations and analyses not now possible. This presentation will briefly trace the path of NAA along its development to its Final Frontier: The ANS.

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*Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

12:00 LUNCH

NOTES

TUESDAY PM: COMPUTER APPLICATIONS IN ANALYTICAL CHEMISTRY

CHAIRMAN: PETER JURS, PENNSYLVANIA STATE UNIVERSITY, University Park, PA 16802

1:30 PREDICTION OF CHEMICAL PROPERTIES OF ORGANIC COMPOUNDS FROM MOLECULAR STRUCTURE. Peter C. Jurs, 152 Davey Laboratory, Department of Chemistry, Pennsylvania State University, University Park, PA 16802.

Relationships between molecular structure and physical or spectral properties can be investigated for large sets of organic compounds using computer-assisted methods. Such structure-property relationship (SPR) studies involve the graphical entry and storage of structures, generation of three-dimensional molecular models, the calculation of molecular structure descriptors, and analysis of the descriptors using multivariate statistical and neural network methods to build predictive capability. Classes of structural descriptors include topological, geometrical, electronic, and physiochemical representations of the molecules. Topological descriptors are calculated directly from the connection table representation of the structure, whereas geometric descriptors are calculated from the 3-dimensional molecular models. The calculated descriptors are related to the desired physiochemical property by multiple linear regression analysis or computational neural networks which yield quantitative predictive ability. The models then can be used for predicting properties for unknown compounds. These studies are carried out with the ADAPT (Automated Data Analysis and Pattern recognition Toolkit) computer software system.

Several specific areas of structure-property relationship studies will be discussed, including studies of chromatographic retention, prediction of the normal boiling points of organic compounds, and studies of other physical properties such as surface tension and autoignition temperature.

1:50 **THE NIST CONSORTIUM ON AUTOMATED ANALYTICAL LABORATORY SYSTEMS.** Gary W. Kramer, National Institute of Standards and Technology, Chemical Science and Technology Laboratory, Chemistry Building 222, M/S A-213, Gaithersburg, MD 20899.

The National Institute of Standards and Technology has joined with interested parties from the private sector, the Department of Energy, and other government agencies to form the Consortium on Automated Analytical Laboratory Systems. CAALS has undertaken, with guidance from its members and others in the analytical instrumentation community, the task of identifying, defining, and promoting general guidelines and standards in critical areas of sample, data, and control information interchange for analytical instruments. From the CAALS viewpoint, fully automated analytical systems (those which take in raw samples and return chemical information) may be constructed most appropriately by interconnecting modular instruments which have been designed specifically as system--instead of user-operated, stand-alone--devices. CAALS is determining the requirements and specifications for interfaces between such analytical modules and their controllers. Current developments include a protocol and syntax specification for communications between modules and their controller and a list of behavior requirements for instrument controllability. This presentation will describe our progress and bring the audience up to date on our current and planned activities.

2:10 STATUS OF THE CONTAMINANT ANALYSIS AUTOMATION (CAA) PROGRAM.

Robert M. Hollen, Sensor Systems and Robotics, Los Alamos National Laboratory, Los Alamos, NM 87545.

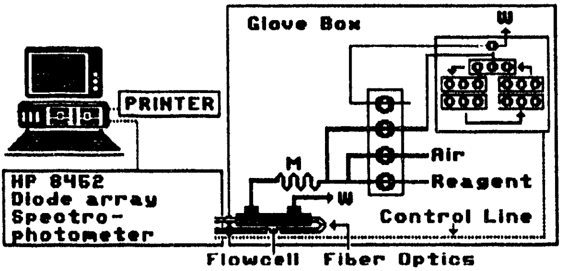
The Department of Energy (DOE) has significant amounts of radioactive and hazardous waste at many of the weapons complex sites within the United States. Most of this waste is yet to be remediated while a significant amount is currently in temporary storage. National regulatory requirements in addition to existing tri-party agreements between the specific sites, the state government, and the local Environmental Protection Agency (EPA) region mandate that remediation must begin typically before 1995. However, before remediation is possible, these wastes must be chemically characterized to determine the elemental, isotopic, and compound content. Sampling requirements to provide this characterization are projected to generate more than 10 million samples by 1995 which will far exceed the capabilities of DOEs current analysis capability. To address this problem the Contaminant Analysis Automation (CAA) program within the Office of Technology Development (OTD) is demonstrating laboratory sample analysis systems which will automate the environmental chemical laboratory. The current laboratory automation paradigm consists of limited capability islands-of-automation that do not integrate into a systems architecture which could provide the path from sample-in through interpreted-data out. Thus today the chemist must still perform many aspects of the analysis manually.

By designing and transferring to industry systems based upon the Standard Analysis Method (SAM) architecture, the CAA group is working towards a standardized and modular approach to laboratory automation. Each SAM system will automate a specific chemical method, from the initial sample preparation through analytical analysis and subsequently generate knowledge of the remediation site via knowledge-based data interpretation. The building block of a SAM is known as the Standard Laboratory Module or SLM. The SLM, being either hardware or software, automates a sub-protocol of an analysis method. This concept allows the chemist to assemble an automated environmental analysis system using standardized SLMs easily and without the worry of hardware or software incompatibility or the necessity of generating complicated control programs. Hardened for the rigors of on-site remediation, these systems will be designed with use within transportable laboratories directly at the remediation site.

2:30 FROM LIQUID SAMPLE TO PRINTED REPORT: A FULLY AUTOMATED PLUTONIUM ANALYZER.

Donald A. Burns, Elmer Lujan, and Lawrence E. Wangen, Los Alamos National Laboratory, Los Alamos, NM 87545.

A totally automated analytical system for plutonium solutions has been assembled from several commercially available instruments. The included computer has been programmed in QuickBASIC 4.5 (incorporating routines from a Hewlett Packard programming library) and provides for both instrument control and data reduction. Modules inside a glove box (see diagram) are interfaced via fiber optics to a HP8452 diode array spectrophotometer. The system is based upon segmented flow analysis (SFA) using an Alpkem multichannel peristaltic pump and a 5 mm pathlength flowcell from Vitro Technologies. Samples and standards are aspirated from an ISCO sampler and diluted on-line 20-fold. The reagent is ascorbic acid, which reduces Pu to Pu^{+3} for spectrophotometry at 400-700 nm. The system operates at 40 samples/hour using only 0.074 mL of sample and generating about 1.5 mL/minute of waste. Sample concentrations to date have been in the range 40 - 240 g/L Pu. One version of the system even permits leaving the peristaltic pump outside the glove box. The system can be modified to provide substantially higher sensitivity: longer pathlength flowcell, lower dilution factor, alternative chemistry (oxidation to Pu^{+6} with detection at 831 nm). The presentation will address those details which will permit others to duplicate our precision of 0.05-0.10% RSD.



2:50 BREAK

3:20 AUTOMATED TEST APPARATUS FOR THE MODELING OF VOC TRANSPORT IN LAB-SCALE SIMULATED WASTE DRUMS. G. L. Gresham, C. Rae, K. J. Liekhus, and M. J. Connolly, EG&G Idaho, Inc., Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415.

The Idaho National Engineering Laboratory (INEL) is currently participating in pretest waste characterization of waste drums for the bin-scale tests at the Waste Isolation Pilot Plant (WIPP). The Environmental Protection Agency (EPA) has issued a Conditional No-Migration Determination (NMD) for the WIPP which requires that a representative drum headspace sample and that all layers of confinement be sampled of the transuranic waste until it can be demonstrated that sampling is no longer necessary. A test program has been initiated at the INEL to demonstrate that VOC concentrations in the void space of each layer of confinement (the drum headspace, the 55-gal. poly bag, and the small inner layers of confinement) can be estimated without extensive sampling of the waste by using a model incorporating theoretical diffusive and permeative transport principles and limited waste drum sampling data. In order to test the model, a series of lab-scale experiments were performed in which the VOC concentrations were measured in simulated lab-scale waste drums under different conditions. Test variables included the type of VOC gas mixture introduced into the innermost layers of confinement, the bag closure type, and the presence or absence of a variable heat source. The Automated VOC Transport experimental apparatus and initial results of the unsteady state experiments will be discussed.

3:40 MULTI-MEDIA ANALYTICAL PROCEDURES -- SOUND, GRAPHICS, VIDEO CLIPS IN PROCEDURES. W. A. Spencer, K. B. Moore, H. B. Aiken, and B. J. Hudson, Savannah River Technology Center, Aiken, SC 29808.

Multi-media tools are available to enhance plain white paper analytical procedures with sound, graphics, video, and animation. The Savannah River Technology Center explored the use of multi-media computer programs to enhance the teaching and display of analytical procedures. Specifically two procedures, one for "Cold Vapor Mercury Analyses", and another for use of an "Automated Titrator for Aluminate, Carbonate, and Hydroxide Determination", were rewritten to add multi-media clips. Photographs, sound, and video clips were added to the procedures to illustrate the key points. For example, instead of just listing the names of equipment, a photograph of each instrument or tool enhanced the display of the text. We made the procedures interactive by adding animated features that required mouse clicks to me through the procedure. The multi-media procedures were made using MacroMind Director and playback on both MAC and Windows operating systems. We explored the possibilities of distributing the procedures via site networks and CD ROMs. Appletalk networks [1 MB/sec] were shown to be too slow for practical real-time network displays but direct ethernet networks [10 MB/sec], if not loaded, functioned adequately. CD ROM and local high speed networks appeared to be the best platform solutions.

4:00 IMPLEMENTATION OF A LABORATORY INFORMATION MANAGEMENT SYSTEM FOR ENVIRONMENTAL REGULATORY DRIVEN ANALYSES. W. A. Spencer, H. B. Aiken, T. L. Spatz, W. F. Miles, and J. C. Griffin, Savannah River Technology Center, Aiken, SC 29808.

The Savannah River Technology Center created a second instance of its ORACLE-based LIMS to support site Environmental Restoration projects. The first instance of the database had been optimized for R&D support and, although highly flexible, did not implement rigorous sample tracking, verification, and holding times needed to support regulatory commitments. Much of the R&D instance was transferable such as the work control functions for backlog reports, work assignment, and hazard communication.

A major enhancement of the regulatory LIMS was the addition of features to support a "standardized" electronic data format for environmental data reporting. The electronic format was developed by the site environmental monitoring organization and applies to both onsite and offsite environmental analytical contracts. This format incorporates EPA CLP data validation codes as well as holding time and analytical result details. The format was supported by using special SQL queries to the database, automatic transference of data to an Excel spreadsheet where data was validated, and then transference of data to the environmental databases for trending and geological mapping.

6:00 HILLBILLY BUFFET AND COUNTRY-WESTERN MUSIC. Garden area at Park Vista Hotel.

NOTES

Wednesday, October 6, 1993

WEDNESDAY AM: ELECTROSPRAY IONIZATION -- MASS SPECTROMETRY

CHAIRMAN: GARY J. VAN BERKEL, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831-6365

8:30 AN OVERVIEW OF ELECTROSPRAY IONIZATION--MASS SPECTROMETRY. Thomas R. Covey, SCIEX, Division of MDS Health Group Limited, 55 Glen Cameron Road, Thornhill, Ontario, Canada L3T 1P2.

Electrospray disperses a liquid into ions by overcoming surface tension forces with electrical forces. Over the past several years electrospray has been applied to the production of ceramic powders, production of aerosol standards, application of coatings, dispersion of pesticides, space thrusters, and mass spectrometry. The recent breakthrough of electrospray in the field of protein molecular weight determination has lead to an enormous effort by instrument companies, research institutions, and chemical industries to build new atmospheric pressure ionization mass spectrometers, to gain insights into the fundamentals of the ionization process, and to employ and extend the technique for the solution of industrial chemical and biomedical problems.

The presentation will provide an overview of the current status of electrospray mass spectrometry highlighting basic principles of different aspects of the technique.

A. Ionization Processes
    1. Fundamental models
    2. Implications of the models for:
        a. Sensitivity enhancement
        b. Dynamic range
        c. Range of molecules amenable to ionization

B. Ionizing Devices
  1. Electrospray and the Taylor Cone
  2. External energy sources to assist electrospray
    a. Pneumatic nebulization
    b. Ultrasonic nebulization
    c. Heat

C. Ion Sources and Vacuum Systems
  1. Single aperture systems
  2. Multiple aperture differentially pumped systems
    a. Nozzles/skimmers
    b. Ion Pipes (metal and glass)

D. Analyzers
  1. Quadrupoles
  2. Magnetics
  3. Ion Traps
  4. FTMS
  5. TOF

E. Inlet Systems
  1. HPLC
  2. CZE
  3. SFC

9:10 THE ROLES OF SOLVATION AND SURFACE CHEMISTRY IN ION DESORPTION.

Mona Shahgholi and Kelsey D. Cook, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600; Michelle V. Buchanan, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120.

