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ANALYTICAL CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1992

W. D. SHULTS
Director

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INTRODUCTION

W. D. Shults

Director

The Analytical Chemistry Division of Oak Ridge National Laboratory (ORNL) is a large and diversified chemistry organization. As such, it serves a multitude of functions for a clientele that exists both in and outside of ORNL. These functions fall into the following general categories.

1. **Analytical Research, Development, and Implementation.** The division maintains a program to conceptualize, investigate, develop, assess, improve, and implement advanced technology for chemical and physicochemical measurements. Emphasis is on problems and needs identified within ORNL and Department of Energy (DOE) programs; however, attention is also given to advancing the analytical sciences themselves. This effort is composed of medium- to long-term projects and is supported primarily by the DOE.
2. **Programmatic Research, Development, and Utilization.** The division carries out a wide variety of chemical work that typically involves analytical research and/or development plus the utilization of analytical capabilities to expedite programmatic interests. The effort in this category comes from ORNL and DOE programs and from Work for Others agreements. Emphasis here is on "applied" chemistry.
3. **Technical Support.** The division performs chemical and physicochemical analyses of virtually all types. The development of methodology is an inherent part of this activity because of

the variety of analytical problems that arise in a multiprogram institution like ORNL. Consultation, collaboration, and special projects are involved. Much of this work is short term in nature and comes from other division and programs within ORNL, but a significant fraction originates outside of ORNL and involves the use of talent and/or facilities in which the division is particularly strong.

The Analytical Chemistry Division is organized into three major sections, each of which may carry out any of the types of work mentioned above. A fourth section was created last year to manage the wide range of operational programs in effect within the division. Chapters 1 through 4 of this report highlight progress within the four sections during the period January 1 to December 31, 1992. Chapter 5 summarizes our education programs, which have grown in both magnitude and importance. Supplementary professional activities, publications, and presentations are given in Chapters 6 and 7.

INORGANIC AND RADIOCHEMISTRY

Inorganic and radiochemical analysis have been traditional strengths in Analytical Chemistry Division for many years. The Laboratory pioneered the production and study of radionuclides, which fostered much radioanalytical work. Similarly, Laboratory programs in nuclear technology fostered much analytical R&D in inorganic analysis. Neutron activation analysis (NAA) was the first highly sensitive, highly specific, multi-element analysis technique. Other multi-element methodologies have evolved over the years and incorporated into the division's arsenal of analytical tools. In recent years, emphasis has been placed upon environmental and low-level analyses, both inorganic and radiochemical, and the use of methodologies that are acceptable for compliance documentation. Much of the work of this section is in support of ORNL and Energy Systems programs, many of which relate to environmental restoration, waste management, or compliance activities. A large project to analyze approximately 4,000 soil and sediment samples from the East Fork Poplar Creek flood plain by neutron activation analysis was successfully completed this year. A challenging aspect of this work

was to utilize neutron activation analysis and data reporting methods which would comply with the quality assurance requirements of the EPA Contract Laboratory Program (CLP). This, to our knowledge, is the first time that NAA has been used for CLP regulatory analysis and it opens the door to possible use of the technique for other regulatory-type analyses. Another similar project is now being developed to provide background soil characterization data for the Oak Ridge DOE reservation.

We installed a laser ablation sample introduction system on our ICP/MS instrument this year and have used it to perform a preliminary study of trace metals in tree rings. The laser allows us to accurately sample the wood produced during both early and late season growing periods of the tree. We are not trying to provide quantitative analyses but instead are measuring the ratio of carbon-13 to some 20 trace metals. The increase/decrease in ratios will give researchers information about the effects of acid rain on forests in the southeastern United States.

ANALYTICAL SPECTROSCOPY

The Analytical Spectroscopy section is devoted to research and development in chemical measurement science, and to supporting various technical programs of the Department of Energy and other federal agencies. The section is comprised of some twenty-five full-time staff members with expertise in physics, organic chemistry, physical chemistry, inorganic chemistry, instrumentation, computers, and, of course, analytical chemistry. Ten to twenty visitors, including visiting scientists, postdoctoral associates, graduate students, and undergraduates, work with the staff at any given time. These guests benefit from access to state-of-the-art equipment, mentoring by mature research scientists, and participation in exciting research activities while, at the same time, bringing new ideas, new capabilities, and added enthusiasm to the section.

Mass spectrometry has been a central area of expertise within this section since its inception. The early emphasis was on elemental and isotopic analysis, but our mass spectrometry activities have grown in both breadth and diversity. Much current interest lies in ion trap mass spectrometry (for

organics) and in glow discharge mass spectrometry (for inorganics). Laser-based analytical spectroscopy has also been an active research area within this section for many years, and is in many ways synergistic with the research in mass spectrometry. The same is true of our research with positrons, although this is a small activity.

A new method is being developed for chemical analysis using trapped ion laser spectroscopy in a quadrupole ion trap. Molecules are confined in the trap and ionized with a laser or electron beam. Ionization is followed by mass selection of ions of interest. These ions are excited by a wavelength tuned laser beam and their fluorescence is measured. Since the trapped ions remain at the center of the trap for a long period of time, they can absorb and emit many times providing a very high sensitivity. After the optical measurements, the parent ion and the fragment ions are analyzed within the ion trap mass spectrometer. Measurements by both optical spectroscopy and mass spectrometry enable us not only to detect a small number of molecules but also to identify chemical species as well as molecular structures. Using a microparticle levitation/ablation technique developed in this laboratory, a

wide range of molecular ions including heavy involatile biological molecules can be introduced into the ion trap and investigated. This method can be utilized also in studying photodecomposition of organic molecules.

A prototype explosives detector has been developed based on a modified Finnigan TSQ-700 mass spectrometer. One of the important characteristics of this instrument is the ability to easily perform MS/MS experiments under computer control. An MS/MS experiment involves the fragmentation of molecular species to derive structural information in addition to the molecular weight of the ionic species introduced into the mass spectrometer. The ion source for this instrument was removed and replaced with an atmospheric sampling glow discharge source developed in this laboratory. Under the conditions identified for this work, molecular anions of molecules present in ambient air are formed and introduced into the TSQ-700 for mass analysis. This application requires that a positive identification of an explosive be made with minimal intervention from a nontechnical user. Consequently, a turnkey application was written using Finnigan's instrument control language. The system was demonstrated successfully to Federal

Aviation representatives during the summer.

The division entered into its first Cooperative Research and Development Agreement (CRADA) this year, with Dow Chemical Company and The University of Tennessee. We are developing magnesium ion and fluoride ion sensors for use in Dow-type molten salt mixtures that function at temperatures above 700°C. The Raman spectral peak of MgCl_4^{2-} will be used to determine soluble magnesium. An all-silica fiberoptic probe has been developed for this application. We are studying the determination of fluoride as evolved HF. Monitoring of Mg and F in Dow melts during production of magnesium can lead to huge energy savings.

We have designed two circuits which will reduce the number of external electronics modules required for enhanced operation of ion trap mass spectrometers. The first will allow enhanced mass resolution to be attained by reducing the ramp rate of the rf amplitude (rather than scanning the resonance excitation frequency via an external sweep generator). The second circuit provides the capabilities for amplification of the resonance excitation signal and for summing of the random-noise (or other) signals. Printed circuit boards

designed for these functions have been installed and tested. They are mounted in the existing ion trap electronics cabinet. We have also demonstrated that random noise applied to the end caps of a quadrupole ion trap is an effective means for collisional activation (CA) of stored ions. The technique overcomes the problems associated with mass/charge dependent excitation, ion space charge, and limited fragmentation. As such, an ideal application of this technique is with on-line separation applications for which the limitations of discrete-frequency CA are most severe. We have now implemented GC-MS/MS on a bench-top quadrupole ion trap-based instrument using random noise to effect CA. By incorporating additional control logic for the random noise, it is possible to perform CA during alternating mass scans without the need for downloading separate scan functions. Thus, because data acquisition rate is not compromised, both mass and MS/MS spectra can be acquired during the period of peak elution.

Glow discharge mass spectrometry (GD/MS) is one of the most exciting developments in inorganic analysis in recent years. It offers multi-element, isotopic, analyses on a wide variety of sample types, with minimum sample preparation. We have

initiated a strong program in GD/MS which includes research into both dc- and rf-powered discharges, trapped ion techniques, isotopic and isotope-dilution analyses, and methodologies for analyzing soils and solution residues. We find that GD/MS has great promise for replacing older techniques such as spark source mass spectrometry, and for making analytical measurements that are difficult or impossible to do by current approaches.

The elemental distribution of the rare earth elements (REEs) provides important petrogenic information for geological research. We have pioneered a secondary ion mass spectrometric (SIMS) technique that uses odd-mass double charged ions for quantitative analysis of REEs in silicates. The odd-mass, doubly charged ions fall at half mass units, hence peaks are generally interference free. Linear calibration curves are observed for thirteen of the REEs and detection limits are < 10 ppb for most. Relative ion yields are reproducible within 2-6% and are stable for months. This technique offers many advantages over other SIMS techniques. We are exploring its general applicability.

ORGANIC CHEMISTRY

Organic analytical chemistry was virtually nonexistent in the DOE laboratories in the early years. Analytical Chemistry Division pioneered this type of analytical chemistry with DOE some twenty-five years ago by initiating research and development programs in tobacco and tobacco smoke chemistry. These programs led naturally to health-related research, and thence to environmental work. Organic analytical chemistry today is central to many analytical operations within the DOE complex. This type of work continues to be quite diverse within Analytical Chemistry Division, varying from fundamental research to organic service analysis.

Matrix assisted laser desorption ionization (MALDI) is a relatively new, powerful technique in organic mass spectrometry. We have studied the application of the technique, combined with Fourier transform mass spectrometry, to the detailed structural characterization isomeric differentiation of normal and modified biomolecules. We have also constructed a laser-based time of flight mass spectrometer specifically for fundamental studies of the MALDI process. Both ionic and optical

signals will be employed in these studies.

The division has been working for several years now in the general area of direct sampling ion trap mass spectrometry (DSITMS). This work is increasingly successful. Significant refinements have been made in the sample introduction devices and other DSITMS hardware, to enhance general applicability. Field demonstrations were conducted at the Savannah River Site and Portsmouth Gaseous Diffusion Plant, and a fieldable version was sent to the Hanford Engineering Laboratory. The success of our DSITMS systems for environmental analysis suggested that this approach might be extended to other "threatening" chemicals. A so-called "multi-threat analyzer" has been conceptualized and constructed, and is being evaluated. It incorporates all of the features of a full-sized ITMS but is only the size of a small filing cabinet. It is being applied to a wide variety of chemicals, chemical agents, and drugs in various matrices.

An emphasis area within DOE's Environmental Restoration and Waste Management Programs is the development of analytical methodology for radioactive mixed wastes. Development of methods for glove box and hot cell use has been central to our effort. Adaptations of EPA SW-846 and

other methods are made, evaluated, documented, and submitted to the DOE Analytical Methods Compendium. This work encompasses organic, inorganic, and radiochemical methodology.

An important activity this year has been the field testing and demonstration of an arrayed, multisorbent sampler for in-situ collection of volatile species at depths up to 40 meters in the vadose zone. The device can be lowered into a 10 cm diameter borehole to sample volatile organic compounds, then returned to the surface for analysis. This system was deployed and demonstrated successfully at the Savannah River Site on two occasions. It was mated to our DSITMS during some of these tests, to provide near real-time determinations of soilgas concentrations in subsurface regions.

OPERATIONS

The Operations Section was established in 1991 to centralize a number of common functions within the Analytical Chemistry Division, e.g., Quality Programs, Training Programs, Environmental Protection, Radiation Control, Chemical Hygiene, Publications Office, etc. During 1992, the division was besieged with many audits, reviews, surveillances, inspections, and investigation, each of which required response and appropriate action. Prominent among these were two investigations, one by a review Panel from the DOE Field Office and a second by Judge William Webster and firm for Martin Marietta Corporation. These investigations imposed many demands and much stress upon the staff, and led to considerable self assessment within the division. Numerous corrective actions were planned and implemented. Tracking systems were developed and implemented to assure regular and consistent reporting of progress.

CONCLUSION

Calendar year 1992 was an exciting year for the Analytical Chemistry Division. Analytical service work increased somewhat from the prior year and was of excellent quality as measured by internal and external quality control programs. Analytical research and development was also successful, as measured by the number of talks, publications, and proposals produced by division staff, and by their involvement in professional affairs. Analytical Chemistry Division continues to be a major contributor within the field of analytical chemistry.

1. ANALYTICAL SPECTROSCOPY

S. A. McLuckey

The Analytical Spectroscopy section is devoted to research and development in chemical measurement and to supporting various technical programs of the Department of Energy and other federal agencies. The purpose of the section is to contribute to the solution of the nation's technical problems through advances in analytical chemistry and by providing unique problem-solving capabilities. The section is comprised of some twenty-five full-time staff members with expertise in physics, organic chemistry, physical chemistry, inorganic chemistry, instrumentation, computers, and, of course, analytical chemistry. Ten to twenty visitors, including visiting scientists, postdoctoral associates, graduate students, and undergraduates, work with the staff at any given time. These guests benefit from access to state-of-the-art equipment, mentoring by mature research scientists, and participation in exciting research activities while, at the same time, bringing new ideas, new capabilities, and added enthusiasm to the section.

Four groups make up the section: Optical Spectroscopy, Inorganic Mass Spectrometry, Secondary Ion Mass Spectrometry, and Organic Mass Spectrometry. Emphasis is placed on laser spectroscopy and various forms of mass spectrometry. However, a wide variety of other basic and applied research projects are ongoing that involve separations and other forms of particle spectroscopies, such as positron spectroscopy. Each group enjoys research support from the Department of Energy's Office of Basic Energy Sciences. These funds support basic research projects aimed at improving the state-of-the-art of chemical measurement and in improving our understanding of the chemical and physical behavior of matter as they pertain to measurement. Each group is also funded, in part, to address current measurement problems of various government and nongovernment entities. Examples include the development of organic ion imaging of biological tissues, miniature separations technology, explosives detection equipment,

explosives detection equipment, fieldable uranium detector, and many others. Much of the expertise and insight available to solve these problems derives from the new knowledge uncovered by the basic research supported by Basic Energy Sciences.

The Analytical Spectroscopy section and its predecessors have played an important historical role in the analytical support of a wide variety of research and development programs at Oak Ridge and other Department of Energy facilities. This work is currently concentrated in the Inorganic Mass Spectrometry group and involves, *inter alia*, high precision isotope ratio measurements in support of DOE's isotope production programs, and inorganic mass spectrometric and emission analysis of materials from a variety of programs.

OPTICAL SPECTROSCOPY

J. Michael Ramsey

The Optical Spectroscopy group has grown substantially in the past year with several new projects. Some noteworthy accomplishments include the first observation of molecular cavity quantum electrodynamic effects in a spherical cavity, ion trap laser ablation mass spectrometry of an individual levitated microparticle, resonance ionization mass spectrometry of rubidium with two sequential semiconductor diode laser excitation steps, the development of a new fiber optic probe for Raman and other optical spectroscopies over a wide temperature range, and the detection of mutations induced by positron irradiation of

DNA. One major new project is to develop a microchip liquid chromatograph. Separations performance comparable to laboratory instruments is anticipated for this device on postage stamp-sized substrates.

Cavity-Enhanced Emission in Microdroplets

Fluorescence detection in the liquid phase is a highly sensitive method of detection primarily because of the large (but finite) number of absorption-emission cycles a molecule may undergo before photochemical bleaching occurs. The detection limits of this method are determined primarily by the magnitude of background signals such as Rayleigh or

Raman scattering from the solvent. These signals can be minimized by making the probe volume as small as possible. Our approach to ultrasensitive detection of fluorescent materials has been to use levitated microdroplets as the sample "container" where the probe volume (defined by the droplet diameter) can be made as small as 35 femtoliters. We have shown that single molecules of β -phycoerythrin, a protein with about 30 chromophores, can be detected in these microdroplets with a signal-to-noise ratio of about 5. Recently, improvements in our experimental apparatus have allowed us to detect single molecules of the dye rhodamine 6G (R6G), a molecule with only a *single* chromophore, with signal-to-noise ratios greater than 10.

Microdroplets offer an additional sensitivity advantage not possible in bulk solution measurements through spherical resonances; also called morphology dependent resonances, or MDR's. It has been known for some time that the interaction of atoms or molecules in excited states with microscopic cavities can produce enhancement or inhibition of the emission rate for optically allowed transitions to the ground state. The essential condition for this effect is that the cavity mode spacing, which

is inversely proportional to the length of the cavity, must be greater than the linewidth of emission. That is, to achieve a mode spacing of 200 cm^{-1} (roughly twice the typical homogeneous linewidth for polyatomic dyes in solution), a cavity dimension of $10\text{ }\mu\text{m}$ must be obtained. Micron-sized droplets thus offer an ideal environment to observe cavity-enhanced emission rates since such dimensions are easily produced in the laboratory and experimental control over droplet diameter, and therefore the mode spacing, is fairly straightforward.

We investigated this effect by measuring the fluorescence lifetimes of dye molecules in microdroplets of different sizes using a time-correlated single-photon counting technique. Briefly, this involves using a short excitation pulse from a mode-locked Ar^+ laser to induce fluorescence, and then measuring the arrival time distribution of fluorescence photons at the detector relative to the arrival of the excitation pulse at the droplet. The results of this investigation showed that for droplets with diameters greater than $10\text{ }\mu\text{m}$, the fluorescence decay kinetics are well described by a single exponential decay and are essentially the same as in bulk solution. As the droplet size is decreased below $10\text{ }\mu\text{m}$ in diameter, the fluorescence decay becomes increasingly nonexponential showing the

appearance of a fast decay component whose magnitude and relative probability amplitude increase with decreasing droplet diameter. The most striking effect is seen with 4 μm diameter droplets where an emission rate greater than 10 times larger than in bulk medium was observed.

Using a simple model based on redistribution of photon-state density, good agreement between our experimental rate enhancements and those predicted by this model is obtained. Within this model, the emission rate enhancement is approximately equal to the resonance spacing divided by the homogeneous linewidth of the emitting species. Since the resonance spacing is known from a measurement of the droplet diameter, the homogeneous linewidth can be estimated from the experimental emission rate enhancement in the nanosecond time regime, a quantity which could previously only be measured using ultra-fast (femtosecond) optical probes such as spectral hole-burning or photon-echo techniques.

Because the broadband dye fluorescence overlaps several cavity modes, emission rate *inhibition* is also expected to occur in these small droplets. It is therefore unclear whether or not this effect will translate directly into a proportionally large sensitivity advantage. The effect on the integrated

number of photons detected per molecule will depend on the magnitude and relative probability amplitude of this inhibited component. Photon yield experiments are currently in progress to see how these cavity effects influence the total number of fluorescent photons emitted from an analyte molecule.