The remarkable success of electrospray (ES) mass spectrometry (MS) stems in part from its reliance on low-energy solution chemistry to achieve analyte ionization and to overcome the strong intermolecular interactions characteristic of high molecular weight, nonvolatile materials. As with any thermochemical system, these advantages cannot be realized without energetic compensation. In ES MS, this "compensation" comes largely from the solvation of analyte ions, which must be overcome in the course of ES sampling. As a result, desolvation is a major factor in the design and limitations of ES ion sources.

In assessing how various physical and chemical phenomena affect ES sensitivity, some guidance can be derived from earlier fundamental studies of other desorption ionization (DI) methods, including electrohydrodynamic (EH) and fast atom bombardment (FAB) MS. For example, ES studies with diquaternary ammonium salts of various counterions reveal correlation between sensitivity and ion pairing as observed previously in FAB and EH MS. Behavior is also parallel in reflecting correlation between sensitivity to various simple quaternary ammonium salts and their solvation energies.

Unique aspects of ES sampling derive from the droplet formation and desolvation process. These engender, *inter alia*, distinctive dependencies on solution surface tension and analyte surface activity. Effects on the overall efficiency of the sampling process have been noted, along with evidence for competition among analytes for surface sites (affecting relative sensitivities). One practical consequence is that reduction of surface tension by added surfactants offers an alternative approach to ES of aqueous solutions without organic cosolvents. Also important are the resulting caveats necessary for quantitative ES MS.

9:40 BREAK

10:10 PROBING COVALENT PROTEIN ADDUCTS BY MEANS OF ELECTROSPRAY MASS SPECTROMETRY. K. W. M. Siu and Roger Guevremont, Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, Canada K1A OR6; J. C. Y. LeBlanc and J. L. Bolton, Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6.

The various functional groups in a protein can react with a variety of compounds in solution to form covalent adducts, which are amenable to monitoring by means of electrospray mass spectrometry. In the present study, two types of covalent modifications were examined. The first reaction involved the base-catalyzed reversible equilibrium between ketones and free amino groups on proteins to form Schiff bases. For myoglobin in a solution containing 20% *iso*-butyl methyl ketone, the mass spectrum reveals two series of ion distributions reflecting two distinct types of equilibria in solution. First, the acid-base equilibria of the various charged states of myoglobin in solution are reflected by an overall charge distribution which spans a few hundred m/z units. Second, the equilibrium reactions between *iso*-butyl methyl ketone and myoglobin are seen in the form of a multiplet of peaks within each myoglobin charge state. Each multiplet is the result of 5 to 10 ketone molecules (depending on the conditions) reacting with one myoglobin unit. In all cases, the maximum number of ketone molecules observed for each protein equals the number of amino groups (lysine and N-terminal residues) in the protein. The second reaction involved irreversible alkylation of nucleophilic residues on proteins by electrophilic quinone methides which are metabolites of numerous dietary phenols. The series of ion distributions observed depends on the reactivity of the quinone methides: relatively extensive modification of myoglobin was observed with a highly electrophilic quinone methide, whereas minimal alkylation occurred with a relatively unreactive analog. This is the first report (to our knowledge) of the identification of xenobiotic modifications of an intact protein by means of electrospray mass spectrometry, which allows direct comparisons of the relative ability of various compounds to modify proteins and may offer rapid analysis of numerous interactions between biopolymers and xenobiotics.

10:40 HIGH RESOLUTION PRECISION MASS MEASUREMENTS OF BIOPOLYMERS BY ELECTROSPRAY IONIZATION FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY. Steven A. Hofstadler, James E. Bruce, Jon H. Wahl, Brian E. Winger, and Richard D. Smith, Battelle Pacific Northwest Laboratory, Richland, WA 99352.

Recently we have coupled an external source Fourier transform ion cyclotron resonance (FTICR) mass spectrometer to an electrospray ionization source. This combination allows gentle ionization of biologically important molecules with simultaneous ultra-high (*i.e.* >> 10^6) resolution, high precision (*i.e.* < 1 ppm) mass measurements. Resolution adequate to resolve the isotopic envelope is a crucial tool for the unambiguous identification of dissociation products. Presently these capabilities are directed towards the analysis of intact proteins, peptides, and oligonucleotides. Examples of current studies are to be presented which highlight the potential of the technique for bioanalytical analysis. We have recently incorporated the additional capabilities of high performance on-line separations using capillary electrophoresis and packed fused silica capillary liquid chromatography using both sheath flow and sheathless ESI interface designs. Preliminary results obtained with capillary electrophoresis indicate that substantial sensitivity improvements can be achieved when the spectrometer is coupled to an on-line separation prior to ionization. For example, a 20 µm i.d. CE capillary into which approximately 6 fmol/component were injected provided an interpretable reconstructed total ion chromatogram with average mass resolution of approximately 5 x 10^4. The rapid pumping speed of the system allows pressure excursions of >5 orders of magnitude to take place in less than a second, thus allowing high pressure conditions which favor efficient ion accumulation and low pressure conditions necessary for high resolution measurements.

11:10 CHEMICAL DERIVATIZATION FOR SELECTIVE DETECTION BY ELECTROSPRAY MASS SPECTROMETRY[1]. J. Martin E. Quirke,[2] Christopher L. Adams,[3] Department of Chemistry, Florida International University, Miami, FL 33199; Gary J. Van Berkel and Keiji G. Asano, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365.

As a rule of thumb, the electrospray mass spectrometry technique (ES-MS) works best when the analyte is ionized in solution, prior to the ES-process. Therefore, non-ionic molecules cannot be detected directly by ES-MS. Transformation of such compounds into ES-active species requires one of three broad strategies. First, Brønsted acid/base chemistry (e.g. modification of solution pH) or Lewis acid/base chemistry (e.g. complexation with a metal cation) may be employed. This approach is most effective for analytes bearing polar groups (e.g. alcohols, amines and carboxylic acids). For highly conjugated molecules (e.g., PAH's), electron transfer is a powerful strategy. Third, molecules may undergo chemical derivatizations to yield an ES-active species. This method may be used with almost any organic molecule. Many of these reactions are rooted in traditional organic qualitative analysis to produce charged species. In this paper we will discuss experiments that have been done which demonstrate the potential value of the derivatization approach for the selective detection of analytes. We will present examples of the selective detection of priority pollutants, fragrances/flavorings and pharmaceuticals in 'real life' mixtures. The modification of derivatizing agents to enhance flexibility will also be described.

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[1] Research sponsored by U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

[2] ORAU Summer Faculty Research Participant, Oak Ridge National Laboratory.

[3] ORISE Summer Student Research Participant, Oak Ridge National Laboratory.

12:00 LUNCH

NOTES

WEDNESDAY PM: DETECTION AND MONITORING OF AIRBORNE TOXICS

CHAIRMAN: ROGER A. JENKINS, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831-6120

1:30 OVERVIEW OF OPTICAL REMOTE SENSING FOR DETECTION OF AIR TOXICS. William M. Vaughan, Remote Sensing-Air, Inc., 8147 Delmar Blvd., Suite 219, St. Louis, MO 63130.

Beams of infrared and ultraviolet light are now being routinely used at industrial sites and cleanup sites to document the movement of clouds of air toxics in the ambient air. These devises known as optical remote sensors have matured significantly in the past five to six years. With the use of high-capacity, high-speed personal computers, detailed digital spectral libraries, and sophisticated analytical software these units can be used as qualitative and quantitative devises with practically real-time output. Because of their versatility in analyzing for the presence of many compounds simultaneously without the need for sample extraction, collection, transport, handling and all that associated documentation, these methods can provide cost-effective data on gaseous releases from many different sites. This paper will provide a brief introduction to the physical principles behind the techniques, and describe some of the commercially available hardware and its real-world application. It will indicate where the regulatory and research communities are in terms of accepting and cross-validating these techniques and their application, including the development of quality assurance procedures to provide defensible data sets.

1:50 AIR ISSUES DURING SITE REMEDIATIONS: REGULATORY CONSIDERATIONS AND CASE STUDY. Timothy R. Minnich, Vice President, Air Services Division, Blasland, Bouck & Lee, 8 South River Road, Cranbury, NJ 08512-9502.

An overview of the regulatory requirements that drive the air aspects associated with the remediation of hazardous waste sites is presented. The air pathway analysis (APA) concept is explained, including USEPA's hierarchical approach to this process in which the impact to public health and environment is assessed via a series of increasingly less conservative, more refined (and thus costly) analyses until insignificance can be demonstrated. Also discussed is how the APA process is employed to arrive at the most acceptable and cost-effective remediation technology from an air-emissions perspective.

The second half of this talk consists of a slide presentation depicting a recent case study in which open-path Fourier-transform infrared (FTIR) spectroscopy was used to assess the air needs in support of an emergency removal in the Midwest. Path-integrated measurements of target contaminants made immediately downwind of site disturbance activities, coupled with on-site meteorological data, were used to continually assess, in near real-time, compliance with pre-established, health-based fenceline action levels and, subsequently, to support decisions concerning implementation of vapor suppressant techniques.

2:10 **DEVELOPMENT OF ANALYTICAL METHODS FOR TOXIC BYPRODUCTS IN GASES FROM SOIL REMEDIATION SYSTEMS.** Paul F. Daley, Environmental Restoration Division, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550.

Soil and groundwater contamination is widespread throughout this country and in other industrialized areas. As the pace of remediation has increased, recognition has emerged of the importance of air emissions from cleanup operations. Many regional air boards now require removal of all volatiles from remediation air streams, with monitoring of scrubbing equipment. Also, the lack of facilities to process and recycle activated carbon has stimulated interest in the use of high-energy oxidation systems to destroy contaminants as part of the cleanup train. We will describe automated systems of moderate cost for monitoring of trichloroethylene (TCE) and fuel vapors, in use at remediation systems at LLNL. The systems use a computer controlled gas switching sampler, and portable gas chromatograph. We will also describe an on-trap derivatization method under development for analysis of acid chlorides and phosgene, produced by oxidation of TCE and other chlorinated solvents.

2:30 **AIR QUALITY MONITORING BY MEMBRANE SAMPLING ION TRAP MASS SPECTROMETRY.** M. E. Cisper, G. C. Saunders, W. F. Bentley, and P. H. Hemberger, Los Alamos National Laboratory, Los Alamos, NM 87545; L. E. DeJarme, D. A. Solyom, and R. G. Cooks, Purdue University, W. Lafayette, IN 47907.

We are developing field-deployable instrumentation to monitor air quality at boundaries of DOE facilities and remediation sites. This methodology will be used for the characterization of volatile organic compounds (VOCs) that can be potentially released to the atmosphere during site remediation activities.

The methodology combines a Micromist Air Sampler developed at Los Alamos with a transportable gas chromatograph ion trap mass spectrometer (GC/ITD) for the field collection and detection of airborne VOCs. Membrane sampling technology, developed at Purdue University, will be used to introduce the preconcentrated VOCs to the ion trap for near real-time analysis in the primary (fast screening) mode of analysis. The secondary (slower) mode will provide legally defensible GC/MS data to verify air quality at and around DOE facilities and remediation sites. The Micromist Air Sampler provides concentration factors of 1000 to 10,000 for airborne contaminants by entraining these contaminants in a water mist created by a piezoelectric ultrasonic oscillator. Condensed water and dissolved organics are passed through a membrane sampling device which selectively introduces organics to the ion trap mass spectrometer. Detection limits are expected to be in the low parts-per-trillion with this simple methodology. We will describe each component of this instrumentation and present our data to date.

2:50 EVALUATION OF FTIR SPECTROSCOPY FOR THE ANALYSIS OF WASTE DRUM HEADSPACE. W. F. Bauer, J. G. Jolley, and M. J. Connolly, EG&G Idaho, Inc., Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415.

The Idaho National Engineering Laboratory (INEL) is currently participating in the Waste Isolation Pilot Plant (WIPP) Experimental Test Program (WETP). The Environmental Protection Agency (EPA) has issued a Conditional No-Migration Determination (NMD) for the WIPP which requires that a representative drum headspace sample be collected and that all layers of confinement be sampled until it can be demonstrated that this sampling is not necessary. One role of INEL in the WETP is the development and evaluation of methods for the analysis of RCRA (Resource Conservation and Recovery Act) constituents in the gaseous headspace of the waste drums and bins. Currently this analysis is performed by gas chromatography/mass spectrometry (GC/MS) of samples collected in SUMMA canisters. Fourier transform infrared spectroscopy (FTIR) was selected as a GC/MS replacement since FTIR instrumentation is simple, durable, and can be operated "at-line". FTIR analysis times are short and the RCRA analytes expected in the drum headspace have unique IR spectra that can be used both quantitatively and qualitatively over relatively wide concentration ranges. Because the number of potential analytes in the drum headspace is over 29, complex IR spectra are to be expected. To assess the feasibility of using FTIR for such complex samples, a two phase study has been initiated. Because of the large number of analytes and analyte combinations, Phase I of the study involved the analysis of computer generated spectra as well as the analysis of spectra obtained in the laboratory. Phase II of the study will consist of a comparison of "at-line" drum and inner layer of confinement headspace analyses by FTIR to the GC/MS analysis. The results of the Phase I studies will be discussed.

3:10

IS THE SAMPLING OF DRUM HEADSPACE VOCs A VIABLE WASTE CHARACTERIZATION TOOL?

Michael Connolly, Kevin Liekhus, and Gary Gresham, Idaho National Engineering Laboratory, EG&G Idaho, P.O. Box 1625, Idaho Falls, ID 83415-2424.

The U.S. Department of Energy has proposed the use of drum headspace volatile organic compound (VOC) data as a waste characterization tool for TRU waste destined for shipment to the Waste Isolation Pilot Plant (WIPP). The U.S. EPA, in its conditional no-migration determination for the WIPP, requires that DOE must demonstrate that drum headspace is representative of the entire void volume of the drum. This means that the DOE must collect headspace samples from all the layers of confinement until they can demonstrate drum headspace representativeness. We have developed an approach to determine drum headspace representativeness that is based on evolved VOC transport modeling, simulated waste drum experiments, and sampling of real TRU waste drums. The concept of drum headspace representativeness does not address the equilibrium relationship between gas and solid/liquid phases, it only addresses the relationship between gases in various layers of confinement within a waste drum. The approach consists of developing models that describe the transport of evolved VOCs within a waste drum under unsteady state and quasi-steady conditions, laboratory scale simulated waste drum experiments, measurement of VOC permeabilities, and finally the development of transport models for and the sampling of real TRU waste drums. Results of simulated and real waste modeling and experiments will be presented. The potential application of these results to defining drum headspace representativeness and the usefulness of drum headspace as a waste characterization tool will be discussed.

Work supported by the U.S. Department of Energy under the following contract DE-AC07-76ID01570.

NOTES

WEDNESDAY PM: LABORATORY MANAGEMENT AND QUALITY ASSURANCE

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

1:30 PERFORMANCE EVALUATION PROGRAMS -- ALTERNATIVES BASED ON USER NEEDS.[1] Peter C. Lindahl and W. Elane Streets, Argonne National Laboratory,[2] Argonne, IL 60439; Robert Newberry and David Bottrell, U.S. Department of Energy, Germantown, MD 20874; Catherine Klusek, U.S. Department of Energy, New York, NY 10014; Stan Morton, U.S. Department of Energy, Idaho Falls, ID 83402; and Sam Kedayat, University of Illinois, Chicago, IL 60607.

Performance evaluation (PE) programs were a key tool for assessing analytical laboratory performance in environmental investigations in the 1980s. Use of this tool will expand in the 1990s. Numerous programs provide external reference materials to monitor analytical laboratory performance for purposes ranging from accreditation (regulatory programs) and contract monitoring to self and internal assessment programs (other federal agencies and private sector programs). Assessments are generally pass/fail and may affect laboratory participation in broad monitoring program areas, e.g., accreditation by the U.S. Environmental Protection Agency's (EPA) Office of Water, or support to specific environmental programs, e.g., EPA's Contract Laboratory Program. Past PE programs have set parameter-specific acceptance windows based upon a statistical treatment of total participant performance (minus some outliers) and have scored laboratory data on a pass/fail basis, i.e., a set number of points is lost for each reported value outside the acceptable range, resulting in a cumulative laboratory score. There is no "right way" to score laboratory performance. This approach assesses laboratory adherence to contract specifications or prescribed methods. Although pass/fail approaches may identify very poor performers, they have limited power to differentiate participant performance among those who pass. For regulatory programs, the need for this differentiation has historically been less than the concern for consistency, i.e., data comparability.

The U.S. Department of Energy (DOE) Environmental Restoration and Waste Management Program has developed a totally different approach to performance evaluation--one more appropriate to address DOE's needs. As opposed to a simple summation of "unacceptable determinations" and point deductions to develop a composite "acceptability" score, DOE's new approach considers actual cumulative variability across all reported measurements to give an "absolute" laboratory ranking. There are no preconceived notions of acceptability. The actual performance (i.e., accuracy and precision) for each measurement is utilized individually and combined to evaluate the laboratory performance. Each laboratory submission of analytical data is normalized to address the differences in measurements performed, since not all laboratories must determine all test parameters. This is a significant change from the traditional PE program format in which points are deducted based on results falling outside a three sigma window of program "expectations".

This new approach improves differentiation among program participants, with scores ranging from 0 to 100. Quality improvement results from establishing improvement goals based on the combination of corrective action requirements or contractual stipulation on data quality and peer pressure because all laboratories know their relative standing. In some programs, e.g., the DOE Quality Assessment Program at Environmental Measurements Laboratory, all participating laboratories are identified in summary reports and their results are given. Also, key analyte measurements, e.g., plutonium in soil or benzene in water, relevant to actual site remediation problems are highlighted for developing site-specific acceptance criteria, for monitoring whether the support laboratories are meeting the acceptance criteria, and for allocating samples to support laboratories. This presentation discusses the application of the DOE's assessment process to site-specific monitoring.

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[1] Work supported by the U.S. Department of Energy, Office of Technology Development, Program Support Division, Laboratory Management Division.

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

1:50 A QUALITY ASSESSMENT PROGRAM AS A TOOL FOR IMPROVING ANALYTICAL LABORATORY PERFORMANCE.

M. M. Khalil and R. C. Tuckfield, Westinghouse Savannah River Company, Aiken, SC 29808.

The Environmental Monitoring Section (EMS) at the Savannah River Site, in cooperation with the Scientific Computations Section of the Savannah River Technology Center, improved its Quality Assessment Program (QAP) to help prevent subcontracted laboratories from providing unreliable results.

EMS monitors the quality of groundwater in over 1500 monitoring wells on site. This generates approximately 500,000 laboratory analyses annually. This volume of work must be subcontracted to more than one environmental laboratory.

The Mean Relative Difference (MRD) statistic was developed to assist the laboratory QA/QC administrator at EMS to assess both the within-lab reliability and between-lab comparability for the subcontractors. The MRD is composed of the sum of individual relative differences (RDij) between the sample concentration and its corresponding replicate measurement at the jth well and for the ith constituent (Khalil and Tuckfield 1992). That is

$$\mathrm{MRD} = \left[\frac{\sum_{j=1}^{n} \mathrm{RD}_{ij}}{n}\right] \bullet 100$$

The MRD statistic was successfully used in preparing for subcontractor laboratory audits. But in some cases, when analyte concentration measurements were reported as very near zero, the MRD statistic was artificially inflated and tended to suggest a larger problem with the laboratory analysis method than was deserved. An adjusted MRD statistic was subsequently developed which weighted each term in the sum by a value between 0 and 1. Measurements near zero received a weight near zero. Measurements greater than or equal to the level of quantitation (LOQ) (Keith 1992) received a weight of one. Measurements between zero and the LOQ received a weight linearly proportional to the distance from zero. Comparisons of the MRD and the adjusted MRD are given in the presentation.

An additional improvement was recently made to the EMS oversight QA/QC system for subcontract laboratory performance. A table showing the constituents and their associated concentrations of the original sample (S) and blind (R) and laboratory replicates (LS and LR, respectively) of these samples for which any RD_{ij} is greater than 66 percent was created. This table provides detailed information of sample date, well identifier, and the corresponding constituent name and concentration measurements for this subset of very large MRD values. EMS uses this information as a tool to improve subcontracted laboratory performance regarding the unusually poor replicate precision for these given samples.

This improvement in the EMS QAP for subcontracted laboratories has resulted in more productive laboratory audits during 1992. Continuous monitoring of MRD statistics and QC standards proficiency results has allowed previously unidentified problems in subcontracted laboratories to be identified prior to scheduled QA/QC audits.

The EMS QAP built on statistical foundations has led to improved overall performance of EMS subcontracted laboratories. EMS improved its monitoring of subcontracted laboratories performance and its assurance that the reported data are accurate and defensible.

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Acknowledgement

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2:10 **TQM SUCCESS IN THE ANALYTICAL LABORATORY.** Wayne J. Spetnagel, Portsmouth Gaseous Diffusion Plant, Martin Marietta Energy Systems, Inc., Piketon, OH 45661.

TQM has become an effective way of doing business at the Portsmouth Laboratory. Over the last two years, the Portsmouth Laboratory has worked hard to meet the challenges of today's environmental, health and safety needs. We are proud to claim some measure of success. Our roadmap to success is marked with TQM milestones including creating a vision, developing strategy, establishing ownership, assuring feedback and celebrating success. No single TQM element stands alone effectively. However, together, these TQM elements become a powerful, very effective way of doing business.

2:30 UNCERTAINTY IN ANALYTICAL MEASUREMENTS.

James R. DeVoe, Chief, Inorganic Analytical Research Division, National Institute for Standards and Technology, Rm. B206, Chemistry Building, Gaithersburg, MD 20878.

The statement of uncertainty in a chemical analysis should combine a random (statistical) error component with a systematic (bias) error component. When the estimated unmeasured systematic component is small with respect to the random component, intercomparison of results between methods or between a method and a value assigned to a reference material or to a regulatory limit is relatively straightforward. When the systematic component is significant the comparison loses its statistically valid predictability. NIST has recently adopted, with some modification, a formalized procedure suggested by the International Organization for Standardization (ISO) for stating the uncertainty of a measurement which attempts to ameliorate this lack of predictability. A brief summary of this procedure will be presented along with a discussion of how intercomparison of results may be done.

2:50 **VALIDATION OF NAA OF ENVIRONMENTAL SAMPLES.** K. Heydorn, Isotope Division, Riso National Laboratory, Roskilde, Denmark.

As neutron activation analysis (NAA) can analyze environmental samples without pretreatment, this technique is especially attractive for investigations that might lead to far-reaching decisions. As with other analytical methods, NAA must demonstrate that its results enable only valid, but not untenable conclusions to be drawn. Thus, the analytical results are taken to be true within specified limitations of: an accurately known uncertainty, and an absence of significant bias. In validating NAA for environmental analysis, both of these factors are ascertained by identifying and quantifying all significant sources of variability. The validation of any analytical method should include the sampling procedures, and in NAA the individual steps to be brought in statistical control are: sampling, irradiation, counting, and data processing.

Validation must start with computational methods, frequently in the form of computer programs. In some cases, but certainly not all, these programs are validated by the supplier, and the validation must be limited to verifying his claims. The validation method proceeds stepwise by bringing first the counting process in statistical control, then the irradiation conditions, and finally the quality of the sampling, expressed in terms of the homogeneity of the samples obtained. Once the entire procedure has been brought in statistical control, traceability must be established, and the validation is therefore completed by analyzing a suitable number of certified environmental reference materials. Illustrations of this validation method for environmental NAA measurements will be presented.

3:10 QUALITY ASSURANCE IN ENVIRONMENTAL MANAGEMENT. Gloria D. Mencer, Environmental Compliance, K-25 Site[1], P.O. Box 2003, Oak Ridge, TN 37831-7155.

Today environmental management is vital to almost any business. It is the process used by management to assure the organization's environmental goals are met. To meet the ultimate goal of "minimizing adverse impacts to the environment" many processes are employed. Action applied to ensure those processes are carried out to meet the mission is defined as quality assurance. This paper will provide an approach where the integration of the two processes - environmental management and quality assurance - are achieved.

The Environmental Compliance organization of Martin Marietta Energy Systems, Inc., is a central staff organization. The organization is responsible for ensuring that the environmental protection, environmental restoration and waste management functions are performed in a manner consistent with local, state, and federal environmental laws, regulations, corporate policy, and applicable Department of Energy (DOE) Orders. This is accomplished through: (1) interpreting external requirements relative to the company's position and developing policies that will communicate and implement the requirements, (2) providing technical assistance to enhance the effectiveness and consistency of environmental programs, (3) acting as principal interfaces with regulatory agencies on environmental issues, (4) assessing compliance within the environmental disciplines, and (5) planning the overall strategy for the corporation as related to environmental issues.

This paper will address key components of the Martin Marietta Energy Systems Environmental Compliance organization quality management systems and processes. The application of quality assurance is based on DOE Order 5700.6C. Specific areas addressed will be roles and responsibilities, implementing an internal assessment program, auditing, and the defining of processes.

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[1] Managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy.

NOTES

WEDNESDAY PM: INTERACTIVE ANALYTICAL SEMINARS

CHAIRMAN: ARNOLD HARROD, OAK RIDGE NATIONAL LABORATORY, Oak Ridge, TN 37831-6129

3:40 - 5:00 POSTER SESSION

NUCLEAR WASTE ANALYTICAL ROUND ROBINS 1-6: LESSONS LEARNED.

Gary L. Smith, Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352.

The Materials Characterization Center (MCC) at Pacific Northwest Laboratory has conducted Nuclear Waste Analytical Round Robins on simulated waste glasses with and without radionuclides. The Analytical Round Robins have been used to provide analytical laboratories with a forum for improving the accuracy and precision of analytical techniques which will be used for characterizing nuclear waste glasses. Chemical analysis data on glass waste forms produced by the nuclear waste community may need to withstand legal challenges for waste material storage qualification and for the licensing of repositories. Determining the quality of analytical data is important for meeting this criteria, making process operation decisions, and predicting long-term waste behavior.