*M. D. Barnes**, *K. C. Ng***,
*M. A. Miller****, *S. Arnold*****,
W. B. Whitten, *J. M. Ramsey*

*ORAU Postgraduate Research Program

**ORAU Faculty Research Participation Program

***ORAU Professional Internship Program

****Physics Department, Polytechnic University of New York

Digital Analysis

One of the frontiers in the field of chemical analysis is that of continuing to reduce the detectable concentration of molecules in solution. As mentioned above, we have improved the sensitivity of fluorescence measurements on levitated microdroplets so that the presence or absence of a single molecule of fluorescent dye in a given droplet can be discerned. This capability opens the way for digital chemical

analysis with substantial potential advantages over conventional bulk analytical techniques. For dilute solutions where the probability of a dye molecule being in a single drop is less than one and where the total sample volume is fixed, we have shown that the detection limit can be substantially reduced by counting the individual analyte molecules rather than by integrating the signal from the entire sample. The minimum concentration that can ultimately be detected is largely governed by the number of false positive declarations. Statistical methods for predicting the minimum detectable concentration for arbitrary signal and background noise distributions have been formulated.

The errors in digital detection are statistical in nature because of the random emission of fluorescence photons and photolysis of the analyte molecules. We have discovered that some molecules are more detectable than others with the same fluorescence photon yield because of their statistical photolysis behavior. Molecules with more than one independently photolyzable fluorophore have lower statistical overlap with the background noise and thus can be counted with greater confidence than single fluorophores that give the same average signal-to-noise ratio.

These results are important for the design of fluorescent tags that must be detected with a high degree of certainty and in the development of experimental methodology for genome sequencing and other measurements where fluorescent tracers are employed.

W. B. Whitten, J. M. Ramsey

Identification of Individual Microorganisms

Timely identification of potential infectious agents has long been a challenge, especially for single organisms. We have obtained some recent results which indicate that an immunoassay technique based on spherical microparticles may permit the recognition of a large number of species of microorganisms. In the present application, microorganisms to be analyzed are stained with a highly fluorescent dye. Antibody-antigen attractions are used to selectively bind the microorganisms to spheres.

We have used conventional techniques with carbodiimide reagent to attach antibodies to polystyrene microspheres. *E. coli* bacteria stained with Texas Red or

tetramethyl rhodamine have been observed to bind to microspheres to which we had attached rabbit anti-E. coli antibodies. We have demonstrated similar results with monoclonal antibodies to Staph. aureus peptidoglycan attached to microspheres incubated with Staph. aureus stained with Texas Red and have also observed selective attachment when mixtures of these spheres and species of bacteria were incubated together. We are currently investigating the importance of nonselective binding of microorganisms to spheres with antibodies to other species.

*M. J. Shapiro**, *B. V. Bronk***,
W. B. Whitten, *J. M. Ramsey*

*GLCA/ACM Science Semester Program

**U.S. Army CRDEC, Edgewood, Md.

Microchip Liquid Chromatograph

A miniaturized chemical sensor is being developed that integrates separation and detection techniques on a single substrate. The resulting device will be used to determine the presence of a broad range of target species. The miniaturization should

ultimately reduce the cost of such instrumentation with little or no sacrifice in performance.

Our initial efforts have been to demonstrate that separations can indeed be performed and detected with such a device. These efforts include fabrication of columns on a substrate and development of injection and detection schemes. The prototype design incorporates electroosmotic pumping to drive the mobile phase through the column and for sample injection. The initial detection techniques are by on-column fluorescence or absorbance with a laser excitation source.

Significant progress in the development of the liquid chromatographic chip has already been achieved. Wet chemical etching techniques, bonding techniques and capillary electrophoresis with absorbance and fluorescence detection were investigated for implementation into the fabrication process. For the wet chemical etching, the common procedures of ammonium fluoride/hydrofluoric acid in water and nitric acid/hydrofluoric acid in water were examined with the former providing better etch results. In order to compare microchip separation techniques with existing separation technology, e.g., capillary

electrophoresis and open tubular chromatography, capillary systems were constructed and tested employing amino acids and rhodamine laser dyes as test solutes with absorbance and fluorescence detection, respectively. The laser (HeNe, green) fluorometric detection scheme will also be used for preliminary tests on a fabricated chip.

R. Hergenröder, S. Jacobson*,
L. Koutny*, J. M. Ramsey*

*ORAU Postgraduate Research
Program

Fundamental Studies of Chemical Vapor Deposition Materials Growth Processes

Several laser spectroscopic and materials characterization techniques have been developed and applied to foster a fundamental understanding of diamond film growth by chemical vapor deposition (CVD). Although many technologically important materials are synthesized by CVD techniques, little is known about the details of the chemical and physical mechanisms involved in

these film growth processes. We have conducted experiments aimed at a fundamental understanding of film growth wherein the mechanistics are learned and the rate-limiting steps are identified. Diamond films have been produced since the early 1980's, but are only now beginning to find commercial use. Their current and expected applications are tied to the unique physical properties of diamond: excellent thermal conductivity, extreme hardness, chemical inertness, high resistivity, and semiconducting character when doped.

The laser diagnostics developed here were applied to a hot filament reactor. It features a replaceable 76-mm diameter quartz vessel that serves as a molecular beam source for a time-of-flight mass spectrometer. Spectroscopic information is collected in two different regions of the reactor: the bulk reactor gas and the boundary layer immediately above the substrate.

Detection of atomic hydrogen was demonstrated in the bulk reactor gases under diamond growth conditions using [3+1] resonance enhanced multiphoton ionization (REMPI) spectroscopy at 365 nm. The ionization signal strength due to atomic hydrogen was recorded as a function of filament temperature and found to

approximately double between 1860 and 1990 °C.

For investigation of the gas/solid boundary layer, orifice sampling was utilized. A small orifice through the substrate connected the reactor to a high vacuum chamber. The gas phase species sampled through the orifice come from a height up to approximately the orifice diameter; that corresponds here to the boundary layer above the growing film. Expansion of the gases into the vacuum results in suspension of further chemistry because collisionless conditions are rapidly attained. We have detected both acetylene (by electron impact ionization) and methyl radical (by [2+1] REMPI) in the boundary layer above a hot substrate. Both acetylene and methyl radical have been suggested as important carbon-bearing nutrients for diamond film growth. Methyl radical purportedly substitutes for atomic hydrogen in the surface equilibrium between the hydrogen-saturated surface and one with dangling SP_3 carbon bonds. The REMPI detection process is highly selective, due to the combination of both optical and mass discrimination.

With electron ionization (EI), extensive fragmentation of methane was observed; thus electron ionization could potentially lead to

confusing results, indicating the presence of fragment species in the reacting gas mixture. For REMPI this is not a problem, as the optical spectral signature of an intermediate must be observed when the laser is scanned to qualify it as a component of the reactor gas.

Several modifications were made to the diamond growth chamber/TOF mass spectrometer this year. Larger bore molybdenum nozzles were fabricated, an oil diffusion pump was installed for the gas expansion region, and more sophisticated data acquisition programs were developed.

Sensitivity has been a problem for the orifice sampling technique and the film growth reactor. To remedy this situation nozzles were fabricated with a larger bore (0.23 mm) and shorter length. Due to the higher flux of reactor gases into the jet expansion region, the turbomolecular pump we had used to maintain this region at 0.1 to 1 Pa was no longer sufficient. It was replaced with a oil diffusion pump with approximately 2X greater pumping speed. The diamond we have grown to date in the reactor/mass spectrometer has taken the form of nanocrystalline balls, a morphology characteristic of a low substrate temperature. The machinable ceramic nozzle that limited

operation to 1000 °C was replaced with a laser-drilled molybdenum nozzle for higher temperature experiments.

The final reactor region to be probed is the material at the surface of the substrate or growing film. Sum-frequency generation (SFG) is an interesting new approach for probing the surface layer of materials. SFG is quite sensitive to interfacial phenomena while not requiring ultra-high vacuum conditions; it should provide vibrational spectra of molecules on surfaces. We have begun to develop a high-peak-power, picosecond-duration, tunable infrared laser source required for SFG spectroscopy. A picosecond pulsed laser is desired because low average power is necessary to prevent altering the surface chemistry with the laser itself. The most valuable spectral regions for investigation are the C-H and C-C stretching vibration regions at 2900 and 1330 cm^{-1} , respectively. Regeneratively amplified Nd:YAG and Ti:sapphire lasers will be mixed in a nonlinear optical crystal to produce infrared radiation. The overall design of this system is nearing completion; such a laser source is beyond that currently commercially available.

Neutron activation analysis has been used to measure the tungsten impurity in hot filament reactor-grown diamond. Two free-

standing films were analyzed and found to contain 5 and 32 ppm tungsten, an amount that must be reduced if this material is to find semiconductor application utility.

Follow-on funding was sought to support further film growth studies that capitalize on the tools we developed during this Director's R&D Fund project. A joint ACD/University of Tennessee-Chemistry proposal to the NSF has been funded to extend this effort for three years; the UT contribution will involve the application of ultra high vacuum (UHV) surface analytical techniques to diamond films. One student and a postdoctoral appointee will help with our boundary layer sampling and film characterization studies.

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Resonance Ionization Mass Spectroscopy

Sequential, two-diode laser resonance ionization mass spectroscopy (RIMS) has been demonstrated and a graphite furnace for mass spectrometry has been developed this year. Tunable, semiconductor diode lasers are practical sources for high resolution atomic spectroscopy. These lasers

oscillate in a single longitudinal mode without any special arrangements, and thus exhibit very narrow spectral bandwidths (approximately 25 MHz). They are conveniently tunable, with no moving parts, by adjusting their temperature and/or operating current. We have previously capitalized on their narrow linewidth for atomic hyperfine spectroscopy and isotopically selective ionization in RIMS experiments. A single diode laser-promoted excitation step to create an excited state population was used, followed by a pulsed dye laser-driven [1+1] resonance ionization process. Now we have successfully demonstrated a rubidium resonance ionization process that utilizes two sequential diode laser excitations. Our long-term goal is to demonstrate a resonance ionization process, particularly for the lanthanides and actinides, wherein only diode lasers are utilized for the optical steps.

Initially, single diode laser excitation of rubidium atoms at the D2 line (780.0 nm), followed by [1+1] ionization using a pulsed 572.4 nm dye laser was examined. Mass-resolved D2 spectra were recorded for both natural isotopes. The spectral linewidth was 175 MHz, and the excited state hyperfine splittings were evident. While we have not made quantitative isotope ratio

measurements, the 1 GHz spectral isotope shift of rubidium results in excellent isotopic selectivity for this ionization process.

Excitation using two sequential diode laser photons in a three-step overall process was accomplished by counterpropagating the beam from the 780 nm laser and one from a 775.8 nm laser; the latter excites Rb from the $5P_{3/2}$ level to the $5D_{5/2}$ level at 25704 cm^{-1} . A photon from the R6G dye laser then ionized the atom. Spectra resulting from scanning the second diode laser - with the first at an off-resonance fixed frequency - revealed both two-photon and sequential [1+1] diode laser processes. The former is due to a two-photon process and occurs at a frequency where the step 1 and step 2 frequencies sum to the energy of the 25704 cm^{-1} level. The three remaining lines are due to sequential [1+1] excitations, one each from the intermediate hyperfine levels populated. Our agreement with the accurately known rubidium $5P_{3/2}$ hyperfine splittings is excellent. The FWHM of the spectral lines was 110 MHz.

This two-diode laser excitation demonstration is the next stage in a progression toward a resonance ionization process that uses only diode lasers for the optical steps. To date we have been unable to demonstrate a sequential two-diode laser

ionization process for a lanthanide atom. Quite possibly for these more complicated atoms, excited state branching will require higher laser powers. Further experiments are in progress.

Studies of the application of a miniature graphite furnace for the study of inorganic samples by thermal ionization mass spectrometry (TIMS) or RIMS have been completed. The usefulness of the furnace for TIMS of several lanthanides (lanthanum, gadolinium, and samarium) and rubidium has been demonstrated, as has its usefulness for RIMS of lanthanum and rubidium. Most of the laser studies have involved rubidium. For these studies the furnace was loaded with an aqueous solution of RbNO_3 . After drying, dissociation of the salt occurred when the furnace was heated to a relatively low temperature, approximately 600 °C. The evaporated atoms were ionized using a [1+1+1] optical ionization route. The latter process employed one diode laser and a copper vapor laser-pumped dye laser (CVL-dye) as described above. To observe the [1+1+1] spectral ionization route, the diode laser beam was directed in a horizontal direction precisely onto the graphite furnace opening (1 mm dia.), and the vertical CVL-dye laser beam intersected the diode laser beam within 1 mm from the furnace. The

ion signal was extremely sensitive to geometry; this is expected as rubidium atoms should be escaping from the furnace in a directional sense. It was also observed that rubidium ions were generated nonresonantly if the vertical CVL-dye laser beam alone was directed at the furnace opening. This effect was also very site specific; any deviation of the beam eliminated the effect. The effect was a nonlinear function of dye laser power and did not appear to be wavelength dependent; either tuning over the dye lasing range to change the power or varying the dye power at a given wavelength produced the nonlinear effect. At the wavelength of peak power, the laser beam average power was of the order of 400 mW. Ionization might be the result of laser heating, but this heating must only be effective if it occurs at the furnace opening. Whether this effect is observed for other elements remains to be seen. No evidence of a two-photon route to ionize rubidium in the R6G region was seen either at the RIMS beam location or with the beam located at the furnace opening; the laser power was low at the wavelengths required for two-photon excitation, but was of the order of 100 mW average power.

The miniature graphite furnace has proven useful as an alternate mass spectrometer source. The work function of

graphite promotes atom generation over ion generation; the atoms should be emitted in a directional fashion from the furnace, allowing for higher laser beam/atom plume overlap. In addition, this design requires no water-cooling contrary to other graphite furnace designs. The furnace tubes are inexpensive and disposable.

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In-Line Sensors for Electrolytic Magnesium Cells

The final approval by DOE and the official signing of the Cooperative Research and Development Agreement (CRADA), #082290-1, with Dow Chemical Company, The University of Tennessee, University of Tennessee Research Corporation, and Martin Marietta Energy Systems, Inc., occurred this year. We are developing magnesium ion and fluoride ion sensors for use in Dow-type molten salt mixtures ($\text{NaCl-KCl-CaCl}_2\text{-MgCl}_2$, 35-35-15-15 mole %) that operate at temperatures above 700 °C. Some NaF is also present to aid in the removal of Mg metal. It is believed that energy

savings will result if the concentration of these two ions is monitored. We plan to use the Raman spectral peak of MgCl_4^{2-} to determine the soluble magnesium in the melt. Last year we discussed a diamond-windowed fiberoptic probe to make these measurements. Because of the reflectivity of the diamond window, unwanted SiO_2 Raman signals generated in the optical fibers were large. Better design of the fiber-diamond window junction might have reduced this problem, but we have developed an all-silica fiberoptic probe for the application. The probe consists of two or more silica optical fibers sealed within a silica tube; the sealing is accomplished by fusing the tube, under reduced pressure, around the fibers. The probe head is formed by cutting and polishing the fused area. The uniqueness of the probe is that it is essentially a pure silica rod that transmits and collects light as a fiberoptic device. For use in Dow-type melts, it was found that the probe is slowly attacked, but it continues to yield useful Raman spectra since the Raman signal is a scattered phenomenon. We therefore favor a disposable fiberoptic probe concept for carrying out magnesium concentration measurements on the Dow melts. In simulated Dow melts we have generated

information on various aspects of the proposed application, such as stability of Raman signal with time, effect of electrolysis, exciting laser power required, and ways to eliminate destructive attack of SiO_2 by molten magnesium metal present in the melt. All this information is available to Dow in terms of the CRADA.

Studies of techniques for determining fluoride ion in the melt have also been carried out. It was hoped that this could be accomplished by a potentiometric measurement at some electrode, such as aluminum, tantalum, or even molten magnesium. It has been found that these electrodes do not seem to respond to fluoride ion at high concentrations of magnesium ion > 10 mole %. Even at low concentrations of magnesium the response is weak and erratic. We have had some success with a hydrolysis method for determining fluoride ion as evolved HF, and this approach is being pursued.

The all-silica fiberoptic probe conceived by Sheng Dai has found research applications in a number of areas. Since it essentially has the properties of pure SiO_2 , it can be used where SiO_2 can be used. It has been demonstrated that it can be used to obtain Raman spectra to 77 K, fluorescence spectra to 77 K, reflectance spectra of solids from

77 K to 1300 K, solution absorption spectra; it is useful in the area of spectro-electrochemistry if one of the fibers is gold coated. One application currently being considered by others is monitoring amenable components in mixed-waste tanks. Since the probe is composed of only silica, concerns about radiation stability, corrosion, etc., are minimal and predictable. Other applications are being considered.

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Advanced Techniques for the Chemical Characterization of Microparticles

Work was continued on the evaluation of the quadrupole ion trap for the mass analysis of ions produced by laser ablation or desorption from microparticles. We are now able to electrostatically levitate a charged particle in the ion trap and obtain a mass spectrum of the laser-produced ions with the same electrodes. We can alternatively drop a microparticle into the ion trap under

vacuum, hit it with a focused laser beam, and then trap and mass analyze the desorbed ions. To determine the instrumental sensitivity, mass analyses were made for tetraphenylphosphonium bromide (TPPB) adsorbed on free falling 125 μm SiC particles. Samples prepared with progressively lower concentrations of TPPB per microparticle were analyzed in the trap. Memory effects made it necessary to clean the trap between loadings and will necessitate some form of trap heating to eliminate dismantling the trap between samples. A sample loading of about 1 fmole per microparticle is very close to the detection limit for TPPB with the current setup but lower limits are expected when laser desorption is combined with other techniques for ionization.

Several types of plastic explosives have very low vapor pressure and thus are likely to exist as solids under ambient conditions. It was therefore of interest to demonstrate that explosives on microparticles could be mass analyzed in the ion trap. SiC particles were loaded with 2,4,6-trinitrotoluene (TNT). The loading was about 30 nanograms or 0.15 nanomoles of TNT per particle. The detector was set for observation of negative ions expelled from the trap because TNT is

known to form very stable negative ions. The expected mass peaks were observed along with an over abundance of fragment ions. The fragment ion peaks may be real or they may be an artifact of the resolution of our trap. Pentaerythritol tetranitrate (PETN) is an explosive with a vapor pressure of about 4×10^{-10} torr which is four orders of magnitude smaller than that for TNT (5×10^{-6} torr). When compared to methods that detect explosive vapors, it seems that the microparticle laser desorption method should be more sensitive for explosives with very low vapor pressures. PETN was adsorbed onto SiC microparticles with a loading of about 70 nanograms or 0.22 nanomoles per particle. The negative nitrate (62 amu) and nitrite (46 amu) fragment ions were readily observed with both 532 nm and 266 nm laser desorption. The parent ion was observed as a positive ion at 316 amu with 266 nm laser desorption. Particles with adsorbed HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) were also tested. HMX has a vapor pressure which is a few orders of magnitude lower than PETN. The signal was partially masked by organic background peaks attributed to diffusion pump oil. The diffusion pump has subsequently been replaced with a turbomolecular pump.