The MCC has conducted six round robins for the waste management, research, and development community from 1987 to the present time. The laboratories which have participated regularly are Ames, Argonne, Catholic University, Lawrence Livermore, Pacific Northwest Laboratory, Savannah River, and West Valley Nuclear. The glass types analyzed in these round robins have all been simulated nuclear waste compositions expected from the vitrification of high level nuclear waste. A wide range of analytical procedures have been used by the participating laboratories including AA, ICP-AES, DC Plasma, and ICP-MS techniques. The consensus average relative error for round robins 1 through 6 has averaged 5.35% with values ranging from 9.42 to 1.09%. The trend on the average improved with each round robin. When the laboratories analyzed samples over longer periods of time the intra-laboratory variability increased. Lab-to-lab variation accounts for most of the total variability found in all the round robins. To date, participation in the radiochemistry portion has not been 100% and the analytical results have not been as accurate when compared to the non-radiochemistry portion of the round robins. Additional radiochemical work is needed in future round robins.

CALIBRATION AND USE OF Cf SHUFFLERS FOR ANALYZING WASTE DRUMS. Jeffrey C. Gross and Keith M. Wines, Martin Marietta Energy Systems, Inc., MS 2214, P.O. Box 628, Piketon, OH 45661.

As environmental concerns over radioactive waste disposal continue to rise, the importance of Californium shufflers as a versatile waste monitoring and segregation instrument also continues to increase. The extent to which different amounts and types of materials can be measured by the shuffler is directly related to the extent of its calibration. As shufflers become more commonplace and their waste management uses also rise, the importance of a wide ranging and thorough calibration becomes critical. This paper presents the techniques used at the Portsmouth Gaseous Diffusion Plant for calibrating the shuffler to detect levels of U-235 in radioactive waste. While the calibration techniques are similar to those used by Los Alamos, the standards that were used were constructed somewhat differently so that geometric effects are maximized. Also presented are shuffler transmission measurements that are used to determine the matrix type and the corresponding calibration. A discussion of the calibration data is given. This discussion includes specific aspects of the calibration such as overall range, high end limits, and poly shielding range and usefulness.

ESTIMATING ANALYTICAL LABORATORY CAPACITY. Cary M. Seidel, Westinghouse Hanford Company, P.O. Box 1970, Richland, WA 99352.

Laboratory Capacity Working Committee:

Paula K. Clark	DOE-RL WMD
Larry Jackson	MACTEC-Richland
John M. Latkovich	PNL Chem Sciences
John P. Maney	MACTEC-Boston
Dave E. Meredith	MACTEC-Washington, DC
Mike A. Purcell	WHC PAL/OPS
Cary M. Seidel	WHC PAL/NLP

In 1989, the Hanford 222-S laboratory began developing a model to estimate the current and future analytical capacities and capabilities of laboratories. This model was developed to estimate potential laboratory output for key sample analyses by measuring the individual capacities of the *laboratory operations* required to complete a given sample analysis. The capacity of a laboratory to analyze samples is equal to the laboratory's capacity to perform the limiting operation in the analytical sequence. Since an analysis consists of a number of separate, and usually consecutive, operations that are performed on a sample, it is helpful to think of a complete sample analysis as being an operational pathway.

Each operation on an analytical pathway consumes personnel and equipment/facility resources. The availability of these resources will determine the capacity to process samples. To quantitate the capacity of an operation, it is necessary to calculate both the personnel capacity and the equipment/facility capacity. The first input to the capacity model is the estimated number of *operational cycles* or intervals in a year for the operation under consideration. A series of factors then are applied to this number of operational cycles to estimate the capacity for completing the operation on *customer samples*. These factors that reduce a laboratory's capacity are:

- Calibration
- QC Analyses
- Facility Maintenance
- Equipment Availability
- Operational Maintenance
- Reruns
- Lab & Staff Availability
- Competition for Resources

MICROWAVE SAMPLE PREPARATION FOR COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY.

W. G. Engelhart and S. E. Littau, CEM, 3100 Smith Farm Road, P.O. Box 200, Matthews, NC 28106-0200.

Mercury contamination in the environment has become an increasing concern due to the toxicity of this element. The volatility of elemental mercury and organomercury compounds requires precautions be taken to avoid losses during sample preparation.

Analytical results obtained following microwave digestion of standard reference materials and real world samples spiked with organomercury standards will be presented. Sample preparation methods and microwave labware cleaning requirements for trace level mercury determination via cold vapor atomic absorption spectrometry will be described.

EXPERIMENTAL AND THEORETICAL RELATIVE ION YIELDS FOR GLOW DISCHARGE MASS SPECTROMETRY.

R. W. Smithwick III, D. W. Lynch, and J. C. Franklin, Martin Marietta Energy Systems, Inc., Y-12 Plant*, Oak Ridge, TN 37831-8189.

The purpose of this work is to improve quantitative elemental analyses by glow discharge mass spectrometry (GDMS) by predicting the individual sensitivities of the elements. The results reported on this poster reinforce recently published work (**JASMS 1993**, 4, 278-285). Relative ion yields (RIYs), defined in that work, were experimentally measured for 19 elements in NIST steel reference materials (#661-665) using both pure argon and argon containing 1 vol% H_2. RIYs were also theoretically calculated using the following equation:

$$\mathrm{RIY}_s = \frac{(\text{Mass Factor})_s (\text{Ionization Factor})_s (\text{Atomic Weight})_{Fe}}{(\text{Mass Factor})_{Fe} (\text{Ionization Factor})_{Fe} (\text{Atomic Weight})_s}$$

The mass factor, taken to be $1 - e^{0.04\ AW}$, was believed to result mostly from the mass dependence of analog detection. The predicted use of ion counting to eliminate the need for this factor is one of the interesting aspects of the present paper.

The thermodynamic ionization factor, $1/[1 + e^{+(EA+IP-\mu)/kT}]$, involves the electron affinity and the first ionization potential for each element, as well as a chemical potential ($\mu = 9.$ ev), the Boltzmann constant k, and a temperature (T = 14000 K). The atomic-weight factors are necessary to convert atom % to weight %.

When the theoretical RIYs were plotted versus the experimental RIYs, the correlation was found to be strong when the measurements were made using argon that contained 1 vol% H_2.

The following results were obtained using a Concept S32 high-resolution glow discharge mass spectrometer (manufactured by Kratos Analytical, Ltd.):

1. When ion counting was used, theoretical RIYs without a mass-dependent factor correlated well to experimental RIYs when argon was used which contained 1 vol% H_2.

2. When Inconel-steel reference materials (4.5 to 46 wt% Fe) were measured using argon containing 1 vol% H_2, the theoretical RIYs (previously used for low-alloy steels) correlated well. This indicated that the same RIYs apply to a wide variety of steels.

3. When a steel standard was measured using argon containing 5 vol% helium, the results were nearly the same as the results obtained when pure argon was used. This indicated that the physical effect of thermal conductivity (which is similarly high for both H_2 and He compared to argon) does not account for the improved correlation observed for argon containing 1 vol% H_2.

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*The Oak Ridge Y-12 Plant is managed for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400.

ANALYSIS OF FLUORIDE IN MOLTEN SALT MIXTURES USING MICROWAVE DIGESTION.

J. E. Coffield, S. Dai, J. P. Young, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6142; and G. Mamantov, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

Analysis of fluoride ion in molten salt mixtures is of importance to several industries including those involved in the electrolytic production of magnesium metal (1). Dissolution of some of the possible fluoride species (CaF_2 or MgF_2) in these melts, however, can sometimes be quite difficult (2-4). One method reported in the literature involves the digestion of the salt in nitric acid at its boiling point (1 atm) for a period of 2 hours (5). Recent studies in our lab have indicated that this method results in incomplete digestion of the fluoride species in some melt systems. We have developed a modified method which makes use of microwave digestion of the sample. This procedure is carried out at elevated temperatures and pressures in sealed teflon vessels and results in a complete digestion of the more insoluble fluoride species with a heating time of 15 minutes. Details of the analytical method including studies of various acid concentrations, microwave pressures, and times are presented along with procedures for analysis of the resulting solutions.

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Research sponsored by U.S. Department of Energy, Office of Industrial Processes, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

DIRECT ANALYSIS OF OILS BY SOLUTION RESIDUE GLOW DISCHARGE MASS SPECTROMETRY.

C. M. Barshick and D. H. Smith, Analytical Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831-6375.

We have been evaluating the glow discharge solution residue sampling methodology for analyzing "wear" oils. Early results showed that cathode formation could not be achieved simply by drying and pressing, and an additional step (low temperature ashing) was incorporated. The LFE low temperature ashing system that we are using enables the dry removal of organic material from a sample, while retaining the inorganic elements. In this system, the sample temperature never exceeds 120°C, ensuring nearly 100% recovery of trace residual elements. For the work we will report here, we compared two NIST aqueous reference solutions with two SPEX standard reference oils. After drying and ashing the oil, only small differences in relative ion yields (less than 10% average) were observed between the two types of samples; this is well within experimental error. When sensitivity factors were used, good accuracy was obtained (better than 5% average error); this indicates a minimal matrix effect. Good agreement was also observed between these results and the EPA approved ICP-OES calibration curve methodology. Although it is too early to speculate about the degree with which the matrix will influence the analysis of other types of solutions (high brines, volatile organic compounds, etc.), we are encouraged.

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*Research sponsored by U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

DETERMINATION OF RELATIVE SENSITIVITY FACTORS FOR THE QUANTITATIVE ANALYSIS OF CLAYS BY GLOW DISCHARGE MASS SPECTROMETRY.

J. Teng and F. L. King, Department of Chemistry, West Virginia University, Morgantown, WV 26505; C. M. Barshick, D. C. Duckworth, and D. H. Smith, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375.

Accurate quantitative measurements with a glow discharge mass spectrometer require the use of either calibration curves or, as is more often the case, relative sensitive factors (RSF's). These RSF's relate the sensitivity of an analyte element to that of a reference element. RSF's reflect element-dependent differences in atomization (sputtering) and ionization efficiencies. Because the sputter yields in conducting samples are relatively uniform, elemental ionization efficiencies dominate RSF's. However, the factors influencing RSF's for the analysis of nonconductors, such as clays, are not well characterized. Clays contain high levels of both oxygen, up to 40%, and low ionization potential elements. Oxygen can influence both sputtering and ionization; whereas, low ionization potential elements can alter ionization efficiencies. This paper will discuss the influence of these sample characteristics as well as other parameters, such as dc and rf power, on the determination of trace elements in a series of NIST clays.

Research sponsored by the Strategic Environmental Research and Development Program under the U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

SECONDARY ION AND MS/MS IMAGES OF BIOLOGICAL SAMPLES. Peter J. Todd, Robert T. Short, John M. McMahon, and William B. Holland, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365.

For the past four years, we have been developing a secondary ion microprobe with the purpose of determining the distribution of targeted compounds in biological tissue. Since the instrumentation has been operational, our efforts have been directed to methods development. This development includes sample preparation, charge compensation, signal enhancement and image presentation. For example, tissue in living organisms is wet. Unless the tissue is frozen before sample preparation, and kept frozen during drying, compounds can move about the sample surface, causing a loss in the spatial relationships between tissue and analytes. Samples prepared by freeze-drying are often electronic insulators, and since analysis by secondary ionization mass spectrometry (SIMS) involves current flow, we have had to develop a way to null the buildup of electronic charge during analysis. For charge compensation, sample preparation and sampling methods developed, secondary ion images from biological tissue before and after application of a method will be used to demonstrate the level of improvement. Also demonstrated will be the effect that image presentation has on the interpretation of the data.

Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy, under contract DE-AC05-84OR21400.

THE DETERMINATION OF TNT AND TNT DEGRADATION PRODUCTS IN SOIL BY HPLC AND OTHER ANALYTICAL METHODS.

Nancy A. Tomczyk and John F. Schneider, Argonne National Laboratory, Argonne, IL 60439.

On many military bases, the soil has been contaminated with trinitrotoluene (TNT) as a result of either the production or the dismantling of ammunition. Studies of the fate of TNT in the soil, conducted for more than a decade, have shown that TNT is photosensitive and that some microorganisms can break down the TNT in the soil. The interactions with light and microorganisms cause the amount of extractable TNT to decrease over time. The form the TNT takes after either interaction remains uncertain. Some first- and second-order degradation products have been determined, but a mass balance shows that these products only account for approximately 20% of the original contamination. A study that used C^{14}- labeled compounds determined that by far the greater portion of the original contamination was still in the soil.

The usual instrument used for the detection of TNT is a reverse phase-high pressure liquid chromatograph (RP-HPLC), but a gas chromatograph with a mass spectroscopy detector (GC-MSD) has also been helpful in the determination of unknown degradation peaks. The RP-HPLC is more sensitive than the GC-MSD for specific compounds, but the mass spectrum gives more useful information about molecular weight and ion fragmentation. Standards can also be run on the GC-MSD, and their spectra entered into a library against which unknowns can be compared for more positive identification.

Some work has also been done using supercritical fluid extraction (SFE) of contaminated soil. Carbon dioxide (CO_2) is used as the base supercritical fluid. CO_2, as a supercritical fluid, has the approximate extraction efficiency as hexane. Because most of the degradation products are polar, such amendments as methanol or acetonitrile can be added. Adding the amendments to the soil rather than to the fluid has been found to be more effective.

Data for extractions and separations will be presented along with graphs, chromatograms and spectra.

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DETECTION OF CYCLOHEXYLAMINE ON LABORATORY AND ENVIRONMENTAL SURFACES USING STATIC SIMS.

G. S. Groenewold, J. C. Ingram, J. E. Delmore, A. D. Appelhans, D. A. Dahl, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208.

Cyclohexylamine (CHA) is readily detected on a variety of surfaces using a unique static secondary ion mass spectrometer (SIMS) instrument, that is equipped with *pulsed extraction* and a *perrhenate ion gun*. Pulsed extraction alternately transmits anions, then cations to a quadrupole mass spectrometer, thus permitting the simultaneous acquisition of anion and cation SIM spectra, and maintaining the charge neutrality of the sample surface. This latter attribute allows for the direct, surface analysis of nonconducting materials like plastics, minerals, and vegetation. The perrhenate ion gun produces a massive, molecular anion, which is efficient for lifting organic contaminants into the gas phase. CHA is used to inhibit scale formation and pipe deterioration in the lab boiler, which in turn is used to humidify the facility. The mean concentration of CHA in the laboratory air is 210 ppb, assuming that all of the CHA is evaporated into the laboratory air. When a sample is brought into the laboratory for static SIMS analysis, abundant ions derived from CHA are observed on the sample surface: m/z 100, $[M + H]^+$; 83, $C_6H_{11}^+$; 18, NH_4^+. These ion assignments were verified by treating the surfaces with D_2O, whereupon m/z 100 shifted to 103, and m/z 18 shifted to 21, thus indicating three exchangeable protons. Surfaces on which CHA is observed include steel, quartz, and basalt.

SEPARATION OF ACTINIDE ELEMENTS IN ENVIRONMENTAL SAMPLES.

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This presentation discusses the use of an extraction resin for the separation of actinide elements in environmental samples. The optimization of separation of trace level anthropogenic elements from higher level natural elements will be discussed. Also considered will be the relative decontamination ratios between elements. A study of normal soil sample including potential interferents will be presented.

DETERMINATION OF RADIONUCLIDES IN SOILS AND WATERS BY ICP-MS USING FLOW-INJECTION CONCENTRATION AND ULTRASONIC NEBULIZATION.

Mark Hollenbach, James Grohs, and Stephen Mamich, RUST Geotech, Inc.*, U.S. Department of Energy Grand Junction Projects Office, Grand Junction, CO; Eric Denoyer, The Perkin-Elmer Corporation, Norwalk, CT 06859.

The U.S. Department of Energy has a recognized need for improved methods to analyze alpha- and beta-emitting radionuclides. Inductively coupled plasma-mass spectrometry (ICP-MS) has successfully measured radionuclides with relatively long half-lives on the order of 1 million years or longer. However, ICP-MS using conventional sample-introduction techniques lacks the sensitivity or the selectivity to measure shorter-lived radionuclides at levels important for environmental monitoring.

A flow-injection analysis (FIA) system was used to separate and concentrate certain radionuclides by solid-phase extraction. The FIA eluent was pumped directly into the nebulizer of the ICP-MS. A cross-flow nebulizer is suitable to meet the desired detection limits for most applications, but an ultrasonic nebulizer is used when higher sensitivity is required. Using FIA resulted in greater sensitivity and in freedom from interferences compared with direct aspiration. Methods were investigated for determining technetium-99, thorium-230, uranium-234, plutonium-239, and plutonium-240 in soil and water samples.

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*Work performed under DOE Contract No. DE-AC05-86ID12584 for the U.S. Department of Energy.

DIRECT AND SIMULTANEOUS DETERMINATION AND QUANTIFICATION OF RADIUM-226 AND RADIUM-228 BY LIQUID SCINTILLATION COUNTING.

Alvin Eugene Blackwell, AEB Consultants, Inc., 2703 W. 28th Street, Pine Bluff, AR 71603.

Current methods for the determination and quantification of radium-226 and 228 in water employ co-precipitation of radium on $BaSO_4$ and $PbSO_4$. Radium-226 is quantified by co-precipitation on $BASO_4$, followed by two emanations including a minimum of 40 hours ingrowth and finally, counting of radium-226's progeny radon-222, in a gas scintillation chamber. Radium-228 also is quantified by co-precipitation of radium on $BaSO_4$ and $PbSO_4$. The radium is then purified by re-precipitation from EDTA solution. After a 36 hour ingrowth period of actinium-228 from radium- 228 the actinium is carried on yttrium oxalate and purified and beta counted. Radium-228 is then quantified by the activity of its progeny actinium-228. This process typically requires, at a minimum, one week's time for each radium isotope to complete. Thus, a simple method for the direct determination and quantification of radium-226 and 228 via liquid scintillation counting with alpha beta discrimination without reliance upon the ingrowth of radon-222 and actinium-228 for indirect quantification is presented.

TRU-SPEC and RE-SPEC CHROMATOGRAPHY -- BASIC STUDIES AND APPLICATIONS*. Edmund A. Huff and Doris R. Huff, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

Commercially available partition chromatographic packings have been recently introduced and are finding extensive application in the nuclear fuel cycle and environmental areas. TEVA-Spec and TRU-Spec columns (Eichrome Industries, Inc.) have been used to isolate actinide constituents in soil samples prior to radiochemical determinations. The behavior of nonactinide elements is less well documented.

This presentation will provide distribution coefficients (K_ds) for some 30 common elements on TRU-Spec and RE-Spec columns. Elution experiments and inductively coupled plasma-atomic emission spectrometry (ICP-AES) were used to generate a K_d database as a function of hydrochloric acid and nitric acid concentrations. This information can be used to devise required separation procedures for a wide range of sample matrices prior to analytical measurements.

We will discuss representative separation schemes in the nuclear fuel cycle area that provide quantitative analyte recoveries and minimize spectral interferences in ICP-AES analyses. In addition, possible chromatographic procedures of interest in the environmental field will be briefly addressed.

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

ON-LINE MERCURY IN WATER MONITOR. D. D. Smith, Development Division, Y-12 Plant, Post Office Box 2009, Oak Ridge, TN 37831-8084.

A microprocessor-driven, on-line, low-level, mercury-in-water monitor has been initially tested in a laboratory testbed for three months prior to siting at the Y-12 Plant. The analyzer will sample and analyze process and/or drainage (sump) water containing a broad spectrum of contaminants. The low maintenance monitor uses the anodic stripping voltammetry method with a glassy carbon working electrode for the analysis of water containing mercury in the 2ppb to 2ppm range directly. One requirement was to limit spent analysis solution volumes and provide for its recycle. Sample volumes are small, < 10 ml with equal amounts of electrolyte. Without digestion, water samples must be filtered to remove clay or other small particles from interfering with the test. A single analysis requires several minutes for completion. In routine operation, a mercuric chloride standard is used to calibrate the cell output. Data as concentration is registered as a number of counts generated over a defined potential stripping range and compared with those from the standard. Actual sump water samples have been analyzed with this instrument and compared with EPA protocol atomic absorption analysis. Data agreement from the two techniques was reasonable, 140ppb Hg for the electrometric vs. 150ppb for the AA technique. Some modifications are needed to extend the analysis range of the instrument and improve the calibration techniques.

ELEMENTS OF BENCHTOP QUALITY CONTROL.

C. R. Horton, J. M. Meszaros, and T. N. Ternes, Analytical Services Organization, Y-12 Plant*, Martin Marietta Energy Systems, Inc., Oak Ridge, TN 37831-8189.

The DOE concept of quality assurance has grown from the rigor of NQA-1 to the Total Quality Management style of DOE Order 5700.6C. This most recent directive relaxes none of the rigor of NQA-1 but does provide analytical laboratories with an opportunity to formulate a quality assurance program better suited to the particular needs of the laboratory setting. Depending on the particular laboratory and the prevalent type of work, influences on the quality assurance program may range from local and corporate management to federal regulatory agencies.

This presentation will offer guidance on benchtop quality control, a small but vital part of any laboratory's quality assurance program. A survey of requirements and best management practices (elements in a comprehensive benchtop quality control program and training required to implement such a program) will be presented. The quality control that will be discussed is that which is performed by the technician in the preparation and analysis of samples. The discussion will include calibration verification, laboratory controls, sample duplicates and spikes, and method and calibration blanks. The preparation, usage, and acceptance criteria determination for quality controls will be discussed. Special emphasis will be given to the use of control charts.

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*Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

NEW TECHNIQUES FOR IMPROVING ICP-OES SAMPLE THROUGHPUT.

K. J. Fredeen, C. Anderau, D. A. Yates, K. M. Barnes, T. J. Gluodenis, Jr., and Z. A. Grosser, The Perkin-Elmer Corporation, 50 Danbury Road, Wilton, CT 06897-0219.

This study explores improvements in inductively coupled plasma optical emission spectrometry (ICP-OES) sample throughput that can be realized through the use of recent advances in ICP-OES instrumentation and data collection/processing techniques. ICP-OES is used extensively in environmental trace metal determinations and even small improvements in throughput may impact cost per analysis. Factors that affect overall data collection speed and figures of merit such as detection limits, precision, accuracy, and dynamic range were studied for an ICP-OES system that incorporates an echelle polychromator with a segmented-array charge-coupled detector (SCD). These factors included sampling time, interference correction methods, and sample introduction parameters. By understanding the effects of these factors, it was possible to maximize the sample throughput for several applications, such as RCRA Method 6010A, while meeting the required data quality objectives.

HOW WE DEVELOPED A DATA VALIDATION PROGRAM.

Janice Engels, Analytical Environmental Support Group, Martin Marietta Energy Systems, Inc., P.O. Box 2003, Oak Ridge, TN 37831-7606.

We developed a validation program to enhance our capabilities to provide validation oversight, to provide validation services for "emergency" and small projects, to advise project managers requiring data validation, and to facilitate monitoring of development of electronic data validation systems. Most of the effort was directed to non-CLP methods. The validation program allows contribution at the project planning stage in the form of deliverables lists and reporting forms. Checklists have been developed to accommodate nonstandard methods, especially radiochemical methods. Checklist development is not simply a clerical exercise; checklists reflect project and regulatory requirements, and modifications to them may be necessary to address specific data quality objectives. The EPA Functional Guidelines were a starting point for the design of the checklists, and the topics and format from them were followed to the extent possible to assure consideration of all factors. An organizational structure of review, peer review, oversight review, and review coordination was established to assure the validation activities themselves were technically correct, reasonable, and complete. Tracking, reporting, and other administrative systems needed to be established and in place.

RADIOACTIVE SAMPLE ANALYSIS BY ICP/MS. E. J. Wyse, M. R. Smith, O. T. Farmer III, D. W. Koppenaal, and J. P. Bramson, Pacific Northwest Laboratory*, P.O. Box 999, Richland, WA 99352.

Inductively coupled plasma mass spectrometry (ICP/MS) is becoming an increasingly accepted method of measuring many long-lived radionuclides. Its use in this capacity, however, has been limited to "environmental" (i.e., nonradioactive) samples, because commercial instruments are generally not configured to accommodate radioactive material. Pacific Northwest Laboratory has successfully modified an ICP/MS so it can effectively process radioactive samples. The shielded instrument has been used to measure both radionuclides and stable elements in many sample types, including contaminated waters and soils, nuclear fuel, and radiolabeled samples. Although the technique provides versatile capabilities previously unrealized for the comprehensive analysis of radioactive material, processing complex radioactive waste samples by ICP/MS has introduced a new dimension in molecular ion and isobaric interferences. The typical sample examined is one produced from a variety of nuclear and chemical processes; the resulting mass spectrum represents a veritable potpourri of fission products, molecular ions, and stable elements with isotopic abundances varying significantly from those found in nature.

Instrument modifications and performance will be presented. Application discussion will highlight capabilities, unique interferences, methods currently under investigation that are intended to minimize or eliminate problematic interferences (e.g., on-line separation and preconcentration via ion chromatography), and general limitations of the ICP/MS technique.

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LASERS AND ION TRAPS.

M. E. Cisper, G. C. Eiden, N. S. Nogar, and P. H. Hemberger, Los Alamos National Laboratory, Los Alamos, NM 87545; J. D. Williams and R. G. Cooks, Purdue University, W. Lafayette, IN 47907; and J. E. P. Syka, Finnigan MAT, San Jose, CA 95134.

We will present recent results from two projects based on laser ion trap mass spectrometry. The first is what we term "ion tomography" where a pulsed laser, which causes photodissociation of a target ion, is used to map ion trajectories in the ion trap. These studies provide spatial and kinetic energy maps of ions in the radial and axial dimensions of the ion trap. The effects of buffer gas mass and structure, resonant excitation, and higher order fields on ion trajectories can be conveniently studied with this technique. One goal of these experiments is to understand the cause(s) of ion structure dependent mass shifts in the ion trap.