The ion trap detector (ITD) with its outboard electrode chamber used for the previous experiments has been modified to investigate alternative methods of ionization for materials laser desorbed from microparticles. Possible alternative methods are chemical ionization, electron impact ionization, or ionization with a second laser. In addition to constructing a new vacuum system with a turbomolecular pump, we have mounted an electron gun on the ring electrode (instead of within one end cap) for ionizing neutral molecules laser desorbed from particles falling through the trap along the rotational symmetry axis. We have also acquired the electronics and software for an ion trap mass spectrometer (ITMS) and constructed a second apparatus. This system permits sequential mass spectrometry with collisional dissociation of selected ions for more positive identification. The new setup also has a ring-mounted electron gun and a mesh end cap for mass spectroscopy and optical measurements on gas molecules. This work is described in this report under "Chemical Analysis with Trapped Ion Laser Spectroscopy".

A new approach has been used for levitating a microparticle in the ion trap prior to subsequent mass analysis of desorbed ions.

For levitating a relatively heavy microparticle or trapping a light ion, the dynamic equilibrium restoring force is inversely proportional to the square of the frequency of the applied voltage. For microparticles the required frequency is a few tens of hertz while that for ions is of the order of one megahertz. We trap and levitate charged microparticles with both end caps at the same 60 Hz ac potential but different dc potentials. The 1.1 MHz rf potential applied to the ring electrode for ion trapping and mass analysis varies too rapidly to affect the microparticle trapping so it need not be disconnected. For ion trapping and mass analysis, the 60 Hz ac and the dc potentials are turned off. An electronic phase-controlled high-voltage switch grounds the end caps during the period of mass analysis of the laser desorbed ions. The switch is synchronized with the ion trapping time and used to trigger the Nd:YAG laser. The switching period can be controlled so that the falling microparticle may be recovered and levitated again for another measurement. A nickel isotope mass spectrum has been measured by laser ablation/ionization of a levitated nickel microparticle. The parent ion peak was also observed for tetraphenylphosphonium bromide adsorbed

on a levitated nickel microparticle. These spectra were obtained with a single laser shot.

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Chemical Analysis with Trapped Ion Laser Spectroscopy

A new method is being developed for chemical analysis using trapped ion laser spectroscopy in a quadrupole ion trap. Molecules are ionized in the trap with a laser or electron beam followed by mass selection of ions of interest. These ions are excited by a wavelength tuned laser beam and their fluorescence is measured. Since the trapped ions remain at the center of the trap for a long period of time, they can absorb and emit many times providing a very high sensitivity. After the optical measurements, the parent ion and the fragmented ions are analyzed by the ion trap mass spectrometer. The measurements of both optical spectroscopy and mass spectrometry enable us not only to detect a small number of

molecules but also to identify chemical species as well as molecular structures. Using a microparticle levitation/ablation technique developed in this laboratory, a wide range of molecular ions including heavy involatile biological molecules can be introduced into the ion trap and investigated. This method can be applied also in studying photodecomposition of organic molecules.

In order to measure the fluorescence of ions inside the ion trap, it is necessary to collect the emitted radiation from a large solid angle. For this reason, one of the original end cap electrodes has been replaced with a highly transparent mesh with a surface that conforms to the original hyperbolic shape. Two fluorescence-collecting lenses have been mounted above the top mesh electrode to make an image at the entrance slit of a half-meter grating monochromator. The photomultiplier tube (PMT) can be mounted either at the other end of the monochromator or directly on the ion trap cube with a narrow band filter. An electron gun has been mounted on the side of the ring electrode. It has been confirmed that the ion trap with the new mesh electrode and the side mounted electron gun yields a mass spectrum with comparable resolution and sensitivity to the original ion trap in which the electron gun was mounted on the

top electrode. A set of pulse timing electronics has been completed. Three-gated boxcar averagers, one for PMT signal, one for the laser intensity monitoring, and one for the mass selected ion intensity measurement, are connected to a computer interface with which an IBM PC can accumulate up to 16,000 data points and seven parallel channels.

In the first measurements of HBr ion absorption spectra, it was found that the laser scattering background was too high even with a narrow band filter. The inside of the ion trap has been treated with graphite paint and the window modified to minimize the laser scattering background. The wavelength scanning system of the dye laser has been modified to allow for the accumulation of data up to 4096 laser shots at one wavelength position. After the test measurements of HBr ion spectra, an experiment is planned for the optical characterization of nitrocellulose.

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The Fragmentation of Large Organic Molecules by Positronium Formation

The ejection of an electron from a molecule requires that energy equal to or greater than the ionization potential be imparted to the molecule. If the ionization is done by means of collisional interaction with positrons there is an interaction channel through which positronium is formed. This is an exothermic process that liberates 6.8 eV of energy, which is transferred to the molecule being ionized. For the large organic molecules that have been studied, the ionization potentials were 9 - 10 eV. The thresholds for ionization by positronium formation were 6.8 eV lower than this, typically 2-3 eV. This can be shown more clearly by means of a Born-Haber cycle:

Over 20 organic molecules have been studied. For all cases a rapid rise in ionization cross section was seen when the positronium formation threshold was exceeded.

The fragmentation patterns of three molecules, butylbenzene, decane, and tetraethylsilane, have been measured in detail as a function of positron energy above the positronium formation threshold. Butylbenzene exhibited the simplest behavior, producing only one ion fragment, $C_6H_6CH_2^+$. The C_3H_7 fragment was produced as a free radical; propyl ions were not observed. For positron energies less than one eV above the positronium formation threshold, only the parent ion was produced as a free radical; propyl ions were not observed. The intensity of parent ions rose sharply with energy, reached a maximum, and decreased. For positron kinetic energies greater than one eV above the positronium formation threshold, the $C_6H_6CH_2^+$ ion began to form. Its intensity also went through a maximum and decreased.

It is useful to note that the fragmentation of the butylbenzene occurred only in the attached butyl group. For positron energies less than 10 eV, no fragmentation of the aromatic ring was observed. This is in keeping with observations of the ionization of benzene and toluene. For these compounds only the parent ions were produced for positron energies less than 10 eV. Compounds having sigma bonds were observed to undergo

fragmentation, as will be discussed below.

Fig. 1.1 shows the mass spectrum of decane produced by 7 eV positrons. For decane also, the parent ion and the ion fragments exhibited distinct thresholds of formation as shown in Fig. 1.2.

Fig. 1.1. Mass spectrum, decane fragment ions.

Fig. 1.2. Decane fragment ion yields vs. β^+ energy.

When the positron kinetic energy exceeded the threshold by only a few tenths of eV, primarily the parent ion was formed, with very little fragmentation. As the kinetic energy was increased beyond the threshold, the parent ion went through a maximum and decreased. When the positron energies exceeded the positronium formation thresholds by more than one electron volt, the intensity of the $C_8H_{17}^+$ fragment began to rise sharply, go through a maximum, and decrease. For positron energies greater than one eV beyond the positronium threshold, successively smaller ion fragments were produced. Their intensities also exhibited maxima, similar in form to those of the parent ion. The C_9 ion fragment was not observed.

For decane, a very clear correlation could be drawn between the thresholds for ion generation and their respective enthalpies of formation. We will define the overvoltage for an ion as the difference between its threshold of formation and the threshold for positronium formation. A plot of overvoltages for the ions, versus their enthalpies of formation, was linear, having a 45° slope.

For tetraethylsilane the fragmentation behavior was similar to that of decane. Fragmentation occurred primarily at the Si-C

bonds. For positron energies only slightly above the positronium formation threshold, primarily the parent ion was formed. As the positron energy was increased, higher proportions of fragments were produced. Plots of ion intensities versus positron energy showed distinct thresholds, followed by maxima, for the parent ion and the fragments.

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Kinetic Studies of the Ionization of Large Organic Molecules by Positrons in a Penning Trap

The ionization of large organic molecules was done using a Penning trap in order to make maximum use of the available number of slow positrons. The slow positrons were retained in a Penning trap for periods of time ranging from 50 to 1800 microseconds, effecting very long collision paths. Depending on their kinetic energies, the positrons traveled distances ranging from 40 meters to several kilometers. The ion

products generated were pulsed out for mass measurements by time-of-flight spectroscopy. Ionization studies were done using positrons with energies above and below the positronium threshold. The fragmentation patterns were strikingly different. Also, the kinetics of ion accumulation were totally different. By studies of the kinetics we can make certain conclusions about the mechanisms of ionization.

The Penning trap did not have perfect retention time for the positrons and ions. The ion accumulation in the trap evolves as a time-dependant balance between the generation, consumption, and loss of the positrons and ions. For the case of the ionization of decane and butylbenzene by positronium formation, we have found that a common kinetic equation will fit the data for the parent ions and all of the fragments. The general equation can be written as follows:

$$I_m = C_m * f(t) \quad (1)$$

where

$$f(t) = (B_0 kp / (kp + r - w)) \{ \exp[-wt] - \exp[-(kp + r)t] \} \quad (2)$$

In equation (1) above, I_m represents the intensity of an ion of mass m , where m may correspond to the parent ion or one of its fragments; C_m is the fraction of ions that fragment to the ion of mass m . In equation (2), B_0 denotes the number of positrons initially injected into the Penning trap; k is the rate constant for ionization of the molecules by the positrons; p is vapor pressure of the organic molecule; r is the rate at which the positrons are inelastically scattered out of the Penning trap; w is the rate at which ions are lost from the Penning trap; and t is the time of residence in the Penning trap of the positrons and ions.

The above equations were derived by assuming that the fragment ions are generated from an excited state of the parent ion immediately after the parent ion is produced. The differential equations that went into the derivation are as follows:

$$dB/dt = -(kp + r)B \quad (3)$$

$$dI_m/dt = C_m kpB - wI_m \quad (4)$$

By solving equations (3) and (4) simultaneously, equations (1) and (2) are generated. The data for the parent ion were fit with equation (1) by choosing appropriate values of C_m , k , r and w . The data for the ion fragments could then be fit by varying only the C_m parameter, with no changes in the others.

The ion accumulation kinetic curves showed pronounced maxima when ionization was done by positronium formation. The maxima and the rest of the points could be matched very well with equation (1).

When the positron kinetic energies were reduced to an average magnitude of about 1/2 eV, which is far below the positronium formation threshold, ionization still occurred, but the distribution of mass fragments was totally different. We have designated this type of ionization condition as 'sub-positronium'. For decane no parent ion was produced, and for the other compounds the magnitudes of the parent ion peaks were greatly reduced. The ion accumulation kinetic curves rose monotonically over a period of 1800 microseconds, with no maxima. The proportion of parent ion to fragment ion remained constant for sub-positronium conditions, but the data could not be fit with equation (1). We conclude

that the sub-positronium ionization kinetics are distinctly different from those for ionization by positronium formation.

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Defect Analysis of Solids by Positron Lifetime Spectrometry

Positron lifetime studies are being applied to problems in materials science dealing with highly perfect single crystals of copper, iron aluminide alloys, and detector materials important to the Superconducting Super Collider project.

Positrons injected into solids are thermalized within a time of less than 10 picoseconds. They then diffuse through the solid with a velocity of approximately 10^7 cm per second. If the solid is perfect, with a negligible defect content, the positrons are annihilated rather quickly; their mean lifetimes are 150 - 200 picoseconds. Defects, such as vacancies, voids, and free volumes in the solid act as traps for the positrons. Such

defects act as potential energy minima for the positrons because of the absence of nuclear charge. For metals and other inorganic solids the lifetimes of positrons trapped in monovacancies and small vacancy clusters are appreciably longer because of the decrease in electronic densities. For inorganic solids having free volumes, the positrons become trapped as positronium atoms. These have lifetimes as much as 5-10 times longer than the positrons that annihilate in the more perfect portions of the solid.

Highly perfect single crystals of copper have been irradiated with neutrons to a fluence of 10^{17} nvt. Comparing their positron lifetime spectra with that from unirradiated copper crystals, it can easily be seen that a large portion of the positrons are trapped at the defect sites. From electron microscopy studies, it is known that the crystals contain high concentrations of defect clusters, 1-10 nanometers in diameter. Positron lifetime spectroscopy can detect defects in the monoatomic form as well as in condensed configurations. Lifetime spectra are also being measured for iron aluminide alloys that have been given different heat treatments. Small differences in defect contents have been seen.

Neutron damage to radiation detector components is a major concern to the Superconducting Super Collider project. Preliminary studies are being done on the effect of neutron damage to silicon single crystals and to plastic fiberoptic material. In preparation for this work, our group has taken spectra of irradiated and unirradiated polyethylene. Decreases in the amounts of free volume have been observed. The average size distribution of the free volume cells appears to be about the same, but the density of free volume cells has decreased. Our present interpretation is that irradiation increases the amount of cross linking between the polymer chains. This leads to a closing up of the regions of free volume between the molecules.

Silicon single crystals of the type used in detectors have been irradiated with neutrons. These will also be examined by positron lifetime spectroscopy to assay the vacancy contents.

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Positron Stimulated Desorption

Attempts have been made to study the desorption of ions from solid surfaces by positron bombardment. The first experiments have been conducted using the combined Penning trap-TOF mass spectrometer that was used in the ionization of gases and vapors. The substrate consisted of a grid situated at the mid-point of the Penning trap. The plan was to capture positrons in the Penning trap and force them to make multiple passes back and forth through the grid. On each pass some of the positrons should strike the grid and perhaps desorb some of the material from its surface. After only a few microseconds the positrons in the trap should be consumed in their repeated collisions with the grid. During that period, any ions that are desorbed would not have time to escape from the trap.

We found that no ions were produced when low energy positrons were introduced in the trap. Ions were produced only when high energy positrons (>10 keV) were injected. The reason for this is not clear at this time. Also, it is not clear whether the ions came from the gas phase or the grid. Ions due to the ionization of background

water vapor are produced if the energy of the positrons exceeds the positronium threshold (~ 6 eV). However, when the grid was introduced, no water ions were produced by low energy positrons. The water vapor ions produced by high energy positrons had a higher proportion of OH^+ when the grid was in place. More work is necessary on this project.

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Mutations in DNA Induced by Positron Bombardment

Plasmid DNA has been irradiated with fast positrons to a fluence of about $10^{12}/\text{cm}^2$. The DNA was instilled into *E. coli* bacteria, which were then cloned and exposed to an antibiotic. Control experiments were done in which unirradiated plasmid DNA was instilled into *E. coli*. Unirradiated plasmid DNA enables the bacteria to acquire immunity to the antibiotic. The irradiation of the DNA by fast positrons destroyed its ability to do this.

The rationale behind the above experiments is to explore the possibility of inducing controlled mutations in the DNA by exposing it to low energy positrons. Experiments with low energy positrons have not yet been done.

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ORGANIC MASS SPECTROMETRY

Scott A. McLuckey

The overriding goal of the Organic Mass Spectrometry group is to advance the state-of-the-art of analytical organic mass spectrometry. This goal is pursued through instrument development, through studies into the fundamental aspects of organic chemistry relevant to mass spectrometry, and through challenging new applications. This year's efforts were concentrated on fundamental aspects of electrospray ionization, gas-phase ion chemistry of biomolecules, separations of biologically relevant species and coupling of separations to ion trap mass spectrometers, quadrupole ion trap research and development, matrix-assisted laser desorption coupled with the ion trap, and various applications such as explosives detection and porphyrin analysis.

Electrospray Ionization

The best results using electrospray ionization-mass spectrometry (ES/MS) are achieved for compounds that are ionic in solution. This is in direct analogy to fast-

atom bombardment and secondary ion mass spectrometry where best performance is observed for preformed ions. Species that are ionic in solution and have been analyzed by ES/MS include, for example, metal and organic salts as well as compounds with functionalities that can be ionized via solution phase acid-base chemistry, such as carboxylic acids and tertiary amines. The latter category of compounds includes peptides and proteins which contain basic amino acid residues and oligonucleotides which contain acidic phosphate groups and are usually detected as the $(M+nH)^{n+}$ and $(M-nNa)^n$ species, respectively. Some polar molecules are also ionized efficiently by ES via attachment of ions other than a proton. For example, Na^+ or CH_3COO^- ions, that are either added to or already present in the analyte solution, are sometimes observed to attach to the analyte molecules. Since the applicability of ES/MS is limited to compounds that are ionic in solution or that can be ionized in solution by acid-base chemistry or by adduct formation, many simple organic molecules containing only one or two functional groups, or nonpolar compounds, such as the polycyclic aromatic hydrocarbons (PAH's) are not typically amenable to analysis by ES/MS.

The short term objective of this work was to open up to analysis by ES/MS simple organic molecules, i.e., those containing one or two functional groups, that are not typically amenable to analysis by the method. The particular approach we have taken is the development of derivatization methods that convert the common organic functional groups to moieties that are ionizable in solution. Using those derivatization methods identified and tested, we can now analyze molecules bearing the following functional groups: lactones, amides, nitriles, acid chlorides, acid anhydrides, aldehydes, ketones, primary and secondary alcohols, phenols, primary, secondary and tertiary amines, primary secondary and tertiary alkyl halides, alkenes and alkynes. In several cases we have found derivatization methods that allow a particular functional group to be analyzed in either positive or negative ion mode. The only functional groups we have been unsuccessful in studying are the simple alkanes, carboxylic esters and ethers as intact molecules, and tertiary alcohols. A potential method to overcome the problem with the tertiary alcohols has been identified, but it appears unlikely that the alkanes and the ethers and esters as intact molecules can be studied using derivative methods.

The initial work on this project has been highly successful. Currently we are working to refine methodologies already identified and tested, and looking to use these methods in specific applications. We are also pursuing our longer term goals in this project which include: (1) development of derivatizing agents for nonspecific fast screening of mixtures, (2) development of derivatizing agents for a particular compound class or a particular compound, (3) development of derivatizing agents that allow a compound to be ionized in a highly specific manner (e.g., electrochemically or via charge-transfer complexation), and (4) development of on-line/automated derivatization procedures.

We recently observed molecular radical cations in the electrospray (ES) ionization mass spectra of various alkyl-substituted metalloporphyrins. This observation is significant because molecular ions, formed by loss or gain of an electron, i.e., radical cations and radical anions, are generally not observed in true ES mass spectra, i.e., when no gas-phase ionization processes are at work. Although details of the ES ionization mechanism are at issue, best analytical results with ES are obtained for compounds that are ionic in solution. Such species include, for

example, metal salts, organic salts, and compounds incorporating functionalities that can be ionized via solution-phase Bronsted or Lewis acid-base chemistry. The latter species are typically observed as protonated, sodiated or otherwise cationized molecules in positive ion mode and as the deprotonated molecules or as molecular adduct anions in negative ion mode. Ionization of neutral, relatively nonpolar compounds, such as aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAH's), and alkyl-substituted metalloporphyrins, by means of solution-phase acid-base chemistry is inefficient. Most compounds of this type either show reduced sensitivity or are not detected under normal ES/MS conditions. Therefore, we were interested in understanding the processes leading to radical cation formation, hoping to expand the utility of ES mass spectrometry to compound types not currently amenable to the technique.

Our most recent data have shown that electrochemical oxidation at the metal-solution interface of the ES needle, or metal connector used as a high voltage contact, is the mechanism for formation of the molecular radical cations. Electrochemical formation of radical cations from organic molecules in the ES needle is consistent with

the recent description of the ES process by several workers as resulting from electrophoretic charge separation. That is, the spray in ES results from field-induced separation of charge in the liquid at the needle tip. For the electrophoretic charge separation mechanism to be operational in the positive ion mode, charge balance requires that an oxidation reaction, resulting in electron flow into the needle, must occur at the metal-solution interface within the ES needle (or at the metal high voltage connection to the solution) to balance the positive ion charge leaving the needle in the spray. Our data show that for some types of analytes, under the appropriate conditions, a major oxidation product can be the molecular radical cation of the analyte.