We are also developing laser sampling ion trap mass spectrometry as a tool for the rapid screening of environmental samples. This methodology has several potential advantages over conventional analytical techniques. Little or no sample preparation is required for complex samples. This reduces the time, money, and additional chemical wastes associated with sample preparation. The technique is fast and can provide characterization of both organic and inorganic contaminants. We are exploring ways to both improve the process of laser sampling and ion capture in the ion trap, and methods for simple, rapid sampling of contaminants for laser desorption. Selective sorbents and microfiber sampling are two such methods.

MICROSCALE LIQUID PHASE SENSORS: CHROMATOGRAPHY ON A CHIP.*

R. Hergenröder, S. C. Jacobson, L. B. Koutny, and J. M. Ramsey, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6142.

Our approach to liquid phase chemical sensing is to create miniaturized analysis systems that function identically to benchtop chromatographic systems. We are using traditional micromachining techniques to etch channels into glass substrates. The open channels are covered by bonding a second glass substrate onto the etched one.

Capillary electrophoresis is being performed in channels that form either a crucifix or serpentine pattern. Channels are typically 10 microns deep and 90 microns wide, and up to 16 cm long for the serpentine pattern. Device performance has been evaluated by injecting fluorescent dye mixtures and monitoring the separation with laser induced fluorescence.

Separations have been performed at field strengths ranging from 100 to 1500 volts/cm. Injections are made by electroosmotically pumping sample through an injection channel that crosses a separation channel followed by a switching of the potentials to force a plug into the separation channel. Separations of two components have been achieved in less than 300 milliseconds, and up to 18,500 plates per second have been generated in separate experimental runs.

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DIODE LASER SPECTROSCOPY FOR PRACTICAL ISOTOPE RATIO MEASUREMENTS*.

R. W. Shaw, J. P. Young, C. M. Barshick, and J. M. Ramsey, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6142.

Tunable semiconductor diode lasers are practical spectroscopic sources that can be used to perform isotopically-selective excitation of gaseous atoms[1]. Detection of this excitation should serve as the basis for measurement of isotope ratios using relatively simple and inexpensive instrumentation. We are exploring the feasibility of such a method for measurement of the U-235/U-238 ratio for a variety of sample types. Samples were fabricated into hollow cylinders by mixing them with silver powder and compressing the mixture in a press. Analyte atoms were sputtered into the gas phase by means of a hollow cathode glow discharge. Light from a single mode titanium:sapphire laser at 778.4 nm, for example, was passed through the cathode to excite uranium atoms from the metastable level at 620 cm^{-1} to the state at 13463 cm^{-1}. Due to its broad tunability in the same range as off-the-shelf diode lasers, the Ti:Sapphire laser is a useful surrogate when acquiring survey spectra for selection of optimum analytical wavelengths for diode laser experiments. Absorption was detected by the optogalvanic effect, wherein the discharge equilibrium is disturbed by optical excitation, resulting in an altered cathode voltage. The U-235-U-238 isotope shift of this uranium transition is 0.1 cm^{-1}, substantially greater than the Doppler-broadened linewidth of 0.025 cm^{-1} we have observed. Optogalvanic spectra relevant to this isotope ratio determination will be presented and our measurement accuracy and precision discussed.

(1) R.W. Shaw, J.P. Young, D.H. Smith, A.S. Bonanno, and J.M. Dale, *Phys. Rev. A*, **41**, 2566 (1990).

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*Research sponsored by U.S. Department of Energy, Office of Arms Control and Non-Proliferation. Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

DETERMINATION OF OIL AND GREASE IN WASTEWATER BY SOLID-PHASE EXTRACTION.

Dave M. Ferguson, John C. Green, and Martha J. M. Wells, Center for the Management, Utilization and Protection of Water Resources and Department of Chemistry, Tennessee Technological University, Box 5033, Cookeville, TN 38505.

Industrial and municipal wastewater dischargers rely upon periodic determination of oil and grease content to monitor compliance with National Pollutant Discharge Elimination System (NPDES) permits and to provide feedback for proper wastewater treatment. Standard protocol for the determination of oil and grease in wastewater currently utilizes liquid-liquid extraction (LLE) with trichlorotrifluoreoethane followed by gravimetric or infrared determination. However, such chlorofluorocarbons (CFCs) or Freons™ have been implicated as agents in stratospheric ozone depletion. Environmental concern over the use of this chemical class has prompted investigation into alternative procedures for testing oil and grease content of wastewater.

Solid-phase extraction (SPE) protocol for the determination of oil and grease content in wastewater is an attractive alternative to liquid-liquid extraction with Freon™. Research with EnvirElut™ solid-phase extraction columns found the protocol developed to be efficient for the determination of oil and grease content. This presentation reports the results obtained upon comparison of the recovery observed for oil and grease analyses of industrial wastewater by solid-phase extraction to conventional liquid/liquid extraction procedures.

Freon™ is a trademark of DuPont Corporation.
EnvirElut™ is a trademark of Varian Sample Preparation Products, Inc.

IMPROVED METHOD FOR THE DETERMINATION OF ACTINIDE ELEMENTS IN SOILS*. Lesa L. Smith and Judith S. Yaeger, Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439.

Over the past decade, the Department of Energy's (DOE) environmental restoration and waste management mission has increased in importance and, subsequently, in cost. DOE has budgeted billions of dollars for this effort and has estimated that over a million analytical measurements would be required annually. It is only through the development and implementation of new technologies that the anticipated high costs of these remediation programs can be contained.

The introduction of extraction chromatography methods to environmental radiochemistry has produced promising results. Preliminary studies of TruSpec and TevaSpec resins (Eichrome Industries, Inc., Darien, IL) demonstrated the feasibility of the use of these materials in the determination of the actinide elements.

Both the acid concentrations and volumes utilized in these systems are significantly lower than those required for the traditional methods as described in HASL-300. Whereas this feature is ideal from a waste minimization viewpoint, the combination of dilute nitric acid and limited solution volumes creates a challenge to maintain many soil samples in solution. Laboratory experience at ANL has also indicated potential matrix effects in soil analyses on these columns. Additionally, experience has shown that the sample dissolution technique influences the behavior of the sample on the columns.

Therefore, a preconcentration step of the actinide and lanthanide elements utilizing Diphonix resin (Eichrome Ind., Inc.) is being investigated to address the previously mentioned problems. Preliminary studies indicate that this material exhibits excellent selectivity for the actinides and lanthanides out of hydrochloric acid media. Larger solution volumes may also be employed. To ensure widespread applicability of this preconcentration method, a wide variety of soils are being processed by several dissolution techniques, namely a hot plate, mixed acid leach procedure, a microwave digestion procedure, and a total dissolution fusion technique.

Subsequently, a separation scheme for the actinide elements utilizing extraction chromatography resins which satisfies the requirements of both radiometric and nonradiometric detection methods is being developed.

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DOE METHODS FOR EVALUATING ENVIRONMENTAL AND WASTE MANAGEMENT SAMPLES: NEW METHODS. S. C. Goheen, S. K. Fadeff, D. S. Sklarew, G. M. Mong, B. L. Thomas, M. McCulloch, G. K. Ruebsamen, W. C. Cosby, and R. G. Riley, Pacific Northwest Laboratory*, Richland, WA 99352; W. P. Brug, Los Alamos National Laboratory, Los Alamos, NM 87545; J. A. Poppiti, U. S. Department of Energy, Germantown, MD 20874.

DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods) is a guidance/methods document for sampling and analysis activities in support of DOE sites. It is intended to fill the gap between existing guidance documents (e.g., SW846), which apply to low-level or nonradioactive samples, and the complexities of DOE site matrices. The first issue, completed in October 1992, contained QC, safety, sampling, organic analysis, inorganic analysis, and radioanalytical guidance as well as four methods. Revision 1, completed in March 1993, had an expanded guidance section and three additional validated methods. Revision 2 is a significantly expanded document with greater applicability. It includes approximately 20 new methods as well as guidance on quality assurance. The quality assurance chapter is written to be in compliance with DOE order 5700.6C. The new methods include sampling and field as well as laboratory analysis methods to determine organic, inorganic and radionuclide constituents. Many of the new methods are labeled "draft" methods. The peer review process has not yet been completed for the draft methods. Further, the draft methods may or may not have QC data associated with them to meet the requirements of method validation. Draft methods were added to speed the release of methods to field personnel. After appropriate QC data are obtained and the peer review process is completed, the draft methods will become validated.

DOE Methods is available at no cost to the user and is supported by the Laboratory Management Division of DOE. As a living document, *DOE Methods* provides a vehicle for technology transfer within the EM community. As *DOE Methods* evolves, its usefulness and applicability is anticipated to grow to meet the demands of the DOE EM mission.

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*This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy.

METHODS FOR SAMPLING WASTES AND ENVIRONMENTAL MEDIA AT DOE SITES. R. G. Riley, S. K. Fadeff, G. M. Mong, D. Sklarew, M. McCulloch, B. L. Thomas, and S. C. Goheen, Pacific Northwest Laboratory*, Richland, WA 99352.

Procedures for sampling waste and environmental media are being acquired from DOE and DOE contractor laboratories, reconfigured and reformatted, and incorporated as methods into *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods).* Initial emphasis is being placed on methods that address sampling in radioactive environments (e.g., waste disposal sites, surface and subsurface soils and groundwaters, treated waste, tanks and repository wastes) to complement other published documents that contain guidance for sampling waste and environmental media. A sampling method is planned for inclusion in Revision 2 of *DOE Methods*, scheduled for release in October 1993.

Over the years, much has been done to refine analytical methodology and improve analytical data quality. In contrast, less emphasis has been placed on addressing the impact of the sampling process on overall data quality. To address this issue, a sampling method submission format has been developed. The format is similar to that used for analytical methods. The purpose of the format is to provide guidelines to authors submitting methods for inclusion in *DOE Methods*. Authors are encouraged to (1) consider those factors that influence the methods performance and impact of the specific sampling process on analytical data quality; (2) make additional/modifications to the sampling method format to improve its general applicability. Examples will be given in which sampling procedures have been rewritten into this format for release in *DOE Methods*.

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*Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

THE DETERMINATION OF ^{230}Th IN SOILS BY LASER ABLATION ICP-MASS SPECTROMETRY.

Richard Ediger, The Perkin-Elmer Corporation, Norwalk, CT; A. P. D'Silva, Ames Laboratory, Ames, IA 50010.

The U.S. Department of Energy desires to evaluate methods for the rapid on-site determination of ^{230}Th in soils for potential use in the characterization of remediation activities at uranium mine tailing sites. The Perkin-Elmer Corporation and Ames Laboratory are collaborating in evaluating laser ablation ICP-MS in a mobile laboratory for this application. The goals are the demonstration of an analysis at a remediation site that will provide a 15-minute total analysis time with a ^{230}Th detectability of 1 ng/g and an accuracy consistent with the precision of sampling.

Using a series of seven reference soils having known ^{230}Th concentrations prepared as pressed pellets, it has been shown in a feasibility study at Perkin-Elmer that the ^{230}Th detection limits are 0.04 ng/g using 30-second data acquisition. Preliminary quantitative results indicate an accuracy of about 0.02 ng/g at concentrations less than 0.1 ng/g and 15 to 20% at concentrations near 1 ng/g. The precision of replicate measurements without internal standardization at different locations on the same pressed pellet is 10 to 15% at concentrations near 1 ng/g. The analysis time for five replicate measurements of each prepared sample is less than four minutes. The total analysis time for a finely-ground soil sample, including binder addition, soil-binder mixing, pelletizing, and five replicate analyses is less than 15 minutes.

The feasibility data described above do not address critical issues such as representative sampling of the soil, whether grinding to a small particle size is necessary, whether the binder addition is required, the optimum laser wavelength and energy, and long-term performance characteristics. These items and others will be evaluated by the Ames Laboratory in the coming months and progress will be reported in the presentation.

NEUTRON ACTIVATION ANALYSIS FOR LARGE-SCALE ENVIRONMENTAL STUDIES. D. C. Glasgow, F. F. Dyer, and L. Robinson, Analytical Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831-6128.

The current emphasis on understanding the role and degree of anthropogenic contamination of the environment has produced a great need for analytical methods that are sensitive, accurate, and low in cost. For measuring the chemical elements, neutron activation analysis (NAA) has many of the attributes of the desired method. During the past two years, the ORNL NAA laboratory analyzed a large number of samples in three major environmental projects. In one, mercury, uranium, and other toxic elements were measured in 5000 soil samples from the flood plains of the East Fork Poplar Creek (EFPC) in Oak Ridge. In another project mercury was collected on activated charcoal from the atmosphere in and around EFPC. The samples were then analyzed for Hg by NAA. In the Background Soil Characterization Project, about 40 trace elements were measured in over 200 field and QA samples from areas thought to be free of contamination by humans. Formal procedures that described the methods of measurement and quality assurance were written for the two soil analysis projects. Considerable effort was made to ensure that the analyses were made with suitable accuracy, sensitivity, and economy. Details of these analyses and means to extend their usefulness and economy will be discussed.