In general, those analytes for which we have observed radical cations can be characterized as species that are known to undergo facile oxidation in solution by loss of an electron; the radical cations formed are known to be relatively stable in solution. Compounds with these properties, for example, porphyrins, aromatic amines, PAH's, and phenothiazines, typically contain π -electrons and/or heteroatoms with lone pair electrons. To observe the radical cations formed, however, relatively nonnucleophilic

ES solvents and solvent additives must be employed. Proper solvents and additives, e.g., methylene chloride and trifluoroacetic acid, extend the solution lifetime of radical cations.

The ability to generate radical cations via the ES process clearly has significant potential in analytical applications. First of all, ionization via electron transfer opens to ES/MS the analysis of compound types not typically amenable to the technique. These are neutral, nonpolar compounds, such as the PAH's, that cannot be charged by conventional solution-phase acid-base chemistry. Also, molecular species other than the normal molecular adduct ions can be produced for selected types of compounds. In the best cases, such as for the metalloporphyrins and relatively unreactive PAH's such as perylene and rubrene, the levels of detection for the ES produced radical cations, based on flow injection experiments, are comparable to those limits we have obtained on our instrument with preformed ionic species (< 1 pmol).

For compounds amenable to electrochemical oxidation in solution, the greatest challenge to utilization of this ionization phenomenon in analytical

applications appears to be constraints placed on the solvent systems to minimize radical cation-solvent reactions that would interfere with the analysis. The best solvent systems for producing and preserving the radical cations (e.g., methylene chloride/0.1% TFA) are more difficult to spray than a solvent comprised largely of methanol, for example. While this limitation is minor in continuous infusion or flow injection experiments, the solvent constraints will more severely impact analyses where on-line separations are involved. Also, our data indicate that the potential gradients at the metal-solution interface might be limited under the present conditions to about 1.5 V. Such a limit in potential gradient will confine the range of compounds that can be oxidized to form radical cations. Changing solvent flow rates, needle dimensions (and possibly needle material), and applied voltages, for example, might be explored as ways to extend these potential gradients. One method we have explored to overcome this possible gradient limit is incorporation of an electrochemical cell, normally used as an HPLC electrochemical detector, into the ES system rather than a needle or other metal high voltage contact. Initial results with this setup demonstrated some degree of control over

the oxidation reactions and analyte ions observed suggesting that additional control over potential gradients at the metal-solution interface is possible.

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Matrix-Assisted Laser Desorption Ion Trap Mass Spectrometry

Matrix-assisted laser desorption (MALD) has been shown to be a very sensitive technique for production of protonated high molecular weight biomolecules. Due to its high mass range and inherent suitability for use with pulsed ionization methods, the time-of-flight mass spectrometer (TOF/MS) has been widely used for mass analysis of such ions. However, TOF/MS does not lend itself to tandem mass spectrometry experiments that might be highly useful for structural characterization. The inherent suitability of the ion trap for use with pulsed ionization and its intrinsic capability for performing multistage mass spectrometry is well known. Moreover, the demonstrated mass resolution

in the ion trap is several tens of thousands and improves with m/z . These capabilities suggest that the ion trap can be a viable alternative to the TOF/MS for use with MALD.

We have coupled MALD with the ion trap and have obtained mass spectral and MS/MS data for several peptides and proteins. For example, using the frequency-quadrupled output of a Nd:YAG laser (266 nm) to effect desorption, we have obtained mass spectra of peptide ions, such as bradykinin and neuromedin, and small proteins such as bovine insulin. Conventional single-frequency resonance excitation was used to effect collision-induced dissociation (CID) of the $[M+H]^+$ ions from several polypeptides, including leucine-enkephalin, bradykinin, and neuromedin. The MS/MS efficiency, which was difficult to measure accurately due to relatively large fluctuations in the parent ion signals, ranged between 50-95%. MALD-MS³ and -MS⁴ spectra, which were also obtained for bradykinin, contained additional product ions similar to those seen from low energy CID on a BEqQ instrument. This is a general observation in the ion trap mass spectrometer (ITMS) which is presumably due to the fact that internal energy

deposition in the initial MS/MS stage with the ITMS is somewhat lower than in the BEqQ. Because single-frequency excitation is generally used, product ions fall out of resonance and subsequently are not kinetically excited. When this is combined with the relatively slow nature of ion internal energy deposition during resonance excitation, ion trap CID frequently produces only a few different product ions. Therefore, structural information inherent in the MS/MS spectrum may be limited. The use of single-frequency excitation for CID has other ramifications for tandem mass spectrometry in MALD/ITMS. The parent (and subsequent target) ion mass/charge must be known to be collisionally activated. Because the exact secular frequency is also dependent on the number of ions stored in the ion trap, tuning of the excitation frequency is required to optimize CID. The latter characteristic is particularly relevant to MALD/ITMS as the shot-to-shot variation in the desorbed ion number can often be large. Thus, although the ion trap is capable of multiple stages of CID, it may be undesirable to be forced to resort to MSⁿ with its added complexity.

We have found that the use of a random noise signal for resonance excitation reduces

many of the aforementioned limitations associated with single-frequency CID in the ion trap. The technique is simple to implement and has been used successfully with a wide variety of ions generated by electron ionization, chemical ionization, glow discharge ionization, and electrospray ionization. We have now implemented random noise CID in the ion trap to generate an MS/MS spectrum for bradykinin $[M+H]^+$ ions produced via MALD ionization. Although only one stage of tandem mass spectrometry was performed, extensive structural information similar to that acquired from the single-frequency MSⁿ spectra was obtained without the need for frequency tuning. These results indicate that MALD ionization coupled with CID/tandem mass spectrometry in the ion trap extends the utility of MALD mass spectrometry beyond molecular weight determinations to structural analysis.

Structural investigations of proteins frequently involve peptide mapping, where chemical or enzymatic digests are used to degrade the protein into smaller peptides that are more easily characterized. In addition to facilitating sequence analysis, maps may be used in comparative studies to examine mutational variants and to

determine microheterogeneity (i.e., identifying differences in amino acid residues at single positions in the sequence) or post-translational chemical modifications including site-specific glycosylation. The technique is also routinely used to determine the purity of proteins produced by recombinant DNA methods. Various mass spectrometric techniques have been used to obtain peptide maps without first separating the individual peptides. These include secondary ion mass spectrometry (SIMS), field desorption (FD), plasma desorption (PD), fast-atom bombardment (FAB), and matrix-assisted laser desorption (MALD). The advantages of the latter include high sensitivity, speed, and relative insensitivity to impurities such as salts and buffers. We have applied MALD/ITMS to the analysis of tryptic digests of various polypeptides and proteins.

Tryptic maps were obtained for 60 to 400 picomoles of glucagon, apomyoglobin, and tuna, horse, rabbit, and dog cytochrome C using either nicotinic or sinapinic acid as the matrix. All major peptide fragments previously reported by CF-FAB were identified for the glucagon digest with the exception of two products at m/z 1352 and 1357 which could not be distinguished due to limited mass resolution. These were detected

in a separate analysis by high performance liquid chromatography/electrospray ionization/ion trap mass spectrometry (HPLC/ES/ITMS). Major peaks in the remaining samples were identified as either tryptic or chymotryptic fragments (derived from residual chymotrypsin found in trypsin). Differences in the cytochrome C digests were readily apparent despite the highly homologous nature of the proteins. Overall, the data show that MALD/ITMS is a useful, rapid technique for peptide mapping. Future efforts will be directed in determining sensitivity requirements for acquiring data on these complex mixtures.

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On-line Condensed-Phase Separations and Ion Trap Mass Spectrometry

Mass spectrometry has, for several years, been found to be extremely useful in molecular weight determination and structural analysis of peptides and small

proteins through the use of desorption ionization techniques such as fast atom bombardment (FAB) and ^{252}Cf plasma desorption in conjunction with tandem mass spectrometry (MS/MS). The more recent introduction of matrix-assisted laser desorption and electrospray ionization techniques has made possible the molecular weight determination and structural characterization of much larger biopolymers ($> 100,000$ daltons). Several groups, including our own, have demonstrated the potential of on-line separation and ES/mass spectrometric analysis of protein enzymatic digests as a convenient, rapid, and sensitive method for protein structural characterization. The ES-determined molecular weight and the MS/MS analysis of the individual peptides resulting from the digest, along with the ES-determined molecular weight of the protein, can often provide enough information from which to determine the complete amino acid sequence of the original protein.

We have been using bradykinin ($\text{MW}_r = 1060$) and neuromedin U-8 ($\text{MW}_r = 1111$) as models for protein trypsin digest-produced peptides (i.e., they are observed as $(\text{M}+\text{H})^{2+}$ in ES spectra). In our present system, which pneumatically assists the ES process, the

total effluent from a microbore HPLC (ABI Model 140B), up to a flow rate of 40 $\mu\text{L}/\text{min}$, is directed toward an atmospheric sampling orifice of the trap. One limitation, which is especially apparent when using an ion trap, is the need to know the mass-to-charge ratio of a given peptide ahead of time in order to carry out the MS/MS experiment. With the ion trap, the normal method of CID is mass selective and can require a great deal of tuning (and time) to optimize. Furthermore, these ideal conditions change with the number of ions in the trap. As a result, MS/MS analysis of unknowns on the chromatographic time scale using the normal CID method is not practical. We are currently studying two nonmass selective methods of accomplishing CID as a means to overcome this problem. In one technique, random noise is applied to the end-cap electrodes of the ion trap to effect CID of ions stored in the trap independent of mass-to-charge ratio and number of ions. The second method, which has shown the most promise in the present application to date, fragments the ions via CID in the atmospheric sampling interface as they elute from the HPLC. The parent ions and fragment ions are then injected into the trap, stored and mass analyzed. The degree of

fragmentation in this case is easily controlled by adjustment of the interface lens voltages. Interface lens voltages can be selected so that $(M+2H)^{2+}$ ions are the only species observed whereas a different set of lens conditions (typically about 50 V more on each interface lens) yields sequence specific fragments in high abundance. On-line separation experiments have demonstrated that molecular weight and structural information can be obtained in this fashion at the low picomole level using a microbore system. (Of course lower levels could be reached with capillary columns or capillary zone electrophoresis (CZE) which operate at much lower flow rates.)

We have further increased the utility of the interface fragmentation by using the dc output of the ion trap mass selective storage module to supply the voltages to the three interface lenses in our system. In this way the lens voltages can be computer controlled via the ITMS software, and therefore varied during data acquisition. Thus, alternate ES mass spectra acquired across an eluting peak, first using "low" interface lens voltages and then using "high" lens voltages, are obtained. The respective mass spectra contain only molecular species (low voltages) or both molecular species and structurally significant

fragment ions (high voltages). Now both molecular weight and structure information can be obtained for the components in each eluting peak from one sample injection.

Our experiences with on-line separations coupled with the ion trap indicate that, while the sensitivity of the on-line condensed-phase separation/ES/ITMS is excellent, this coupling can compromise many of the other desirable features of the ITMS. In this report, some of the problems faced with dynamic range, mass accuracy and calibration, mass resolution, and single-frequency collisional activation (CA) and MS/MS are overviewed. The remainder of the discussion focuses on three methods other than single-frequency CA that we have investigated to obtain structure information in on-line applications.

Automatic gain control (AGC) which automatically varies the ionization (or ion injection) time to avoid accumulating "too many" ions in the trap, was developed to increase the dynamic range for separated compounds entering the trap. However, an inherent compromise in increasing the ionization time for minor component detection is a loss of peak resolution. As ionization or ion injection time increases, the number of data points across a peak will

decrease. The analysis of high mass biomolecules by ES often necessitates extension of the nominal m/z range of the trap from 650 to as much as 3000. This is most easily accomplished using the technique of resonant ejection. When resonant ejection is used to multiply the m/z range, peak position is dictated by a number of factors including the m/z of the ion of interest, the resonant ejection frequency and amplitude, the speed of the fundamental rf amplitude scan, and the He pressure in the trap. Since power absorption in resonant ejection has a z/m dependence, the mass scale is slightly nonlinear. Therefore, calibration must be done with ions of known m/z over the range of m/z of interest using as similar experimental conditions as possible. Obtaining high resolution spectra in on-line applications is problematic for several reasons. First, because resolution and scan speed are inversely related, a decrease in scan speed reduces the data points per peak. Second, signal/background decreases as resolution increases (i.e., less ion current per unit time). Third, the number of ions in the trap have a significant effect on resolution and this number changes as the peak elutes.

A practical limitation in obtaining structurally informative fragmentation using

the normal single-frequency method of CA is imposed by the mass-selective nature of the process. The m/z ratio of an ion must be known in advance so that the parameters affecting CA can be optimized (e.g., well-depth, tickle amplitude, time, and frequency). When an on-line separation involving compounds of unknown mass is performed, CA cannot be pre-optimized or optimized at present on the chromatographic time scale. The compounded tuning requirements in MS^n experiments, which are often needed to obtain additional structural information, make acquisition of such data on-line highly impractical. As with other ES interfaces, the voltages on the aperture plates and lenses in our interface can be adjusted so that the molecular species generated by ES can be fragmented through energetic ion-molecule collisions in the interface region upon transport to the ion trap. Fragmentation may also be induced upon injection of ions from the interface into the ion trap by adjustment of the rf voltage amplitude (low mass cutoff) on the ring electrode during ion injection. In reference to on-line applications, interface fragmentation and injection-induced fragmentation are of added utility because they both are nonmass-selective means to promote fragmentation. In addition, the variable parameters used to

control fragmentation in these two techniques may be controlled automatically as components elute using the ITMS software. Thus, molecular weight and structure information may be obtained in one analysis for each component as it elutes from the chromatographic column.

Recently our group has demonstrated that random noise applied to the end caps of the ITMS is an effective means for CA of trapped ions in MS/MS experiments. This technique is a simple and inexpensive approach to overcoming the single-frequency CA drawbacks of frequency tuning, space charge effects, limited fragmentation, and the inability to activate parent ions over a range of m/z values. The relaxed tuning requirements associated with random noise CA make this dissociation technique ideal for MS/MS in on-line separation applications for which the limits of single-frequency CA are most severe. To demonstrate on-line microbore HPLC/ES/ MS/MS using random noise CA, two injections of the porphyrin hematin were made, the first with the random noise signal off, the second injection with the noise signal on. The resulting ion current profiles and mass spectra demonstrate acquisition of the hematin mass spectrum, which is devoid of fragment ions, and the structurally informative product ion

spectrum produced via random noise CA. As with interface and injection-induced fragmentation described above, random noise MS/MS product ion spectra may be obtained for alternate mass scans allowing for the acquisition of molecular weight and structure information in a single experiment. However, by adding additional control logic it was possible to perform random noise CA during alternate mass scans without the need to download separate scan functions. All data are acquired into a single data file, but can be deconvoluted following the experiment to yield a data file of mass spectra and another data file with the MS/MS spectra of each eluting component. By performing experiments in this manner, the rate of data acquisition is not compromised, as is the case when a key sequence program is used due to computer overhead, allowing more data points to be acquired across an eluting peak.

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Ion Trap Instrumentation

Several recent advances have occurred in the field of quadrupole ion trap mass spectrometry. Among these are enhanced mass resolution, extended mass/charge range operation, and the use of random-noise collisional activation for MS/MS. However, each of the improvements has required the use of external electronics modules. For example, high resolution operation requires a frequency-sweep generator, high mass/charge range employs an amplifier for the resonance excitation signal, and a summing amplifier is needed for random-noise collisional activation. Thus, incorporation of these features in multiple ion trap instruments necessitates duplicate acquisition of electronics.

We have designed two circuits which will reduce the number of external electronics modules required for enhanced operation of the ion trap. The first will allow enhanced mass resolution to be attained by reducing the ramp rate of the rf amplitude (rather than scanning the resonance excitation frequency via an external sweep generator). The scan rate will be selected via panel-mounted thumbwheel switches. The second circuit provides the capabilities for

amplification of the resonance excitation signal and for summing of the random-noise (or other) signals. Printed circuit boards designed for these functions have been installed and tested. They are mounted in the existing ion trap electronics cabinet.

The first commercial quadrupole ion trap, which employed *in situ* electron ionization (EI), was introduced in 1983 as an inexpensive and sensitive mass spectrometric detector for gas chromatography (GC). The latest commercial versions of the device incorporate advanced capabilities such as chemical ionization (CI), automatic gain control (AGC) in EI, automatic reaction control (ARC) in CI, and axial modulation. The next logical step in the advancement of quadrupole ion traps as GC detectors is implementation of routine methods for performing MS/MS analysis. The protocol for MS/MS has been well established in the ion trap mass spectrometer, a sophisticated version of the ion trap GC detector, with collisional activation (CA) being the most generally employed method for inducing fragmentation. As currently practiced, CA in the ion trap is accomplished via application of a discrete, supplementary rf signal to the end cap electrodes to kinetically excite ions based on their mass/charge. Although GC-

MS/MS using CA has been demonstrated with the ITMS, the complex time (and sample) consuming "tuning" involved with discrete-frequency CA limits the practicality of ion trap MS/MS experiments for on-line GC/MS applications.

Recently, our group demonstrated that random noise applied to the end caps of a quadrupole ion trap was an effective means for CA of stored ions. The technique overcomes the problems associated with mass/charge dependent excitation, ion space charge, and limited fragmentation. As such, an ideal application of this technique is with on-line separation applications for which the limitations of discrete-frequency CA are most severe. We have now implemented GC-MS/MS on a bench-top quadrupole ion trap-based instrument using random noise to effect CA. By incorporating additional control logic for the random noise, it was possible to perform CA during alternating mass scans without the need for downloading separate scan functions. Thus, because the data acquisition rate was not compromised, both mass and MS/MS spectra could be acquired during the period of peak elution.

The method was demonstrated for applications using both EI and CI in order to illustrate two important scenarios in which

MS/MS coupled with GC separation is of utility. The first case involved analytes that, when ionized by EI, show very little fragmentation. Consequently, though the molecular weight of such compounds could be determined from the mass spectra, little structural information was available. However, the MS/MS spectrum of the molecular species could be used to confirm the presence of a specific analyte. A second scenario concerned analytes which, when ionized by EI, fragment extensively so that no molecular species is readily discernable and only low-mass fragments offering little useful structural information are observed. However, CI gave a molecular species from which the molecular weight was ascertained, and its MS/MS spectrum yielded structural information which was not present in the CI mass spectrum.

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Multiply Charged Biomolecules-Oligonucleotides

Electrospray typically forms multiply charged species from biopolymers such as peptides, proteins, and oligonucleotides. Our group has taken a particular interest this year in the behavior of multiply charged oligonucleotides. We have characterized this class of compounds phenomenologically with respect to their activation and dissociation in the quadrupole ion trap. The observations were condensed in terms of a set of rules and guidelines to help sequence the oligonucleotide in question using the MS and MS/MS spectra. Also, mechanisms have been proposed and tested to rationalize these rules and guidelines.

The first decomposition step involves the loss of a base with the order of preference being A->>T->G->C-. We hypothesize that this order follows that of the relative gas-phase acidities of the bases. We also hypothesize that coulombic repulsion is responsible for the loss of negatively charged bases in highly charged oligonucleotides. MS/MS spectra of each of the four monomeric nucleotides, which were phosphorylated at either the 3' or the 5' carbon, were examined and the loss of the

base as a neutral was observed to dominate. This suggests that, without the presence of other nearby negative charges, the base tends not to carry the charge. The situation for various charge states of a tetramer was simulated using a commercially available graphical software which included a molecular geometry optimization package. The $d(A)_4$ oligonucleotide was modeled and its geometry optimized using an MNDO algorithm. The intramolecular coulombic forces in the triply and doubly charged forms of the $d(A)_4$ molecule were each estimated. It was found that the triply charged ion relieved a large portion of its coulombic repulsion by allowing one charge to reside on one of the adenines (through intramolecular proton transfer). This energy minimization was not as large in the case of the doubly charged molecule because the two negative charges could be separated if the phosphate group in the center was neutralized and the two phosphate groups on either side kept the charges. The combination of these estimations and the monomer data support the hypothesis that coulombic repulsion plays a key role in promoting the loss of negatively charged bases.

The oligonucleotide $d(A)_4$ is also being studied in greater detail to characterize the

behavior of multiply charged biopolymers. Energy-resolved and time-resolved MS/MS of triply and doubly charged $d(A)_4$ were carried out and the data clearly indicate that the former is far more fragile in the gas phase. This presumably is due to its larger intramolecular coulombic repulsion: the triply charged molecule requires less energy to fragment. A procedure is being developed to combine the energy-resolved and time-resolved MS/MS data in order to quantitatively compare the relationship between charge state and threshold for dissociation.

The ions produced by ES of sodium salts of oligonucleotides have the form $(M-nNa^+)^{n-}$ and $(M-nNa^++mH^+)^{(n-m)-}$. A multiplicity of charge states for molecular anions and CID product ions is often observed. The large number of possible fragment ions and charge states in the MS/MS spectra increases the interpretation burden on the spectrometrists. Thus, a program has been written which performs a number of useful calculations for an input oligonucleotide sequence and finds useful features in the MS/MS spectra of unknown oligonucleotides.

Program options currently include calculation of molecular weight, possible

ES/MS ions, and possible MS/MS product ions for an input sequence. These calculations are useful in the empirical exploration of the fragmentation pathways of this important class of ions. Program options to facilitate analysis of unknown oligonucleotides include the calculation of possible base compositions for an input ion m/z and charge state, identification of ions corresponding to base loss with charge retention ($-B^+$) and neutral base loss ($-BH$), and the identification of complementary ions produced by charge separation fragmentation.

Our experience to date indicates that a significant fragmentation pathway for these ions involves cleavage at the 5'-sugar-phosphate bonds in the oligonucleotide. Ions coming from the 5' end of the molecule have been designated "a" ions and the ions coming from the 3' end of the molecule have been designated "w" ions. The charge on the oligonucleotide anions usually resides on the phosphate groups; however, charge may also reside on the bases (e.g. $-B^+$). In some cases, "a" and "w" ions are observed with different charge states in the same spectrum due to intramolecular proton transfer. A working model for the mechanism of this important fragmentation pathway that accounts for the

proton transfers has enabled accurate m/z calculation of the MS/MS product ions.

It is anticipated that as our knowledge of the fragmentation pathways of these ions increase, we will be able to develop a set of interpretation rules that can be used for unknown oligonucleotides. Generation of candidate sequences using constraints obtained by applying the rules to the MS/MS spectra of a unknown oligonucleotide should then be possible.

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Program

Micellar Electrokinetic Capillary Chromatography

The initial step in measuring base damage in DNA generally involves enzymatic digestion or chemical hydrolysis to yield small fragments that may be resolved from normal unmodified constituents. The digestion products may contain fractions of unhydrolyzed DNA (long and short-chain oligonucleotides), deoxyribonucleoside

monophosphates, and nucleosides. Separations of these mixtures have been obtained by ion-exchange or size-exclusion liquid chromatography. Micellar electrokinetic capillary chromatography (MECC), however, is an attractive alternative to these methods because of the high efficiency and speed of analysis. Recently the separation of mono-, di-, and triphosphate nucleosides using anionic and cationic detergents has been demonstrated. The positively charged micelles electrostatically attract the negatively charged nucleotides and also adhere to the negatively charged fused-silica capillary walls, altering the electroosmotic flow. This results in an expansion of the time window available for separation and increases the peak capacity. For neutral solutes additional selectivity in the separation process is provided by differential partition mechanisms between the hydrophobic interior of the micelle and the aqueous buffer. In view of these advantages we are investigating the use of cationic surfactants for the separation of phosphorylated photoproducts, mono- and di-nucleotides, and nucleosides. Using dodecyltrimethylammonium bromide we have been able to obtain rapid separations (within 5 minutes) at -25 to -30 kV for a

variety of these compounds including dinucleotides differing only in the relative position of the bases (e.g., dCpT from dTpC). The effect of the hydrophobic character of the surfactant will be examined using detergents with different structures.

Investigations on the separations of nucleosides and nucleotides in MECC have primarily focused on the use of phosphate buffers containing sodium dodecyl sulfate (SDS). Since increased interactions between positively charged micelles and negatively charged solutes may provide additional selectivity, we have examined cationic detergents (dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide) for the separation of structurally similar phosphorylated photoproducts, dinucleoside and mononucleoside monophosphates, and nucleosides. The highest column efficiency and overall best resolution for all charged solutes under investigation were obtained using tetradecyltrimethylammonium bromide (TDTAB). Three of the four photoproducts of dUpT including two geometric isomers were resolved and separated from the remaining 20 solutes in less than 6 minutes at -25 kV. Differences in selectivity between the cationic detergents were observed but improvements in resolution were not found

to correlate with the length of the alkyl chain of the surfactant. The photoproducts and all the dinucleotides were found to coelute using SDS, although this anionic surfactant offered the best resolution of neutral nucleosides. We conclude that MECC using TDTAB may be an effective means of examining DNA digests for base damage following exposure of isolated DNA to UV radiation. Concentration detection limits for the photoproducts were determined to be in the low μM range and these base-modified compounds were found to migrate prior to all other normal constituents that could interfere with an analysis.

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Explosives Detection by Tandem Mass Spectrometry

Our group has been involved in the detection of vapors of explosives by tandem mass spectrometry for several years. A variety of activities took place within the context of this application. Automation of a

triple quadrupole instrument for explosives detection and fundamental studies concerning the role of gas dynamics on the formation of anions in atmospheric sampling glow discharge ionization (ASGDI) are described herein.

A new ASGDI source used in conjunction with mass spectrometry for direct air monitoring was designed so that several key instrumental dimensions as well as operating parameters could be readily changed. Such flexibility permitted the study of ionization processes in ASGDI and the parameters that can be controlled to favor a particular ion product. One aspect of ASGDI that was found to influence ionization yield was the hydrodynamic properties of the sample inlet free-jet expansion. From these investigations it was found that mean molecular flow of species expanding toward the skimmer could be manipulated to favor kinetically fast reactions over more thermodynamically preferred reactions. In the case of 2,4-dinitrotoluene, observations of the M^+ ion could be enhanced relative to anions derived from the air-matrix background.

A mechanism for ion formation was discerned from source pressure experiments. Because source conditions that favor optimal

DNT anion signals can be achieved without the presence of background species, electron capture is believed to be the primary ionization mechanism. The high gas density environment near the expansion may promote associative electron capture and subsequent stabilization through third-body collision; it may also provide a means to moderate electron energy through inelastic collision for resonant electron capture.

A prototype explosives detector has been developed based on a modified Finnigan TSQ-700 mass spectrometer. One of the important characteristics of this instrument is the ability to easily perform MS/MS experiments under computer control. An MS/MS experiment involves the fragmentation of molecular species to derive structural information in addition to the molecular weight of the ionic species introduced into the mass spectrometer. The ion source for this instrument was removed and replaced with an atmospheric sampling glow discharge source developed in this laboratory. Under the conditions identified for this work, molecular anions of molecules present in ambient air are formed and introduced into the TSQ-700 for mass analysis. This application requires that a positive identification of an explosive be

made with minimal intervention from a nontechnical user. Consequently, a turnkey application was written using Finnigan's instrument control language (ICL).

The top level menu of the ORNL Explosives Detector software displays three "buttons". The options represented by these buttons are Tune and Calibrate System, Start Monitoring, and Reset Background. The user selects options by clicking a button with a mouse-controlled cursor. If the first button is selected, an automated tune procedure is invoked to maximize ion transmission in negative ion mode. This procedure is followed by one that calibrates m/z assignment. If the second button is clicked, a procedure begins to monitor the conventional mass spectrum for the presence of parent ions indicative of the explosives of interest (i.e., m/z 176 - RDX, m/z 182 - DNT, m/z 227 - TNT and m/z 240 - PETN). If one of these ions is detected above a specified threshold, a warning is issued to the user and the instrument switches to MS/MS mode. The parent ion is then fragmented by collisions with a neutral gas within the collision octapole. The collision-induced products are then analyzed by a second quadrupole mass filter. If CID product ions indicative of the explosive molecule are

observed, an alert is issued to the user and a warning light flashes. The third main menu option characterizes normal background ions. This system was successfully demonstrated to Federal Aviation Administration representatives this summer.

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Comparison of Electron Ionization and Chemical Ionization

The following generic equation can be used to determine the number of analyte (A) ions formed in EI and CI experiments:

$$A^+ = I_0(1 - e^{-\beta l(A)})$$

In EI, I_0 is the number of ionizing electrons and β is the product of the ionization cross-section and the path length. In CI, I_0 is the number of reagent ions and β is the product of the reaction rate constant and the reaction

time. In typical beam instruments, the only variable in the equation that is easily changed is the number of ionizing electrons, which is achieved by changing the emission current. In a quadrupole ion trap the number of ionizing electrons can also be changed by varying the length of the ionization pulse. In CI experiments on an ion trap, the reaction time can be readily varied as well, whereas most beam instruments have a set reaction period. EI experiments on a beam instrument and an ion trap are similar, but there are fundamental differences in the CI experiment. First, the reagent gas pressure is several orders of magnitude lower in the ion trap experiment. More importantly, I_0 is a couple of orders of magnitude lower in the ion trap. This can be partially compensated for by increasing the reaction time, though this is limited because the number of reagent ions continually decreases in the ion trap experiment. New reagent ions, however, are continually being generated in the beam instrument.

To evaluate the relative sensitivities of the two ionization methods, we studied two compounds on the Finnigan MAT TSQ 700 (beam) and the Finnigan MAT ITS-40 (ion trap). Varying levels of benzophenone and N,N-dimethylaniline were injected onto a

Varian 3400 GC coupled to the instruments. The ionization time (EI) and the reaction time (CI) were varied on the quadrupole ion trap experiments. The EI and CI experiments on the TSQ 700 were carried out without any parameters being changed. Methane was the CI reagent gas on both instruments.

On the quadrupole ion trap, as the ionization period was increased for 160 pg of benzophenone, the response of the major ions increased linearly. When the response of the molecular ion is plotted as a function of the amount injected, a tenfold increase in response is observed when the ionization time is increased from 1 ms to 10 ms. The response of the higher analyte level begins to tail off because of space charge effects in the ion trap. This effectively reduces the dynamic range available and reduces sensitivity. A corresponding plot for CI shows a tenfold increase in the response of the protonated molecule of benzophenone when the reaction time is increased from 10 to 100 ms. To overcome problems of space charging, the AGC and ARC scan functions were used to obtain good sensitivity without compromising dynamic range for comparing EI and CI sensitivities and detectability.

ITS-40 data show that the sensitivity (slope) of the molecular ion (EI) and the protonated molecule (CI) for N,N-dimethylaniline are nearly equal. But EI would seem to offer better detection limits given that the intercept is higher (provided that the background is the same, the line with the higher intercept should give the better detection limit). This is in contrast to the result obtained on the TSQ 700 where CI has the better detection limit. Data for benzophenone on the ion trap also show EI detection limits about 50 times better when comparing molecular species and about 100 times better when looking at the total ion current. Hence, it appears that the detection limits for CI on the ion trap are hindered by the lower number of reagent ions, I_0 .

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**Geoporphyrin Analysis
Using Electrospray Ionization
Mass Spectrometry**

One general theme in our research over the last several years has been the development of new and better ways to analyze porphyrins by mass spectrometry (MS). Some of our recent work has demonstrated the general utility of electrospray (ES) ionization combined with MS for the analysis of a wide variety of free-base porphyrins and metalloporphyrins. In our most recent work, we have been evaluating the use of ES/MS for geoporphyrin analysis. Results from the initial work indicated that ES offered several advantages for geoporphyrin analysis when compared to some of the other ionization techniques currently in use. First, because of their nonvolatility, geoporphyrins are generally introduced to the mass spectrometer for analysis by EI or CI via heating from a solids probe. Molecular weight and structural data can be obtained from pure compounds in this manner, but fragmentation, differential volatilities of the porphyrins in the mixture, and condensation of the porphyrins on the walls of the ion source inhibit the analysis of mixtures.

Fragmentation is reduced in EI, allowing the analysis of mixtures by lowering the electron energy (12-14 eV) used for ionization. However, ionization efficiency is reduced resulting in poorer detection limits, and the problem of differential volatilities remains. In addition to the volatility problem, mixture analysis is hindered with CI-MS because a plethora of molecular species and fragment ions, the abundances of which depend on a difficult to reproduce ion source phenomenon, can be formed. With ES the porphyrin ions are transferred from a solution-phase to the gas-phase without heating, circumventing the problem of differential volatilities. Also, in most cases only one molecular species is produced from each porphyrin by ES and no fragment ions are generated. Thus, the technique has several advantages. First, it may be used to determine porphyrin molecular weights and might possibly be used to accurately determine the relative abundances of the porphyrins within complex porphyrin mixtures. Second, a wide variety of solvents can be sprayed so that the solubility of the porphyrins, which can sometimes limit the applicability of fast atom bombardment (FAB), flow-FAB, and thermospray, is usually not a problem with ES/MS. And

third, ES is readily coupled with any of several separation techniques, including microbore- and packed capillary-HPLC and capillary electrophoresis, so that on-line separation/mass analysis of the analytes of interest is possible with ES ionization.

Geoporphyrin-like standards, e.g., free-base, nickel, and vanadyl chelates of octaethylporphyrin (OEP) and etioporphyrin-III (etio-III), as well as geoporphyrins isolated from Gilsonite bitumen were analyzed by ES/MS using continuous infusion, flow injection, and on-line microbore-HPLC. As expected, a single molecular species was produced from these porphyrins and no ES produced fragment ions were observed. Detection limits using continuous infusion at 1-5 $\mu\text{L}/\text{min}$ required sampling as little as 1 femtomole of material, while at these same flow-rates, 18 femtomoles of OEP could be detected via flow injection. However, because of sample impurities, spectra with suitable signal-to-background for unambiguous identification of unknowns required injection of about 400 femtomoles. Detection of 500 femtomoles of mesoporphyrin IX dimethyl ester was demonstrated using on-line reverse-phase microbore-HPLC at solvent flow rates of 40 $\mu\text{L}/\text{min}$. Spectra obtained at these levels

had good signal-to-background such that the molecular weight of the eluting component was easily determined.

The ability to use ES/MS to accurately determine the relative abundances of the porphyrins within geoporphyrin mixtures was demonstrated using standard solutions containing known molar ratios of OEP and etio-III as determined by weighing and UV/visible spectrophotometry. With this methodology established, the porphyrin distribution in Gilsonite bitumen was determined via three sequential flow injection experiments. Average data from three injections, requiring about 5 minutes total analysis time, matched literature values for the porphyrin distribution within this sample. The major advantage of the ES/MS for this determination is the sensitive, rapid and reproducible nature of the measurement.

A reverse-phase separation (300 Å ODS (1 mm X 100 mm), 40 $\mu\text{L}/\text{min}$, 75% methanol/25% water/0.1% trifluoroacetic acid to 95% methanol/5% water/0.1% trifluoroacetic acid in 15 min) was used in the on-line HPLC/ES/MS analysis of the total free-base porphyrin mixture isolated from Gilsonite bitumen. The two porphyrin structural types in the mixture, etioporphyrins and those containing an exocyclic ring,

i.e., cycloalkanoporphyrins (CAP), were completely separated from one another with the etioporphyrins eluting first. Within each structural type the porphyrins separated by carbon number with the higher carbon number species eluting at longer times. All the known porphyrins in the mixture were detected including the major isomeric species of the etio type. In addition, minor DPEP components of high carbon number (i.e., C₃₄ and C₃₅) were also detected in the mixture. Nickel Gilsonite porphyrins separated on-line using different reverse-phase conditions showed similar elution behavior.

Based on results obtained to date, ES/MS and HPLC/ES/MS are proving to be superior mass spectrometric methods for the determination of geoporphyrin molecular weights and the relative abundances of geoporphyrins within complex porphyrin mixtures.

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INORGANIC MASS SPECTROMETRY

D. H. Smith

The Inorganic Mass Spectrometry Group carries out both research and support activities. Several kinds of mass spectrometers are available to be used as indicated by the analytical problem. These include glow discharge, thermal emission, spark source, gas, and secondary ionization instruments.

Last year at this time, we reported that funding had been obtained to renovate space in Building 5505 (Transuranium Laboratory) for our use. The design phase is now finished and a contractor selected. Work, begun in November, is expected to be completed in the first quarter of 1993.

A new gas mass spectrometer, a VG1401, was obtained and installed this year. After a few months of service at Y-12, it was moved to Building 5510A, where it is now in the last stages of installation.

We added two new members to the research staff this year, Doug Duckworth and Chris Barshick. They are working in glow discharge mass spectrometry and have made significant contributions to this exciting area.

Their presence has resulted in increased collaboration with outside scientists. Work with George Swihart of Memphis State University in boron isotopic analysis continued, as did collaboration with Ken Marcus of Clemson University in rf-powered glow discharge development. Work with Fred King of West Virginia University in the area of graphite analysis was initiated.

Work continued on converting our lutetium double-spike method for use at the Power Reactor and Nuclear Fuel Development Corporation (PNC) in Japan.

An isotope dilution technique to assay lithium in a lithium-aluminum alloy was developed in support of a Savannah River project. Our IMMA secondary ion mass spectrometer was used in this application. We also developed techniques to analyze many (a dozen or more) elements using either thermal emission or secondary ion mass spectrometry.

RF-Powered Glow Discharge Mass Spectrometry on the VG9000

Several recent advances in the development of the rf glow discharge source for the VG9000 have been made this year. Modifications to the source have allowed more consistent operation at the desirable 8 kV accelerating potential, where an improvement in ion extraction over lower voltages is realized. Large ion energy distributions, once a limitation, have been minimized through electrical filtering of rf interference from the dc accelerating potential. Ion energy distributions have been reduced from > 30 eV to ~ 11.5 eV, consistent with that observed during dc operation. Similarly, mass resolving power under rf operation is nearly equivalent to that of the dc glow [~ 4000 (5% peak height) at 60% beam intensity]. At present, the limiting feature is sample presentation, which is cumbersome due to the small size of the samples (4.8 mm diameter); an rf source that will accommodate much larger samples is being designed.