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*Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

AUTOMATION OF A GAMMA RAY SPECTROSCOPY SYSTEM USING LABORATORY ROBOTICS.

D. H. Brown, L. Robinson, and F. F. Dyer, Neutron Activation Analysis Facility, Analytical Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831-6128.

The use of a laboratory robot, pneumatic transport tube, and a gamma ray spectroscopy system to automate gamma ray counting is described. A Zymark laboratory robot is used to transport samples pneumatically to high purity germanium (HPGe) detectors. A PC-based multichannel analyzer (MCA) system is then used to accumulate and store spectra. After data accumulation and storage, the robot then transports the sample to a storage area and repeats the process for a predetermined number of samples. Upon successful completion of this project, the overall cost effectiveness, efficiency and safety of performing neutron activation analysis (NAA) will be enhanced.

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*Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

MAXIMIZING THE COLD NEUTRON FLUX FROM A CALIFORNIUM-252 SOURCE.

L. Robinson, Neutron Activation Analysis Facility, Analytical Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831-6128; E. Johnson and L. D. Robles, Transuranium Research Laboratory, Chemistry Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831.

The primary goal of this work is to find the materials and geometrical arrangement which will produce a maximum flux of cold neutrons from a californium-252 source. Some of the materials being studied are water, deuterated water, and deuterium. The optimum conditions are being sought by calculations using the Boltzmann equation. This equation is being solved using Monte Carlo integration. Solving the Boltzmann equation by this Monte Carlo integration procedure has not been done before. Monte Carlo trajectories is the usual Monte Carlo procedure used. The accuracy of the calculations is being checked by comparison with some experimental results. The experimental results available are relatively limited.

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A COMPARISON OF EXTRACTION OF SOILS USING THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND TOTAL METAL DIGESTION *

Dean A. Bass, Analytical Chemistry Laboratory, Chemical Technology Division, and John D. Taylor, Energy Systems Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

The Resource Conservation and Recovery Act (RCRA) was established in 1976 to protect human health and the environment. This regulation provides definitions for hazardous waste. Hazardous waste is waste that is ignitable, corrosive, reactive, or exhibits toxic characteristics. Toxic characteristics are determined using the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP is used to simulate, in a laboratory, conditions which could be present in a sanitary landfill to determine if any inorganic elements, pesticides or herbicides could be leached from the waste in a sanitary landfill. A provision in this procedure also allows determining the total amount of contaminant. If the total concentration of the contaminant is so low that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

This study looks specifically at determining the concentrations of inorganic elements (As, Ba, Cd, Cr, Pb, Hg, Ag and Se) in extracted soil. A comparison is made of the concentrations of metals extracted from soils using TCLP and total metals extraction. The TCLP is more time consuming and costly than measuring the total concentration of metals present. In some cases, it may be known that contaminants are low in the waste or that the waste would be so completely extracted by the TCLP, that a total measured concentration would be representative of what is extracted. The results provide insight into how the environmental hazard in soils can be assessed in a cost-effective system.

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

CHARACTERIZATION OF HEPA FILTERS FOR DISPOSAL*.

Alice M. Essling, Irene M. Fox, Florence P. Smith, Donald G. Graczyk, Analytical Chemistry Laboratory, Chemical Technology Division, and Christopher W. Grandy, Environmental and Waste Management Programs, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

Because of their bulky construction and potential for radioactive as well as hazardous chemical contamination, used HEPA filters present a challenge to both waste-management operations and the analytical chemistry laboratory in efforts to minimize waste volumes and characterize the waste for proper disposal. In this presentation, we will describe our experience in analyzing filter media from used HEPA filters to satisfy waste acceptance criteria established for shipment of waste to the Westinghouse Hanford facility. We will address difficulties encountered in preparing composited filter samples for representative subsampling as well as adaptation of established analysis methods to accommodate the low density and high liquid absorbency of the filter-medium matrix. Results obtained with actual contaminated filters will be shown with an evaluation of the data.

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

RADIOSTRONTIUM ANALYSIS USING COMBINED CATION EXCHANGE-EXTRACTION MEDIA METHODS.

Ross W. Williams, CompuChem Laboratories, Inc., P.O. Box 12652, 3308 Chapel Hill/Nelson Highway, Research Triangle Park, NC 27709.

I have developed a simple, two-step method for purification of strontium that both increases sample throughput and improves the quality of radiostrontium analyses. The method uses well-known cation exchange techniques for initial separation and pre-concentration, followed by a purification step using Sr•Spec™ extraction media. Strontium recoveries are determined by ICP emission spectrophotometry, and ^{90}Sr and ^{89}Sr are quantified by liquid scintillation counting.

Following appropriate sample-specific digestion steps, samples for radiostrontium analysis are spiked with one milligram of stable strontium and dissolved in 1 M HCl. The sample is passed through a cation exchange column (BioRad AG50W-X8, 100-200 mesh, hydrogen form) in 1 M HCl, and the Sr fraction is collected in 2.5 M HCl. This column removes 99 + % of the Cs, Ba, Co and REE, about 60% of the Ca, and about 80% of the Fe and Y. After conversion to nitrates, the final purification of Sr is achieved with a Sr•Spec™ column run in 3 M HNO_3, which eliminates the remainder of the Ca, Fe and Y.

The advantages of this method include: (1) the techniques are easily learned; (2) no extremely hazardous or chelator-laced reagents are used, which minimizes waste handling and management concerns; (3) there are no time-consuming, repeated precipitation steps; and (4) chemical recoveries are high (average is about 85%) and are measured more accurately than by gravimetric techniques. Compared with proportional counting for radiostrontium analysis, liquid scintillation counting has higher background levels, but this disadvantage is offset by higher counting efficiencies and more stable and reproducible counting sources, so that minimum detection limits of the two counting methods are comparable.

MANAGING A SUBCONTRACT LABORATORY PROGRAM.

Joe Pardue, K-25 Site, Oak Ridge, TN 37831-7169.

(NO ASBTRACT RECEIVED.)

LASER MASS SPECTROMETRY FOR OLIGONUCLEOTIDE ANALYSIS*. K. Tang, S. L. Allman, and C. H. Chen, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6378.

Matrix-assisted laser mass spectrometry has been successfully used to detect single-stranded and double-stranded oligonucleotides. Parent ions of homopolymer single-stranded DNA of $pd(A)_{60}$, $d(T)_{130}$, $d(G)_{40}$, and $d(C)_{40}$ were successfully detected without any significant breakup. A random sequence of mixed-base single-stranded DNA of 150 mer was also successfully measured. Polymer ions of poly-A with sizes as large as 420 mer were also observed. The detection sensitivity for oligonucleotides has reached 80 femtomole. Double-stranded DNA segments with sizes up to 128 base pairs, which were produced by polymerase chain reactions (PCR), were also detected by laser mass spectrometry. We also demonstrated that laser mass spectrometry can be used to analyze DNA segments in a PCR buffer solution and Sanger's solution for DNA sequencing. Thus, the application for laser mass spectrometry for fast analysis of PCR products and fast sequencing looks promising in the near future. Kinetics of desorption and ionization mechanisms were also pursued. The effects of various isomers, laser wavelengths, and laser fluences on matrix-assisted laser mass spectrometry have been studied. Details will be presented in the meeting.

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*Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

NONDESTRUCTIVE MEASUREMENT OF COMBUSTIBLE WASTE CONTAINING URANIUM IN A B-25 BOX*. R. L. Mayer II, J. F. Harris, and R. C. Hagenauer, K-25 Site,** Oak Ridge, TN 37831-7319.

The Oak Ridge K-25 Site is a shutdown uranium enrichment facility which processes and stores a large variety of radioactive wastes. Measurements to identify and quantify radioisotopes present in this waste are performed using nondestructive assay techniques. A measurement substation, consisting of four sodium iodide γ-ray detectors, is used for measurement of low- to medium-density waste contained in B-25* boxes. Regions of interests are defined and used for quantification of ^{235}U and ^{238}U as well as the identification of ^{137}Cs and ^{237}Np. A software program (GAMMAEFF) was developed to estimate the overall detection efficiency, including effects from B-25 box walls, waste matrix, item size, and detector positioning. Items which exceed a preset threshold are also measured using a high-resolution γ-ray detection system to determine enrichment and to estimate the relative amounts of nonuranium radionuclides. Results indicate that the target measurement sensitivity of 32 ρCi/g of waste is achievable in most 900-sec measurements for most items.

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*The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-84OR21400.

**Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

*This is a common term used at the Department of Energy sites managed by Martin Marietta Energy Systems, Inc., to describe a 4x4x6 ft. "strong, tight" container. It is, in fact, a container designation of the Container Products Corporation. Its use in this document does not mean or imply that only the containers of Container Products are acceptable or the only ones in use. Various manufacturers have and will continue to supply "strong, tight" containers to the Department of Energy sites.

HIGH SPEED SEPARATIONS TO MEASURE IMPURITIES IN PU-238 OXIDE AND TRACE RADIONUCLIDES IN HIGH ACTIVITY WASTE AT SRS.

Sherrod L. Maxwell III, Matthew R. Nelson, and Robert N. Mahannah, Westinghouse Savannah River Company, Aiken, SC 29808.

High speed ion exchange and extraction chromatography techniques have been developed at SRS to solve a wide range of lab separation problems. The measurement of metallic impurities in Pu-238 oxide and trace radionuclides in high activity liquid waste are several recent examples. The determination of metallic impurities in plutonium-238 oxide, traditionally measured by less precise d.c. arc emission spectrometry, is a key product specification measurement. A high speed ion exchange technique to rapidly and effectively remove the Pu-238 was developed that enables the use of plasma emission spectrometry. Plutonium levels are lowered by a factor of 100,000 to enable safe handling of the samples. Trace radionuclide measurements in high activity liquid waste are important measurements for waste processing. High speed column techniques to separate strontium-90 and neptunium-237 from high activity alkaline waste solutions have been developed using Sr-Spec™ and TEVA-Spec™ resins, respectively. In the Sr-Spec™ method, strontium-90 is rapidly and successfully separated from barium-140 and other interfering isotopes prior to liquid scintillation counting. In the TEVA-Spec™ method, plutonium, uranium and thorium isotopes are removed successfully prior to Np-237 measurement by alpha spectrometry. Very small particle resin is used to enable column flow-rates of 2 to 10 milliliters per minute and to enhance separation capabilities. The rapid flow rates also reduce sample analysis times, enabling higher sample throughput and significant cost savings.

HIGH SPEED COLUMN REMOVAL OF RADIOACTIVE CESIUM AND STRONTIUM TO LOWER EXPOSURE DURING ANALYSIS OF HIGH ACTIVITY WASTE AT SRS.

Matthew R. Nelson and Sherwood L. Maxwell III, Westinghouse Savannah River Company, Aiken, SC 29808.

The Central Laboratory at SRS has developed a high speed column extraction technique to lower sample radiation levels prior to analysis of high activity liquid waste samples, dissolved glass and sludge. This simple, rapid technique can be applied in shielded analytical cells to remove cesium-134, cesium-137 and strontium-90 prior to analysis of samples for metals by plasma emission spectrometry. The technique employs a mixture of fine particle size resins, ammonium molybdophosphate (AMP, 5 μm) and a crown ether extractant (Sr-Spec™ resin, 20-50 μm) to remove cesium and strontium. A mixture of nitric acid and ammonium nitrate is used to separate metal ions from the cesium and strontium. The method uses applied vacuum to enable rapid flow rates, requires minimal space in the shielded cells and significantly lowers cesium and strontium levels prior to analysis.

INTEGRATION OF MOBILE LABORATORIES INTO AN ANALYTICAL SERVICE STRATEGY FOR ENVIRONMENTAL RESTORATION. George Brooks and Chris Leibman, Environmental Chemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545.

Mobile laboratories for radiochemical and chemical analysis have been developed and deployed at LANL to support the Environmental Restoration Program. Shortcomings in our initial mobile laboratory design and unanticipated operational details were evident after on-site support was initiated. While subsequent refinements in the mobile laboratory design and operations have improved data throughput, mobile laboratories still present a challenging work environment. Mobile laboratory operations may best be limited to those site operations that can use analytical data immediately to support on-site decision making. Dedicating mobile laboratory instrumentation and personnel to sites not needing real-time data should be avoided since limited analytical resources are squandered if sample collection activities are interrupted. Fixed base laboratories are less impacted if site operations stop since other work can be undertaken. Mobile analytical support should be viewed as part of a complete analytical services plan that includes quick turnaround and more rigorous methods provided from a fixed base laboratory. Field experiences since the implementation of mobile laboratory support at LANL and integration with fixed base laboratory operations will be discussed. Aspects of our current mobile laboratory design related to operational requirements we have identified will be presented.

APPLICATIONS OF EXTRACTION CHROMATOGRAPHY IN RADIOCHEMICAL ANALYSES.