We have also performed preliminary comparisons between our standard 13.56 MHz and 40.68 MHz excitation frequencies. These studies revealed that

there may be an advantage in working at the higher frequency. Sputter yields were a factor of 3-5 times greater at 40.68 MHz owing to a better coupling efficiency of power to the discharge. The higher sputter yields contribute to an increase in ion beam intensity. Operation at 40.68 MHz is more difficult, however, due to rf interference, and the evaluation of higher frequency operation is still in progress.

D. C. Duckworth, D. H. Smith

Glow Discharge/Ion Trap Mass Spectrometry

A new and promising collaborative project between the inorganic and organic groups of the Analytical Spectroscopy section involves the coupling of glow discharge sources (rf and dc) to a quadrupole ion trap mass spectrometer (GD/MS). The benefits of the glow discharge are direct solid analysis, similar elemental sensitivities, broad elemental coverage, and low cost; these complement the versatile, compact, and relatively inexpensive ion trap mass spectrometer.

There are several advantageous features

of the technique which have been demonstrated, including a relatively high temperature environment in which many loosely bound polyatomics (a common problem in GD/MS) are spontaneously dissociated. Of the more tenaciously bound species, nearly 100% can be dissociated in the trap via axial modulation. Gas phase reactions were also observed and promise to be a source of interesting fundamental gas phase chemistry studies.

Our most recent studies have focussed on extending the dynamic range of the trap for quantification of glow-discharge-generated species. It is necessary to accumulate the ions of interest using several isolation techniques during injection. Undesirable ions, such as those derived from argon (utilized as the discharge support gas) and the matrix which tend to fill the trap preferentially, are discriminated against by judiciously selecting appropriate trapping conditions. This has been done quite successfully, increasing the dynamic range of the technique from $< 10^1$ to nearly 10^6 .

Because these selective accumulation schemes only work over a small mass range, we have developed means of coupling these single-element scan functions into a multiramp function. Such a scan function

provides a possible means of quantification, and standard materials are currently being investigated.

We are also in the process of assembling a second quadrupole ion trap in the Inorganic Mass Spectrometry group which will be dedicated to GD/ITMS development. This system should be on-line in early 1993.

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Solution Residue Analysis

Although GD/MS has traditionally been used to analyze solid samples, many instances arise where the sample of interest is in an aqueous medium. Previously, this type of analysis has been accomplished using atomic absorption, inductively coupled plasma emission, or, more recently, inductively coupled plasma mass spectrometry. There are instances, however, where the sample volume is too small for conventional solution nebulization, or the analyte concentration is already too low to allow dilution of the sample to a suitable volume; with these samples, thermal atomization approaches (graphite furnace atomic absorption, or

electrothermal atomization in conjunction with inductively coupled plasma emission spectroscopy) are often employed. It is well recognized, however, that one of the shortcomings of these thermal atomization approaches is the transient nature of the analyte signal. We have, therefore, been evaluating new ways of preparing glow discharge sample cathodes that permit the acquisition of data for several hours (instead of minutes) using small aliquots of solution. To date our most successful cathode preparation technique involves mixing a 200 μL aliquot of the sample solution with a pure conducting powder, followed by drying and pressing prior to conventional GD/MS analysis. Preliminary results indicate that the analyte signal is stable to better than 5% for the duration of the analysis. Internal and external reproducibles were also evaluated and found to be better than 5%. The ion signal intensity was linear with concentration over at least 4 orders of magnitude, and preliminary detection limits are on the order of 0.3 ppm in a 200 μL volume of solution. Quantification was demonstrated using user-defined relative sensitivity factors, and relative standard deviations were better than 15% for the elements investigated; there was no preconcentration of the analyte.

This method, because it is solution-based, is well suited for analyzing samples where conventional GD/MS cathode preparation has a shortcoming (< 1 mg of sample). Although the results were obtained from solution residues, we hope to be able to analyze small samples originating as solids using similar techniques, and we are continuing to investigate this possibility. We also believe that this technique has a yet-untapped potential for application to environmentally important samples where only small amounts and low concentrations are available.

C. M. Barshick, D. H. Smith

Isotopic GD/MS

We continue to evaluate how well the VG9000 glow discharge mass spectrometer measures isotope ratios by compiling a data base on the accuracy and precision of the technique for a wide range of elements at various concentrations. Although it is well recognized that GD/MS isotope ratio precision will not rival that of thermal ionization mass spectrometry (TIMS), some applications do not require the high precision

of the TIMS technique, and GD/MS could therefore present a great cost savings in sample preparation time. An example of one such instance is the $^{10}\text{B}^+ / ^{11}\text{B}^+$ ratio. Performed with a 1% boron sample, this ratio was measured with the hope that good enough precision could be obtained to warrant measuring several samples of interest to Dr. George Swihart (professor of geology at Memphis State University). Preliminary results indicate that a 0.15% relative standard deviation and < 1% isotopic bias can be routinely obtained (good enough for samples exhibiting a 1% - 5% variation in boron composition).

Another area where isotopic GD/MS is important is in the development of isotope dilution as a complementary technique for our solution residue project. Preliminary results indicate that much of the associated error comes from the measurement of isotopes near the detection limit, and various counting schemes are presently being evaluated to improve this measurement. Our goal is to obtain a better than 5% relative standard deviation, which will be a significant improvement over calibration curve methods.

A third challenge of isotopic GD/MS is the measurement of elements in difficult matrices such as soils. A preliminary

measurement of the $^{235}\text{U}/^{238}\text{U}$ ratio of uranium (~ 65 ppm) in a soil of unknown origin showed a good correlation to TIMS data. It is the ultimate goal of this work to use an rf glow discharge to determine these ratios directly without first having to mix the soil with a conducting matrix.

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UTI Quadrupole Evaluation for NASA

Work continued this year for the National Aeronautics and Space Administration in evaluating a UTI quadrupole mass spectrometer configured for gas analysis. This instrument is being considered as a possible replacement of the present system to monitor hazardous gas levels during launch operations of the space shuttle fleet. To test the instrument's capability in accurately measuring gas compositions, standards were commercially prepared to approximate what is expected during launch operations. After numerous measurements of these standards, relative levels of sensitivity, accuracy, and precision

for the instrument were determined; these met the acceptance criteria NASA has mandated. In addition, studies have been made of data acquisition rates to determine the minimum times appropriate for a useful analysis. Currently, three averages of 1 second per mass for each mass of interest yields relative standard deviations of $\pm 0.2\%$. With some software manipulation, shorter dwell times per mass are possible, which could shorten the time necessary for an acceptable analysis.

Some problem areas were noted in the studies. One is the difference in sensitivity factors for gases having the same elemental components, and differing only in the abundance of these components. This may be due to pressure differences among gases in the ion source when calibration scans are taken. Another possibility is that the composition of the gas may actually be different from that certified by the manufacturer. A second problem is a tendency for reactive gases to require longer inlet conditioning times as compared to nonreactive gases. This problem in sampling, however, is a universal analytical problem and is attributed to the various degrees of adsorption of gases in the sampling stream to metal surfaces. These problems seem related

to factors other than instrumental performance, and can usually be compensated for. Recommendations will be made to NASA on how to minimize these effects.

Recently the instrument has been moved to its new location in Building 5510A and is now operational. A gas inlet modification is planned to compensate for ion source pressure variations among the differing gas standards caused by poor control of the gas bottle regulators. In-line particulate filters will be installed for each gas line to protect and extend the lifetime of the 16 position rotary inlet valve. In the coming months we plan to evaluate the instrument's clearing times between the closing off of one gas and the admission of another. Experiments will also be made to establish the times required for a gas to reach 90% of its certified value once admitted into the inlet system.

E. H. McBay, D. H. Smith

Tank Calibration Using a Lutetium Double Spike

The lutetium double-spike method addresses one of the most difficult areas in the nuclear fuel cycle for which to obtain a fissile-isotope inventory: holding tanks containing solutions of spent reactor fuel. Demonstrations of the utility of our technique have been described in previous Annual Reports.

The focus for research efforts in 1992 was to eliminate elements from the tank sample that interfere with isotopic lutetium analysis. Particular emphasis was placed on a chemical separation technique that would isolate lutetium from tank solutions specific to PNC in Japan in a manner that met PNC hot cell requirements. Specifically, the isolation procedure would have to remove relatively large quantities of gadolinium and uranium from a sample without the use of solvent extraction or hydrochloric acid-based chemistry. In addition, a majority of the radioactive nuclides must also be removed from the sample to allow PNC staff to load the final sample into the mass spectrometer for isotopic analysis.

A series of commercially available, solid phase extraction (SPE) columns have

replaced the conventional solvent extraction techniques used to isolate lutetium from tank samples. The separation columns eliminate the need to agitate the solutions during the chemical processing of samples, the need to separate small volumes of transparent liquid phases using hot cell manipulators, and does not require the use of hydrochloric acid. Lutetium isolation is accomplished by introducing a 1:100 dilution of the initial tank sample at the head of a U/TEVA™ prepacked column (ElChroM Industries, Inc.). The effluent is allowed to drain directly into a RE.Spec™ column. The U/TEVA™ column is then rinsed with 2 mL of 2M HNO₃ to transfer the tank sample into the second column while retaining uranium and other actinides. The U/TEVA™ column is discarded at this point. A 0.5 mL post-column of inert support material is then positioned to the exit of the RE.Spec™ column to remove trace organic material that is washed from the SPE columns. An additional 5-10 mL 2M HNO₃ is used to wash all elements except rare earth elements from the RE.Spec™ column. Lutetium is then separated from the remaining rare earths by washing the RE.Spec™ column with a final 10 mL 2M HNO₃. The 10 mL acid fraction contains greater than 80% of the initial lutetium

added to the tandem SPE columns and can be evaporated to incipient dryness prior to isotopic analysis.

D. A. Bostick, D. H. Smith

SECONDARY ION MASS SPECTROMETRY

Peter J. Todd

The research of this group is directed toward improving the scope of analyses that can be performed by secondary ion mass spectrometry (SIMS). This includes analysis and development of spectrometer systems and methods, as well as fundamental research related to the performance of analysis by SIMS. Collaborations within ORNL, Energy Systems, national and international communities have been consistently encouraged because the need for development is mainly determined by the difference between analytical needs and existing technology.

Instrumentation and direction within the group are roughly divided between organic and inorganic SIMS. Two new organic instruments have been brought on-line during this year. They are the secondary ion tandem microprobe (SIMS/MS), which was designed and built at ORNL, and the JEOL SX-102A high resolution mass spectrometer. These instruments complement the existing Cameca ims 4f used for inorganic SIMS, and two prototype instruments under

development. These instruments serve not only as experimental test benches, but unique assets for collaborative research.

Inorganic SIMS Particle Search and Analysis Using Digital-Imaging SIMS

Using a digital-imaging interface and software upgrade from Charles Evans and Associates for our Cameca ims 4f ion microscope/microprobe, we are characterizing chromium-rich soil particles by size, position, and semiquantitative analysis. Two routines are being used. The first employs an automated two-dimensional step scan (2DSS). In this routine a selected sputter area or raster scan is stepped back and forth across the sample in a two-dimensional pattern by moving the sample stage a pre-selected step size. The total secondary ion counts of up to 14 elements or isotopes in each field (defined by the scan size) can be collected and displayed as a line graph of ion counts versus field or cycle, or as an element map. Variables include the collection time for each isotope, the scan size ($< 500 \mu\text{m}$), the step size (usually chosen to match the scan size), and the number of steps

(maximum of 10 x 10). By examining the element maps of the X,Y fields or the plot of ion counts versus cycles, the operator may step the sample stage to any of the (X,Y) fields to collect digital images of selected elements and analyze selected particles by line scans or area sums. For example, using a 5 nA O_2^+ primary beam accelerated by 8 kV and a secondary ion mass resolution of 5000, we collected the total ion counts of Al and Fe (60 s) and Cr and Ni (120 s) in a 4 x 4 array using a 250 micron scan and step size (1 mm² area) from soil particles self-cemented on a carbon planchet. Examination of the digital images of the (1,3) field of those four elements reveals two Cr-rich particles. Element area sums indicate that one particle contains primarily Cr, while the other particle appears to be a Cr-rich clay.

The major advantage of the 2DSS approach is that it provides a means of pre-screening fields for a particular element or combination of elements without collecting images for 14 different elements. The major disadvantage is that it is difficult to distinguish between a field which may contain a few particles rich in an element of interest and another field which may contain many particles poor in the element of

interest if their total count rates are similar.

The second routine, Particle Search (PS), also collects data from a selected raster scan which is stepped in a two-dimensional pattern across the sample with the same options for step size, raster size, collection time, and array size as the step scan routine. In PS, however, ion images of only two elements are collected in each field of the array. Particles composed of either or both of those two components are identified if they exceed an operator-selected value for the minimum number of ion counts from a set of contiguous valid pixels. Valid pixels are set by the operator to represent a certain number of ion counts above the noise. All valid pixels from the two image fields are represented in registration on a third field. Comparison with the two image fields allows the operator to adjust the particle and pixel thresholds to mirror the actual shape and size of the particles. Particles are also tabulated by their physical location on the sample, ion counts for each element, a count ratio, and the number of valid pixels in the particle. A maximum of 254 particles can be identified in each field. For example, using the same conditions and scanning the same area as the 2DSS routine, 10 Cr-rich particles were identified in the (1,3) field, including

the two particles identified with 2DSS, and 211 particles with radii ranging in size from 3 to 15 microns in the 1 mm², 4 x 4 field array. Radii were calculated by assuming that each particle was spherical. A plot of Cr signal intensity per pixel vs. radius revealed at least three groupings of particles based on the strength of their Cr signal intensity. The advantages of the Particle Search routine are clear. If operator-controlled parameters can be adjusted to mirror the actual particle shape and size, a complete list of particles in an array can be rapidly identified by ion counts, number of pixels, and physical location on the sample. The disadvantages are that it requires prior knowledge of the particles to determine which two elements to image and it generates a large amount of data by collecting two images per field in the array.

Although it may be time consuming, additional analysis of the individual particles found using either routine is readily accomplished by reducing the beam size or raster size and beam intensity. For example, the mass spectra of the two larger particles identified in the (1,3) field reveal that one particle is nearly pure Cr and the other is Cr-rich clay (Mg, Al, Si, Fe, etc.). Future work will be required, however, to improve

classification of the particles. It will also be necessary to develop standards for semiquantitative analysis.

T. M. Rosseel, W. H. Christie

Analysis of Rare Earth Elements Using SIMS and Doubly Charged Ions

The elemental distribution of the rare earth elements (REE) Z's of 57-71 or lanthanides provides important petrogenic information for geological samples. Unlike bulk analytical techniques (instrumental neutron activation, isotope dilution mass spectrometry) which generally require at least a milligram of sample, SIMS offers the possibility of quantitative analysis of the REE on a fine scale (< 20 microns) while preserving important textural relations. Previous attempts to use SIMS have utilized three techniques to overcome analysis problems caused by the interference of oxide peaks in the secondary ion spectra: high mass resolution, specimen isolation, and moderate energy-offset, spectral-stripping. The intensity of the secondary ion spectra is so reduced using high mass resolution that sensitivities are too low for practical use.

Specimen isolation utilizes sample charging to provide a form of extreme energy filtering, which eliminates the interfering oxide peaks. However, proper charging conditions cannot be maintained for beam sizes < 100 microns, limiting the applicability of this technique to large samples. The moderate energy-filtering spectral-stripping technique is the most commonly used technique. However, the need to analyze all 55 REE and interfering oxide peaks makes this technique very time consuming, and matrix deconvolution can lead to the propagation of relatively large errors in the analysis of the heavy rare earth elements.

We have pioneered a technique using odd-mass doubly charged ions for quantitative analysis of REE in silicates. Since the odd-mass, doubly charged ions fall at half mass units, the peaks are generally interference-free, allowing analysis without the need for energy offsets or deconvolution of the secondary ion spectra. Using a suite of natural and glass clinopyroxene standards [ideally (Fe,Mg)CaSi₂O₆], we have established linear calibration curves for thirteen of the REE. Estimated detection limits are < 10 ppb for most elements. Only Gd appears to suffer from interferences, and they only become apparent at low abundances (< 1 ppm). Relative ion yields

have been reproducible within 2 to 6% (depending on the element) for a period of over six months. This technique offers several advantages as compared to other SIMS techniques. Our beam spots are much smaller (< 20 microns versus 100 microns) than those needed for the specimen isolation technique, and no instrument or sample holder modifications are required. As compared to the moderate energy-filtering, spectral-deconvolution technique, analysis of doubly charged ions is roughly five times faster for similar precision, and there is no need for complex spectral-stripping data reduction, since the measured peaks are interference-free.

We are continuing this investigation to determine the applicability of this technique to other silicate phases (garnet, feldspar, and glasses). We also plan to investigate the ionization behavior of doubly charged REE ions relative to matrix effects. This technique may also be applicable to the determination of other elements that suffer from interference problems during SIMS analysis.

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SIMS Characterization of a Multilayer Superconductor Film

A ZnSSe multilayer, superlattice, superconductor film grown on a GaAs substrate was characterized by SIMS. The film consists of alternating layers of 12 nm of $\text{ZnS}_x\text{Se}_{1-x}$ and 24 nm of $\text{ZnS}_y\text{Se}_{1-y}$. A depth profile analysis of the sample, using a 14.5 keV cesium beam, revealed the correct number (33) of alternating layers and the correct intensity variations from layer to layer, within 20%, of sulfur and selenium. The concentration profiles, however, were not square, but sawtooth in appearance. This effect may be due to the sample preparation technique or it may be due to ion beam mixing. We found that lowering the sputter rate did not significantly alter the sawtooth profiles of S and Se, but it did remove the upward drift of the signal as a function of depth. Perhaps the most interesting observation was the dramatic (2 - 3 orders of magnitude) decrease in the S and Se intensity when the external optical microscope light was turned off. Examination of the secondary ion kinetic energy distribution of S revealed that with the light off the sample charged 15 - 20 V.

This had the effect of offsetting the secondary ion kinetic energy distribution or conversely the pass energy and thus decreasing the secondary ion signal. By increasing the light intensity, the surface charging was completely neutralized by the apparent microscope-light-induced (photo) conductivity of the film.

Based on these results it may be possible to fabricate a ZnSSe film capable of evaluating the charge compensation ability of various electron flood guns. It may even be possible to use such a film as a standard for comparing flood guns or competing charge compensation schemes.

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Molecular Doping of GaAs

We are collaborating on a program to develop a novel doping scheme for semiconductors. The goal of the work is to study the incorporation of aluminum and oxygen in GaAs epilayers. The method employed is unique in that instead of using

elemental species or atomic doping, it uses molecular doping. The molecular doping of Al and O is accomplished by using dimethyl aluminum methoxide (DMALMO) during organometallic vapor phase epitaxy (OMVPE). Al-O complexes produced along the growth front during pyrolysis are believed to be incorporated into the crystal. Growth conditions such as substrate temperature, DMALMO flow rate and reactor pressure will be varied in order to better understand the factors which control Al and O doping. With this understanding, growth conditions will be optimized so that it will be possible to fabricate high-resistivity buffer layers. These techniques could lead to new device applications such as metal-semiconductor-metal photodetectors.

In the first phase of our SIMS studies, we are measuring the Al and O concentrations in the GaAs epilayers as a function of the growth conditions. Depth profile data of Al, collected using an oxygen beam, and O, collected using a cesium beam, are converted to concentration using relative sensitivity factors (RSF) referenced to a stable matrix element. Accuracy is usually estimated to be within a factor of two. The depth scale is typically measured with a stylus profilometer which has an accuracy of better

than 10%.

Our initial SIMS measurements verified our sensitivity to Al (ppb) and O (ppm) and have shown that while the concentration of oxygen is inversely related to the substrate temperature, the aluminum concentration was independent of substrate temperature over the range we explored.

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Organic SIMS

The triple quadrupole secondary ion tandem mass spectrometer (SIMS/MS) microprobe developed by us is a unique instrument for a number of reasons. These include unparalleled sensitivity, a large field of view, and the ability to produce images using the combination of secondary ionization and MS/MS. The large field of view ($> 1 \text{ cm}^2$) and high transmission permit images to be obtained under static SIMS conditions; i.e., images can be obtained at primary ion doses so low that effects of primary ion damage are nonexistent. The tandem mass spectrometry capability permits

ions to be distinguished on the basis of their structure, in addition to their mass-to-charge ratio. There are a number of applications for this instrument, including analysis of biological tissue samples, DNA sequencing, and analysis of organic surfaces. In addition, there are a number of experimental and fundamental complications that call for further research.

Perhaps the most stunning accomplishment achieved with this instrument has been imaging of epinephrine in dog adrenal tissue. Images produced show that epinephrine is confined to the medulla, consistent with known anatomy. To our knowledge, this feat has only been accomplished at ORNL, and is the harbinger of spatially resolved biochemical analysis by SIMS/MS. As testament to the sensitivity of the instrument, it is known that within the medulla, epinephrine is confined within granules of less than a few microns in diameter. With static SIMS, the membranes of these granules cannot be breached. The epinephrine ions detected reflect only a small percentage of the total epinephrine present. The validity of this was established by using special surfactants to lyse a small portion of the chromaffin granules. Subsequent analysis by SIMS showed a dramatic increase in

epinephrine-characteristic secondary ions.

The instrument has also been used to observe the distribution of solutes dissolved in glycerol; that is, a dynamic organic surface. Glycerol is commonly used in organic secondary ion mass spectrometry to disperse involatile analytes and permit production of intact secondary ions characteristic of the solute. We were able to show that time dependence of spectra produced from such solutions was a direct consequence of evaporation of the glycerol, and the surface-tension-driven spreading and precipitation of the solute. In short, compounds that are surfactants are uniformly spread across the surface of the sample, whereas nonsurfactants migrate to the periphery of the droplet, and precipitate. These results are important for two reasons. First, they clearly elucidate the origin of a controversy that has continued for years within the organic SIMS community; namely, the cause of time dependence of spectra. Secondly, the results show that in addition to the qualitative and quantitative aspects of organic analysis, determining the spatial distribution of compounds provides unique insight into the sample.

In many ways, a more prosaic aspect of the organic SIMS instrument is the ability to

perform a tremendous volume of analyses in a short period of time. Each secondary ion image produced requires about three minutes, and typically reflects the results of 40,000 analyses. Such a rate of analysis is unique, and may well have applicability to the human genome project. We have demonstrated that when spots of nucleic bases are deposited in an array on a sample target, the identities of the array elements, i.e., the bases, can be reproducibly identified, even when each spot contains less than 10^{-15} moles of base. From these data, we estimate that 10,000 bases could be assayed in about 10 minutes. Were assay by SIMS the rate-determining step in DNA sequencing, it is estimated that the human genome project could be completed within one year, at a cost less than 1 cent/base. All that is necessary is a method to successively cleave the terminal base from a selected strand of DNA. Methods to accomplish this are currently under development in the Health and Safety Research Division.

The most vexing problem associated with SIMS in general and organic SIMS in particular is sample charging. Because of differences between primary ion current and secondary ion and electron currents, samples often develop a large static charge during

analysis. The consequences of sample charging include primary ion beam deflection and suppression of secondary ion emission. We are currently modifying the organic ion microprobe to mitigate this problem.

P. J. Todd, R. T. Short,

J. M. McMahon

Mass Spectrometer Data Systems

Many mass spectrometers and microprobes can be operated either manually or under computer control. *Inherently*, the organic ion microprobe cannot be operated except under computer control. The ion optical system must be continually adjusted for optimal performance as an image is generated from secondary ions emitted from the 1 cm^2 area of a sample. A special data acquisition and control system had to be designed to accomplish the myriad tasks of control and data acquisition for this instrument. Because of the instrument's complexity, it was necessary to develop a system that could, by itself, find optimal control parameters for operation; that is, the computer system was developed so that the instrument tunes itself.

The lessons learned in developing this data system have a number of applications. For example, we have subsequently developed data acquisition and control systems for other experimental mass spectrometers. Mass spectrometers are peculiar in the requirements of their data systems because of the large dynamic range $> 10^9$ and the range of data acquisition rates, which can be as high as 1 MHz. One system currently under development is for a combination ion mobility-triple quadrupole (MS/MS) mass spectrometer. Ion currents detected with this system range from microamps to counts of one ion/ 10 s. Furthermore, there are eighteen separate electrode controls. Other work involves developing a data acquisition/control/data reduction system for sector mass spectrometers employed for environmental analysis. We have developed control systems for autosamplers and automatic purge and trap gas chromatograph/mass spectrometers, and interfaced these systems to existing mass spectrometer data systems.

In related efforts, we have developed data file conversion routines that permit using the data reduction features of one program with the data acquisition capabilities of another. The results of this work have

been increases in sample throughput and system reliability that often show an order of magnitude improvement.

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Image Software

The quality of image data taken from the organic ion microprobe has led us to develop high-quality gray-scale display and hardcopy output systems. Analytical image data are different from other types of analytical data simply on the basis of the sheer volume of data necessary to produce an image. For example, for the organic ion imager, each image can be stored in a file of 160,000 bytes. The quality of images produced can be limited either by the microprobe data or the computer system used to display the data. We have found that by using a nearly continuous gray scale, the veracity of the image presented is greatly improved. For example, artificial contrast is reduced, and the transition from black to

white appears more consistent with known chemical distribution. Existing methods of producing hard copy have been limited to eight discrete steps, so several algorithms were developed to produce images on an HP LaserJet III. Enormous amounts of time were required to print images using these algorithms, and the images showed poor quality. We subsequently acquired a printer driver board from the XLI Corporation which disables part of the HP Laserjet III drive mechanism and sends the printer its own driver commands. By using the XLI board we have achieved a print resolution of 2400 dpi and a true 256 shade gray scale with quick output and reasonable cost. The printed images are suitable for publication as they are essentially photographic quality.

Image software development has now moved to some of the other functions necessary for analyzing SIMS/MS imaging data. Programs have been written to convert microprobe data files into a standard image format (TIFF) so that images can be displayed by almost any image processing program and can be correctly read and displayed on both PC's and Macintosh (Apple) machines. Currently, different methods of reducing MS data acquired from quadrupole mass spectrometers are being

developed. For completeness, mass spectral data are presently stored as waveforms, rather than as stick plots. This allows us to evaluate the performance of the mass spectrometer for all samples, even for data taken years apart. Better routines will eventually be combined into a complete package resulting in an improved version of the original instrument control software as well as an off-line image processing package.

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2. INORGANIC AND RADIOCHEMISTRY

J. R. Stokely

The Inorganic and Radiochemistry section consists of five groups: Inorganic Analysis, Radioactive Materials Analysis, Transuranium and Activation Analysis, Low-Level Radiochemical Analysis, and Special Projects. The section supports a large number of Laboratory and DOE programs in the areas of environmental monitoring and remediation, waste characterization and operations, transuranium element and radioisotope production, and basic and applied R&D. The section is continuing to undergo substantial growth and change due to increased demands for environmental regulatory analyses, new analytical chemistry requirements for environmental, safety, and health activities, and start-up of major new projects. Over the past eighteen months, approximately twenty-five new chemists and laboratory technicians have been added to the section, representing about 40% of the current staff.

Recently we have combined our neutron activation analysis (NAA) activities at the High Flux Isotope Reactor with the analytical chemistry support group located in the Radiochemical Engineering Development Center to form the Transuranium and Activation Analysis Group (TAAG). Although this group's primary work has traditionally been to support ongoing ORNL programs, the group has become involved in several major new developmental projects. A large project to analyze approximately 4,000 soil and sediment samples from the East Fork Poplar Creek flood plain by neutron activation analysis was successfully completed this year. A challenging aspect of this work was to utilize neutron activation analysis and data reporting methods which would comply with the quality assurance requirements of the EPA Contract Laboratory Program (CLP). This, to our knowledge, is the first time that NAA has been used for CLP regulatory analysis and opens the door to possible use of the technique for other regulatory-type analyses. Another similar project is now being developed to provide background soil characterization for

the Oak Ridge DOE Reservation. A number of other new developmental projects are being conducted in the TAAG.

The Low-Level Radiochemical Analysis group continues to provide analyses for ultra-low levels of radionuclides in environmental and waste materials. Much of this work is performed for environmental monitoring or waste classification purposes both for ORNL and other Energy Systems facilities. The group continues to conduct both in-field and laboratory radiological support for the annual managed deer hunt on the DOE Oak Ridge Reservation.

A number of improvements have been made in the Inorganic Analysis group to increase technical capabilities. A new Jarrell Ash inductively coupled plasma (ICP) spectrometer was put into routine service. A laser ablation sample introduction system was installed on our existing ICP-MS and two special projects were initiated that utilize the laser system. Major improvements have been made in handling and transfer of data from the ICP systems to the division's data management system.

The Radioactive Materials Analysis (RMA) group continues to characterize radioactive waste from ORNL waste operations groups and special projects on active and inactive waste storage tanks. The group also performs general radiochemical and chemical analyses on a large number of other types of radioactive materials. The RMA group is located in a special facility designed for handling radioactive materials (Building 2026). Recently, as a result of a Laboratory-wide study, the hazard classification of the facility was reevaluated and reduced to a lower classification. The liquid low-level radioactive waste collection and transfer system for the facility is presently being upgraded to meet Federal and State requirements.

TRANSURANIUM AND ACTIVATION ANALYSIS

J. M. Keller

The Transuranium and Activation Analysis group (TAAG) consists of the Transuranium Analysis Laboratory (TAL) located at the Radiochemical Engineering Development Center (REDC), Building 7920, and the Neutron Activation Analysis Laboratory (NAAL) located at the High Flux Isotope Reactor (HFIR) facility, Building 7900.

Transuranium Analysis Laboratory

The principal objective for the TAL operation is to provide around-the-clock analytical support to transuranium isotope production by REDC of the Chemical Technology Division (CTD) and to contribute to the monitoring effort for both nonradioactive and radioactive waste streams which are managed by the Waste Operations (WO) section of the Waste Management and Remedial Action Division. Analytical support is also provided to various projects and programs including radioactive waste characterization projects, remedial action

programs, and health physics support for the identification of nuclides from various contamination incidents. About 18,000 samples were received by TAL with approximately 58,000 analytical determinations completed during FY92. This work load represents a 7.3% increase in samples and a 17.3% increase in analytical determinations over work done in FY91. The work was split mostly between CTD (45%) and WMRAD (45%) with the balance (9%) distributed throughout a wide variety of programs and projects.

Operations in support of REDC/CTD during FY92 included the completion of TRU processing Campaign #68. While the bulk of Campaign #68 was completed during 1991, several processing operations continued throughout the year. Among these, a curium oxide process was performed to provide target material for future irradiations, and final clean-up runs continued throughout the year to recover any actinides remaining in the fission product waste. Actinide product finishing activities, which involve the final purification of various actinides, were supported in parallel with the REDC processing activities. Also, analytical support was provided for two processing campaigns for high specific activity nickel-63 ($> 3.7 \times 10^{11}$ Bq).

Analytical support on the Mark-42 Fuel Assembly process development was continued throughout 1992. The Mark-42 process is a relatively new project for REDC/CTD which involves the recovery of americium-243 from high burn-up plutonium fuel from the DOE Savannah River Site. One project involved analytical characterization of core samples taken from different sections of a fuel assembly. This involved extensive hot cell work for the aluminum/actinide separation and preparation of the recovered actinides. The characterization involved radiochemical measurements for fission products by gamma spectrometry, for strontium-90 measurements, and for actinides by alpha spectrometry. Samples were also prepared on resin-beads for isotopic measurements by mass spectrometry for plutonium, curium, and americium. The characterization data were used to determine the relative burn-up for the segments/sections of the fuel assemblies. The region of the fuel assembly with higher levels of burn-up corresponded to the sections in which the americium-243 enrichment is higher. These characterization data were used by REDC/CTD to plan the processing of the Mark-42 assemblies. The first Mark-42 process has been completed, and a second batch of Mark-42 fuel

assemblies is currently in the early stages of processing. The analytical support requirements for the Mark-42 project are expected to continue for the next four years.

A project was performed for REDC/CTD that focused on removing high amounts of radioactivity from waste solutions. This project involved a series of in-cell filtration and dissolution steps to determine how to best remove a large percentage of the activity from insoluble fission products. The project entailed approximately two weeks of cell work to complete the tests and the products were then analyzed by TAL. Members of the REDC/CTD group received Waste Minimization Awards for this project.

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TAL Special Projects and Development Activities

Development work performed during this period involved studies for clean-up of waste samples for metals analysis, preparation of radiochemical methods for inclusion in the DOE Analytical Methods Compendium, and experimental studies on TAL analytical methods. Group programs focused on the implementation of an improved external quality control program and revision plans for all group Standard Operating Procedures (SOPs) and Standard Analytical Methods (SAMs).

Experiments were continued on solvent extraction using tri-n-octylphosphine oxide (TOPO) and extraction chromatography using the EIChroM™ transuranic specific (TRU-Spec) column for the removal of U and Th to allow for analysis of the EPA target analyte list elements by inductively coupled plasma (ICP) spectrometry. Data on recoveries of all of the target analytes from these two extractions in aqueous acid media were obtained. Studies indicated that these two extraction procedures do not affect recovery of the analytes under the conditions studied. This work was presented orally at the annual Gatlinburg Conference and in an

ORNL TM report which has been designated as a Martin Marietta Award Fee Milestone. Procedures on these two methods in SW-846 format were submitted to DOE/HQ for inclusion in the Methods Compendium. Both were accepted and assigned method numbers. Revisions of these methods will be submitted as necessary.

Drafts of two procedures (Clean-up of Radioactive Liquid Waste for Gross Alpha Determination and Alpha Spectroscopy and Determination of Total Radioactive Strontium in Nuclear Wastes) have been prepared in SW-846 format. The first procedure involves the application of the TRU-Spec column to radioactive wastes for concentration of the actinides and lanthanides to be analyzed for gross alpha determination and alpha spectroscopy. This clean-up reduces mass absorption due to high solids content from various salts typically present in nuclear wastes. The second procedure also involves extraction chromatography using an EIChroM™ column. The Sr-Spec is specific for strontium, separating it from yttrium which interferes in subsequent beta counting. This method can be applied to nuclear wastes for total radioactive strontium determination. Method validation experiments are currently being

performed. After these experiments are performed and the methods are concluded to be valid, the drafts will be submitted to DOE for inclusion in the Methods Compendium.

Development work specific to TAL operations was associated with revisions of group SAMs. The revisions involve experimental studies of the methods to determine validity and areas for improvement. Due dates have been assigned and documented for each SAM revision. Due dates have also been set for all TAL SOPs. Six SOPs have already been revised and submitted to the division for review. The reviews were returned and corrections are currently being made.

An improved external quality control program was implemented in the TAL group in February. This improved program involves more repetition of quality control checks as well as the addition of new checks. This program provides more regulated monitoring of instrumentation, procedural operations, and certification of the analyst. This monitoring is controlled by data entry into AnaLIS and documentation of control results. Quality control charts are received regularly and are filed. Corrective action is taken as necessary. Plans are being made for implementation of an internal quality control program which will also be monitored

through data entry into AnaLIS.

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Training Accreditation at TAL

The Transuranium Analysis Laboratory (TAL) became actively involved in the implementation of a performance-based training program, required by DOE Order 5480.18A, at the beginning of calendar year 1992. Performance-based training (PBT) has been demonstrated to be highly effective in providing the basis to ensure that personnel have qualifications commensurate with performance requirements of their jobs. PBT consists of five phases: analysis, design, development, implementation, and evaluation. The first four phases (analysis, design, development, and implementation) are performed sequentially with the output from one phase providing the input to the next. The evaluation phase is utilized throughout the entire process.

The analysis phase ensures that the training program is oriented specifically to the job tasks of the position (position refers to job title; i.e., lab technician, lab supervisor, etc.). During this phase two major events take place: job analysis and task analysis.

Job analysis results in the identification of tasks that are performed by the position being evaluated and the level of training needed to perform those tasks, based on the frequency, difficulty, and importance of the tasks in question. Once this task list is compiled and validated, a task analysis is conducted to determine the skills and knowledge needed to perform each task.

During the design phase terminal objectives are developed, based on the information from the analysis phase, and training/evaluation standards are developed to provide guidance for on-the-job training. Skills and knowledge associated with a task form the task analysis, and are translated into enabling objectives. These objectives are organized into instructional units and sequenced to aid the learning process. The objectives form the blueprint which guides the development of training materials, tests, and strategies.

During the development phase all training materials are developed based on the results of the design phase. Lesson plans and guides, student materials, and training aids are the products of this phase. Technical and instructional reviews of these products are conducted and recommendations are incorporated as necessary to assure that the program content

is both educationally and technically sound.

Implementation consists of activities related to the actual conduct of training, as well as planning, scheduling, and resource allocation. Instructors and technical staff are assigned, and facilities and training are scheduled. Qualified instructors conduct training during this phase.

Evaluation is an integral part of the performance-based training process providing critical feedback to ensure training is up-to-date and reflective of the job. Results of this phase are translated into action items or recommendations which are factored into the program content.

The current status of this activity is that job analysis has been completed, resulting in a validated list of 46 tasks. The task analysis is in progress and projected for completion in the first quarter of calendar year 1993. Projections for the completion of the subsequent phases are as follows: (1) completion of design phase, 12/93; (2) completion of development phase, 6/94; (3) completion of implementation phase, 06/94; (4) program ready for review, 12/94; and (5) accreditation, 12/95.

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Neutron Activation Analysis Laboratory

During the past twelve months the NAAL has experienced 1100 Research Reactors Division (RRD) operator shift checks, 52 health physics radiological surveys, 4 RRD safety inspections, 4 ACD safety committee inspections, and 6 formal DOE safety audits. Most of the ES&H audits have been positive and none have revealed any serious regulatory violations or threats to the health and safety of personnel working in the facility. In response to one such audit, we are reviewing the suitability of existing Memoranda of Understanding with Research Reactors Division to our present practices, paying particular attention to the matter of occurrence reporting. With regard to sample throughput, in the past twelve months approximately 5000 samples have been irradiated with about 35,000 determinations reported.