Charles D. Good, Portsmouth Gaseous Diffusion Plant, Piketon, OH 45661.

The use of extraction chromatographic materials in radiochemical analyses results in shorter analysis times and minimized waste generation. TRU-Spec™ columns, purchased from ElChrom, Inc., are selective for actinides and allow extraction of the actinides while most non-actinides are not retained by the columns. After extraction, the actinides thorium through americium are sequentially eluted from the column, precipitated as their respective fluorides, and counted by alpha spectroscopy. The ability to analyze for each of the actinides from the same sample aliquot allows realization of shorter analysis times and decreased waste generation. The various matrices analyzed include urine, water, soil, vegetation, air filters and smears, alumina, hydrolyzed uranium hexafluoride, and chromium sludge samples. The sample preparation for each type of sample matrix is discussed, as well as the adjustment of the oxidation states of plutonium, neptunium, and uranium before extraction onto the column. Finally, a brief description of the chemistry necessary to sequentially elute the actinides is presented, and the results for control samples are presented.

TERRATROG SOIL/WATER GAS SAMPLING SYSTEM*. R. H. Ilgner, R. R. Smith, J. H. Moneyhun, and R. A. Jenkins, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120.

TerraTrog is a novel soil/water gas sampling system, designed for implantation into a given matrix under study with minimal disturbance to the matrix during sampling episodes. The device is designed for deployment with the Army Site Characterization and Analysis Penetrometer System (SCAPS). Efforts are under way to re-engineer the existing design to facilitate deployment. TerraTrog is designed for interfacing with a sensitive real-time monitoring instrument such as an ion trap. Current studies focus on the evaluation of the suitability of selected membrane materials for use with TerraTrog. Membrane evaluation experiments are being performed to test membrane permeability with several volatile organic compounds (VOC's): trichloroethylene (TCE), carbon tetrachloride, benzene, toluene, perchloroethylene (PCE), chloroform and meta-xylene. Membranes evaluated thus far have an intrinsic capacity for retaining VOC's resulting in a delay in detected response on the low concentration side of the given membrane. This membrane property is related to the membrane diffusion coefficient (D), which was determined empirically from real-time experimental data to be approximately: $D = 3.0\text{x}10^{-9}\ \mathrm{cm^2/s}$. This quantity is about three orders of magnitude lower than previously expected. Membrane requirements for TerraTrog are: a low permeability coefficient (P_m), approximately $P_m = 1.0\text{x}10^{-9}\ \mathrm{mL/min.\text{-}cm^2\text{-}torr/cm}$ to ensure accurate quantitative results independent of matrix analyte permeability; and a high membrane diffusion coefficient, about $D = 1.0\text{x}10^{-6}\ \mathrm{cm^2/s}$ for rapid TerraTrog response to matrix VOC's concentration gradients. Current studies involve the characterization of a thin film membrane in efforts to find a material with the desired mass transport properties.

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Thursday, October 7, 1993

THURSDAY AM: WASTE AND ENVIRONMENTAL SAMPLING

CHAIRMAN: R. G. RILEY, PACIFIC NORTHWEST LABORATORY, Richland, WA 99352

8:30 OPENING REMARKS. R. G. Riley, Pacific Northwest Laboratory, Richland, WA 99352

8:40 MEASUREMENT AND SPATIAL MODELING OF VOC CONTAMINATION IN SOILS. Olivia R. West and Robert L. Siegrist, Environmental Sciences Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831.

The characterization of a VOC-contaminated soil region typically consists of two phases: (1) measurement of VOC concentrations at discrete points within a three-dimensional soil region; and (2) interpretation of the VOC distribution which may include the development of a spatial model for the soil VOC data set. The current framework, which places a lot of emphasis on high quality discrete point measurements, often results in a small number of "quality" and "formally validated" data points being used to characterize a volume of soil that is several orders of magnitude larger than the combined volumes of the soil samples. Because laboratory analytical equipment are in general more accurate than corresponding field models, proponents of the current approach place me significance on laboratory measurements without considering the larger losses that occur by increased handling and holding times for samples that are shipped to an off-site laboratory.

Using a case study, the presentation will show how the accuracy of discrete measurements can be confounded by the inherent spatial variability of the subsurface VOC distribution. This presentation will also focus on alternatives to the current paradigm of soil VOC measurements. These include the more frequent use of field analytical methods to collect spatially disperse data of "acceptable quality", better chemical preservatives, and improved soil sample collection and handling techniques. The presentation will describe how VOC measurement and spatial modeling efforts conducted at a DOE site pointed to the need for a revised approach to the characterization of soil VOC contamination.

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*Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400 with the U.S. Department of Energy.

9:05 **DEVELOPMENT OF SAMPLING TECHNIQUES FOR INEL STORED TRU SOLIDIFIED/STABILIZED WASTE FORMS.*** Michael Connolly, Al Johnson, Idaho National Engineering Laboratory, EG&G Idaho, P.O. Box 1625, Idaho Falls, ID 83415-2424; Bart Draper, Clay McCurley, Bechtel National, San Francisco, CA; and Carla Dwight, Argonne National Laboratory-West, Idaho Falls, ID 83415.

Characterization of Idaho National Engineering Laboratory (INEL) stored TRU solidified/stabilized waste forms requires the development of sampling techniques. Sampling techniques to collect representative samples from 55 gallon drum waste in an alpha confinement facility have been developed. These techniques were developed using simulated waste in a "cold" mock-up area. Simulated waste recipes were developed to simulate the physical properties and waste packaging configurations found in Rocky Flats Plant generated stored INEL TRU waste. Waste forms were developed to simulate waste water treatment sludges, organic sludges, cemented aqueous liquids, and cemented ion-exchange resins. Results of the simulated waste sampling demonstration and the application of these to the development of sampling techniques for use in ANL-W alpha confinement Waste Characterization Chamber will be discussed.

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*Work supported by the U.S. Department of Energy under the following contract DE-AC07-76IDO1570.

9:30 **ESTABLISHMENT OF MULTIPLE PHASE SAMPLING CAPABILITY FOR CHARACTERIZATION OF NUCLEAR WASTES.** Michael J. Minette, Leonard A. Bunes, and Dale N. Price, Westinghouse Hanford Company, Richland, WA 99352.

More than 227,000 m^3 (60 Mgal) of high-activity radioactive waste has been stored in 177 underground storage tanks at the U.S. Department of Energy's (DOE) Hanford Site in Eastern Washington State since 1944. These caustic wastes consist of many different chemicals, and the waste forms include liquids, slurries, salt cakes, and sludges. A number of safety issues have been raised about these wastes which have generated a need to clearly define the contents and characteristics of the waste.

In response to this need, Hanford Site sampling methodologies have undergone evaluation and enhancement, resulting in the development of a multi-phase sampling system that samples hard salt cake, sludge, and liquid wastes. Significant development effort was given to the system, especially in the areas of drill bit and sampler design, drill bit cooling parameters, dust generation, and the sampler change out approach. Much of this effort was focused toward developing the capability of penetrating and sampling hard salt cake wastes without losing sample characteristics or harming the tank structure. The system performs this task within a conservative safety envelope to ensure heat generation is minimized and retrieved sample is undisturbed and uncontaminated.

9:55 **DRILLING AND SAMPLING METHODOLOGY FOR THE COLLECTION OF HIGHLY RADIOACTIVE SOIL SAMPLES.** Wendy Thompson, Westinghouse Hanford Company, P.O. Box 1970, Richland, WA 99352.

The hazards associated with radioactive and mixed waste soil disposal sites across the Department of Energy Complex challenge traditional sample collection techniques and procedures. Collection methods are required that minimize radiological exposures to the workers and at the same time result in representative samples meeting stringent regulatory requirements and data quality objectives for characterization purposes. In some cases, existing sampling techniques require modification, or new strategies must be proposed, in order to meet performance and safety requirements.

Westinghouse Hanford Company recently completed a CERCLA characterization of ten radioactive waste disposal cribs located within the 200-BP-1 Operable Unit. Contaminated soil cuttings encountered during drilling operations and containerized in waste drums exhibited up to 1.4 R/hr gamma and 12 rad/hr beta radiation. Soil sample jars reading up to 300 mR/hr on contact were collected, packaged, and shipped to laboratories for analysis. A total of 28 boreholes were drilled and sampled through these cribs meeting the requirements of the EPA's Contract Laboratory Program's procedures. Approximately 190 chemical samples and an equal number of physical and archive samples were collected, many of which were highly radioactive and required special handling techniques for sampling and analysis. In spite of the high radiological contamination encountered, stringent data quality objectives for the project were achieved. The collective personnel exposure was less than 650 mrem.

This paper describes the drilling and sampling operations used for the 200-BP-1 crib and vadose zone characterization. To minimize the amount of investigation derived waste, and to meet the radiological requirements for controlling contamination and reducing occupational exposures, cable tool drilling methods were used. The method allowed for completion of the boreholes without the addition of drilling fluids, thereby enhancing the integrity of the samples and minimizing the amount of associated waste. The process for adapting and upgrading procedures and safety controls resulting from changing radiological conditions during the operation are discussed. Methods used for equipment decontamination, contamination control, waste handling, and sample collection, packaging and shipping are also described.

10:20 BREAK

10:35 *IN SITU* CHARACTERIZATION: THE NEXT GENERATION. Troy Farris and Leonard A. Bunes, Westinghouse Hanford Company, Richland, WA 99352.

At the Hanford Site, 177 underground storage tanks (UST) are used for storage of radioactive wastes, including liquids, sludges, and solids (hard salt cake). The tanks range in size from 55,000 gallons to over 1.1 million gallons, while the wastes are the result of decades of various defense materials production processes. A fundamental goal of the Westinghouse Hanford Company is the characterization, retrieval, and stabilization of these wastes. Presently, characterization techniques require expensive and lengthy sampling and analytical processes which we are proposing be replaced by *in situ* technology that is faster, better, and cheaper.

Our vision of *in situ* characterization is the ability to deliver analytical probes to the waste - in place - and subsequently obtain, in real-time, analytical data for a wide variety of parameters. Data validation is a key to the success of such technology in order to meet data quality objectives. Expected benefits from this approach include reduced sampling and analysis costs, reduced turn-around times, lowered employee exposure, statistically improved characterization data, and the elimination of lab waste disposal.

A portfolio of technologies will be required to realize the vision. The probes will be delivered to the waste by either the push mode sampling platform or a cone penetrometer system. Characterization requirements include radiological, physical, and chemical parameters. Leading analytical technologies to meet these needs include neutron activation devices, various penetrometer systems, Raman and infrared spectroscopy, and sample dissolution/capillary electrophoresis.

11:00 RAPID ISOLATION AND MEASUREMENT OF TC-99.

K. A. Orlandini, M. D. Erickson, and J. G. King,
Argonne National Laboratory, 9700 South Cass
Avenue, Argonne, IL 60439.

A method has been developed for the recovery and assay of technetium-99 in aqueous solutions (e.g., environmental waters, extracted soil solutions) using minimum chemical conditioning and operator involvement. It is both rapid and highly selective for this radioisotope.

The method employs a special charged membrane (commercially available) which retains the technetium selectively from an aqueous solution. The membrane, after a quick-dry, is counted directly. Projected average analysis time for initial recovery to final assay is on the order of half an hour including counting time. (Reference sample: 100 pico curies per liter using 50 ml volume). The technique includes a sequential membrane contact allowing the measurement of chemical yield without the addition of a yield monitor. This feature avoids the production of residual mixed waste for most samples. Interferences, potential interferences and a suggested preconcentration step are discussed. Finally, a solid state 4 π scintillation detector (not commercial) is proposed for final assay and identification of the low energy beta spectrum produced by the technetium-99.

11:25 ANALYSIS AND VERIFICATION OF COMPRESSED GAS CYLINDERS. J. E. Alarid, R. A. Garcia, A. P. Lovell, W. D. Spall, and P. H. Hemberger, Analytical Chemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545.

Los Alamos National Laboratory has as many as 4000 surplus gas cylinders that require characterization prior to their disposal. Although many of the cylinders are innocuous (i.e., they contain, for example, compressed air or an inert gas), other cylinders can pose some unique problems. Cylinders containing unknown gases can present health and safety hazards; their content may also be difficult to analyze. We must also ensure that radioactive gases or contaminated cylinders are detected, characterized, and disposed of in a proper manner. Our goal is to provide an efficient analytical service while minimizing any hazards relating to the handling, analysis, and disposal of these cylinders and while complying with local, state and federal regulations.

For this project, a gas analysis laboratory has been equipped with a LB1000 low background counter to detect particulate alpha and beta counts on cylinder swipes; a Berthold tritium monitor is used to detect any tritium or beta emitting gases; and a UTI quadrupole mass spectrometer and a Mattson FTIR are used for gas analysis. We will describe the sampling and analysis protocols we have established and discuss our solutions to the problems presented by reactive, unknown, or potentially radioactive gases. To date, we have analyzed in excess of 500 gas cylinders which subsequently have been disposed.

12:00 ADJOURN

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