Our collaborative activities, designed to increase the use of neutron activation analysis in both the service and research areas, continued in 1992. During 1991/92, NAAL provided research support for one undergraduate student, one graduate student, one postdoctoral fellow, and one college faculty member. Some of these collaborative activities are: (1) East Fork Poplar Creek

soil analysis, (2) background soil characterization, (3) nanogram Hg determination in activated charcoal, (4) gross fissile content in TRU waste, (5) multielement analysis of geological materials, (6) trace element analysis of brain tissue, (7) volatility and extractability of Hg from East Fork Poplar Creek soils, (8) chemical speciation of Hg in soil, (9) nanogram quantities of iridium in fossilized dinosaur bones, and (10) trace element analysis in ceramic materials.

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NAA for Trace Elements in Soil and Sediment from East Fork Poplar Creek

A large project started last year to determine trace elements in soil and sediments from East Fork Poplar Creek was completed during this reporting period. NAA was used to determine Hg, As, Cr, Sb, Se, ^{235}U , and ^{238}U in the soil and sediment samples. The QA requirements for this project approached the EPA Contract Laboratory Program (CLP) protocol and

CLP-like data packages were prepared for it. Regulatory measurements for trace elements by neutron activation analysis was a new application for ORNL.

This project included delayed neutron counting (DNC) to measure ^{235}U , upgrading the software to calculate NAA results from the gamma spectral data, upgrading the PC-based multichannel analyzers, and developing the automated procedures to handle a large number of samples. This effort resulted in a system that functions totally with magnetic media without the need for paper records of analysis.

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NAA Using PC-Based Multichannel Analyzers

The Neutron Activation Analysis Laboratory recently converted from the use of minicomputer-based multichannel analyzer (MCA) systems to PC-based systems. Accompanying this change was the conversion or development of software so that neutron activation analysis can be made from vendor-supplied gamma-ray

spectroscopy analysis data. The PC-based system lacks the multiuser capability of the former system but because it operates entirely in a DOS environment it is able to utilize all of the powerful DOS programming features. For example, one of the PC-based systems allows simultaneous and totally independent accumulation of four different 4096 kilobyte spectra with the use of a multiplexer. Other, single detector input MCAs for high count-rate applications can be operated simultaneously with the same PC. Multiuser capability is nearly achieved by using batch and other executable files which establish the necessary logical unit arrangements and the corresponding data acquisition and display configurations. Within the MCA system, batch files and other executable files can be executed with a single keystroke.

Multichannel analyzer boards are located in the back-plane of IBM compatible 386 (33 MHz) computers. Each board has a capacity of 16K memory which in our operation is partitioned to allow acquisition of up to four 4096 channel spectra for gamma-ray spectroscopy. A single MCA board can be interfaced to a multiplexer which allows four detector inputs to be handled simultaneously using a single analog-to-digital converter. If desired, but not

recommended, up to four multiplexers could be used in the present system. The total cost of a multiplexed system including the computer is about \$11,000. The cost of a mainframe-based system with similar capabilities would have cost as much as \$50,000. It must be emphasized that when using the multiplexer mode of operation, only low count rate spectroscopy can be reliably performed. For this reason, only single input boards are used for gamma-ray spectroscopy measurements of neutron activated samples.

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Automation of Pneumatic Tube System No. 2

The loading station of pneumatic tube No. 2 is being modified to allow automated sample irradiation and delayed neutron measurements to fulfill one of the primary objectives of the NAAL. Automated sample irradiations should reduce the potential for personnel exposure to radiation and decrease the chances for contamination. Ultimately, these changes should result in a cost savings

for our customers and will allow more efficient use of personnel time. The design and safety assessment of the modifications have been completed. Construction is expected to begin in the near future. A brief description of the proposed changes is given below.

A 15.2 cm stainless steel load tube will replace the present approximately 30.5 cm stainless steel load tube that allows samples to be manually inserted into the loading station cylinder. The new load tube will contain two electrically operated solenoids that engage stainless steel pins that extend into the load tube. The two pins ultimately control the movement of rabbits into the loading cylinder of the pneumatic tube by pushing rabbits against the side of the load tube upon instruction from the Gould Programmable Logic Controller (PLC). We intend to ensure that the pins do not under normal conditions have the capacity to penetrate the surface of polyethylene rabbits. An 86.4 cm removable plastic sample magazine will be attached to the sample load tube extending vertically into the hood. The magazine will have the capacity to hold 30 rabbits. A manually operated set screw in the sample magazine will be removed to allow samples to be gravity fed into the stainless steel section of the load tube upon

demand. At this point rabbit movement into the loading cylinder is controlled by the two pins as described earlier. The loading cylinder is designed such that it can accept only a single rabbit at a time.

Accompanying these mechanical changes to the loading station are several modifications to the Gould software and electronics. The operating program will have several features to ensure safe operation in the automated irradiation mode.

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Background Soil Characterization Project

Preparation is under way to analyze soil samples from the Background Soil Characterization Project (BSCP) by neutron activation analysis (NAA). The BSCP, administered by the Environmental Sciences Division, has the objective to characterize the background levels of constituents in soils from three areas. These include the DOE Reservation, a region located in the extreme western side of Roane County, and a region

located in the extreme eastern side of Anderson County. We will be assisting in measuring the elemental composition of the soils. Project personnel are interested in determining as many elements as possible.

Presently, we are attempting to design a procedure that permits the analyses to be performed with efficiency and precision. The procedure will conform to the spirit of EPA CLP protocol as did the soil measurements in the East Fork Poplar Creek project. The analyses will be performed by comparative NAA and will include QA samples in addition to field samples. Schedules of irradiations and counting have been nearly completed. Selections and procurement of laboratory control samples and standards are beginning.

We anticipate being able to measure forty elements. Uranium measurements will include both ^{235}U and ^{238}U . The procedure, which is still subject to modification, would entail the analysis of two samples (each about 0.5 g) per specimen to measure elements that produce short- and long-lived gamma emitters. The first sample will be irradiated in PT2 and analyzed for elements that produce short-lived radionuclides. The second sample will be irradiated in PT1 where the resonance-to-thermal flux ratio is higher than in pneumatic tube No. 2 (PT2).

This increased epithermal neutron flux has an advantage for measurement of several important elements.

The first sample will be irradiated 15 seconds and counted 5 minutes after a 20-minute decay and then counted 30 minutes after a 24-hour decay. The second sample will be irradiated 1-2 minutes in and counted after decay periods of 4 and 20 days. One set of the samples irradiated in PT1 will later be irradiated in PT2 for measurement of ^{235}U by delayed neutron counting.

A technique has been developed to mix and homogenize samples of about 10 grams without introducing any contamination. This technique entails shaking 10-g, air dried samples in 50 ml high-purity polypropylene vials that contain one impactor consisting of a 20 mm long, 12 mm OD quartz rod. The rod is Supersil quartz to prevent contamination of the soil and is rounded on the ends to give an elliptical impactor that beats up the soil particles in an optimal manner. The samples are shaken 30 minutes on a paint shaker in gallon buckets with four vials in each end of each bucket. The shaker will shake two buckets so that 32 samples can be processed per hour.

F. F. Dyer, L. Robinson

Status of Analytical Chemistry Facilities in the Advanced Neutron Source

The final System Design Description (SDD) for the ANS project was completed in 1992. This document contains all of the information, as best we know it, needed by the project architects and cost engineers to develop cost estimates for the reactor project. The following paragraph is a brief description from the SDD for neutron activation analysis facilities.

Analytical Chemistry facilities are divided into prompt radiation materials analysis facilities, neutron activation analysis laboratories, pneumatic tube systems, and gamma irradiation facilities. The prompt radiation materials analysis facilities make use of cold neutron beams to provide trace element analysis of materials. These facilities are comprised of prompt gamma analysis (PGA) facilities and neutron depth profiling (NDP) facilities. The neutron activation analysis laboratories will consist of two facilities, NAAF-1 and NAAF-2, and associated pneumatic tube systems. NAAF-1 must be located in a secure area and will consist of an irradiation control room (ICR) and a counting room (CR). The ICR will contain a shielded work station with manipulators and a chemical fume hood that

contains the loading stations and associated control systems of the pneumatic tubes. Seven pneumatic tubes are proposed to allow neutron irradiations in the heavy water reflector and the light water pool. Five of the tubes will terminate in the heavy water reflector and two in the light water pool. The gamma irradiation facility will be located in the fuel storage area and use the gamma radiation emitted from one or more spent fuel elements to irradiate paints, plastics, and other materials to allow an evaluation of the damage to these materials by high doses of gamma radiation. A 7.62 by 7.62 m area with a chemical fume hood will be provided in the reactor support room to function as a sample preparation area.

L. Robinson, F. F. Dyer

LOW-LEVEL RADIOCHEMICAL ANALYSIS

N. A. Teasley, Jr.

The Low-Level Radiochemical Analysis group (LLRAG) has continued to provide radiochemical analysis and development for the environmental monitoring programs at ORNL and other Energy Systems installations. During the past year, about 8600 samples were submitted to the LLRAG with a total of 23,000 radiochemical results being reported.

We have continued to provide services for the Paducah Gaseous Diffusion Plant (PGDP) in support of their monitoring programs by performing analyses on a variety of sample types. Samples such as corn, green beans, eggplant, squash, tomatoes, and deer muscle, liver, thyroid, and bone are submitted to our laboratory for determination of a variety of radionuclides.

ORNL Waste Operations classifies waste generated at ORNL and submits samples to the LLRAG for radiochemical analyses. A large variety of sample matrices are analyzed to help classify the waste. Some of the determinations performed on the waste samples are gross alpha, gross beta, gamma spectrometry, tritium, and ^{14}C . A large

number of the waste samples are oils requiring tritium and ^{14}C analyses which are difficult to perform. Three aliquots are analyzed on each sample; one contains a portion of the sample, the second is spiked with a known amount of tritium, and the third is spiked with a known amount of ^{14}C . The spikes allow us to calculate an efficiency for each waste oil sample which is then used to calculate the activity in the oil.

The number of analyses reported in support of the air and groundwater monitoring programs at ORNL for FY92 was about the same as FY91. A large number of samples are taken at stacks and water effluent locations in and around ORNL. The data from the samples are submitted to State and Federal agencies for verification of ORNL's permit obligations.

The LLRAG has continued to be heavily involved helping to characterize possible radioactive contamination at the Paducah Gaseous Diffusion Plant. We have received and analyzed an average of 70 samples (10% of group's sample load) per month for gross alpha, total uranium, and gross TRU elements.

In addition to the normal work load in the LLRAG, we had the responsibility of preparing and reporting data on approximately 4000 (36,000 determinations)

soil samples from the East Fork Poplar Creek (EFPC) project. These analyses were performed by neutron activation analysis (NAA) at the HFIR facility. Programs written by personnel in the LLRAG enabled comparative activation analysis on the samples to be handled electronically. The soil samples were prepared as received. At the same time, a sample was taken for a wet/dry ratio of the soil to convert the "wet" results to "dry" weight basis. Once all associated weight and result files were transferred to ACD's VAX, the programs calculated the percent solids, the weight used for NAA, performed the comparative activation analysis, converted wet results to dry results, and created an AnaLIS electronic transfer compatible file that was then transferred into AnaLIS. The samples were run using CLP-type protocol. For every set of twenty samples, a spike, duplicate, blank, two calibration verification standards, and two other independent standards were prepared, analyzed and reported as a sample delivery group.

The LLRAG continues to provide radiological support for the Energy Systems/TWRA/DOE managed deer hunts. This year, during the December gun hunt, an archery hunt was conducted in the area of the Tower Shielding Facility. The total

number of deer taken during the 1992 hunts showed a substantial increase, while the number of deer confiscated because of radioactive contamination decreased.

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INORGANIC ANALYSIS

J. W. Wade

The Inorganic Analysis group provides analytical services and development for many ORNL and Energy Systems programs. We also provide services for organizations outside Energy Systems such as the Nuclear Regulatory Commission and Science Applications International Corporation (SAIC). We reported approximately 90,000 analytical results to our customers during this reporting period. During the past year, many of the major environmental monitoring and compliance programs at Energy Systems installations were forced by the regulatory agencies to require Contract Laboratory Program (CLP) protocols and data packages. Because of this need, a major effort was made by our group to upgrade our abilities to provide the forms and packages required by the program. We worked with personnel from SAIC to successfully complete and implement a software package to generate the CLP forms from our AnaLIS data management system. We had to modify AnaLIS and create databases so that we could store instrument parameters such as detection limits and linear ranges. Controls and QC samples are logged into AnaLIS with

identifications that associate them with a batch of samples. All the information is then written out to files and the forms can be generated by the SAIC programs. The software package will save time and eliminate possible transcription errors.

We installed and put into routine service a new Jarrell Ash (JA) Inductively Coupled Plasma (ICP) spectrometer. System parameters were determined and an EPA performance evaluation quarterly sample was analyzed with acceptable results using the new instrument. A 386 class PC operates the system providing us with a much more flexible controller than we have with the older JY48 spectrometer. Fortran programs were written for the PC to format data so that they can be transferred directly to AnaLIS. Data files in the proper format for AnaLIS are transferred to the ACD VAX via Ethernet. Very large files containing thousands of sample results can be transferred in a matter of seconds through the network. Because of the excellent stability of the JA system, we have begun to determine potassium with it instead of by flame-AA as we have done in the past. Using the JA reduces the cost and increases throughput because we no longer need to set up an instrument for one analysis. We continued to use the JY48 ICP primarily for

the analysis of waste samples. The hard disk on the JY48 crashed once during the past year and had to be replaced. We were lucky to find another disk drive on a computer system that was being salvaged. The electronics on the JY48 are antiquated and replacement parts are hard to find. We have investigated the possibilities of replacing the electronics on the system and will probably acquire the electronics upgrade if we continue to need a second ICP. Approximately 26,000 analyses were completed by the ICP-Atomic Emission Spectroscopy laboratory.

Our ICP-MS laboratory continued to undergo improvements during the past year. In February we installed an OS/2 system software on the PC that controls the VG PlasmaQuad system. With OS/2 running the PC, we can now perform a variety of tasks and acquire sample data at the same time. Another useful function is the ability to add samples onto the end of a run already in progress. With the DOS software suite, we had to abort the samples in acquisition, reenter everything and start over.

We installed a laser ablation sample introduction system and have used it to perform a preliminary study of trace metals in tree rings. The laser allows us to accurately sample the wood produced during

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both early and late season growing periods of the tree. We are not trying to provide quantitative analyses but instead are measuring the ratio of carbon-13 to some 20 trace metals. The increase/decrease in ratio amounts will give researchers information about the effects of acid rain on forests here in the southeast.

The ICP-MS system was down for repairs several times during the past year after running almost non-stop for the first 18 months. Many of the problems were due to wear and tear on moving parts and the vacuum system. A positive side of all the repair work was that we were able to learn a great deal about the mechanical/electrical design of the system. We feel confident now that we can solve most problems with a minimum amount of downtime. An additional PC was obtained for the ICP-MS lab to do data manipulation and transfer from the system. Several FORTRAN programs were written to read data generated by the OS/2 controlled system and manipulate it for transfer to AnaLIS. Ethernet was installed on the second PC to perform the file transfers. During the past year we began using the ICP-MS to perform most analyses that were previously done by graphite furnace AA.

We have procured and put into operation a Questron high pressure asher for the dissolution of solid samples. Our initial use for the system was to dissolve iridium metal and then measure trace metals in the material by ICP-AES. With the technical help of Questron, we were able to completely dissolve the metal. We have also used the system to dissolve soil for the determination of uranium by ICP-MS. We are presently performing a study to determine if the asher is capable of dissolving indigenous forms of natural uranium. Previous results for uranium using the EPA approved nitric acid digestion have indicated that over 50 percent of natural uranium remains insoluble to the treatment. The high pressure asher will be very valuable to us if it proves effective in these experiments.

We moved our mercury preparation and analysis operations from Building 2026 to Building 1505 to make room for the expanding needs at 2026. The perchloric acid hoods at Building 2026 had been shut down for some time before the move because they no longer met ORNL specifications. Because of the Laboratory-wide ban on the use of hot perchloric acid in nonapproved hoods, we had anticipated using approved hoods at the Y-12 plant to prepare

fish samples for mercury analysis. Before we began with the perchloric dissolutions, we received an EPA procedure that used sulfuric and nitric acids instead of perchloric. We ran several comparisons between the two methods and found no bias or anomalies. After checking with our customers, we began to use the method routinely for all fish samples. We have begun to sample our labs in Building 4500S for background mercury contamination in anticipation of moving all mercury preparation and analysis out of Building 1505. If we cannot find a suitable room, we will designate a lab for renovation and replace everything including the floor and cabinets much as we did for the ICP-MS lab.

The major programs at ORNL involving environmental monitoring and compliance such as the National Pollutant Discharge Elimination System (NPDES) and Resource Conservation and Recovery Act (RCRA) continued to place a high demand on our services. Waste Area Group (WAG) groundwater monitoring well samples were delivered daily. Routine measurements such as biochemical oxygen demand, fecal coliform, ICP metals, anions, corrosivity, oil and grease, pH, total organic carbon, and ammonia are determined on these samples. Several of these have short holding times and

require us to log the samples into AnaLIS and begin the procedures immediately after receipt. We were asked again this year to determine metals by ICP-AES and ICP-MS on about 30 area homeowners' well water. These samples are very sensitive and require that strict controls be followed. We continued to perform determinations of metals in blood, air filters, and paint residue for Industrial Hygiene. This will be the last year that our group does the blood analysis. In the future, the samples will be sent to an outside laboratory that is set up to run blood routinely.

A computer interface for our two ion chromatographs was procured and installed during this reporting period. The interface allows a PC to control both systems and is a definite improvement over the integrators that were used previously. The software runs under Windows and is very versatile. It allows us to output data in a format that can be imported into a spreadsheet or read by a program. Preliminary software has been developed in FORTRAN to read the files and set up data so that results can be transferred to AnaLIS. We can also perform multiple point calibrations, something we could not do with the integrators.

Most of the environmental monitoring programs at ORNL report data to branches

of State or Federal regulating agencies. We continued during the past year to participate in external quality control programs that give our laboratory credibility for the analyses that we do for these programs. Examples of the QC programs that we participate in are EPA water pollution studies, EPA performance evaluation (CLP) quarterly samples, Tennessee Department of Health water supply studies, Center for Disease Control, and The National Institute for Occupational Safety and Health.

We have continued to provide technical and service support in the fields of transmission electron microscopy (TEM), X-ray diffraction (XRD), optical microscopy (OM), and electron-excited X-ray analysis (EDX). Asbestos analyses by use of TEM are performed for programs at ORNL, Y-12, K-25, ORAU, and occasionally Paducah. Sample types include air, H₂O, surface, and bulk. All deadlines for both rush and routine requests have been met. In addition, we have reduced charges for TEM-H₂O by 30% and TEM-air by 17%. The use of TEM techniques for examination of samples for man-made fibers has increased, and approximately 5% of this work now concerns these fibers. A second chemist has been trained to perform asbestos determination by TEM. This training was comprised of

extensive in-house instruction, followed by two 1-week intensive courses at McCrone Research Institute in Chicago. Our senior chemist completed a 1-week intensive course at McCrone in order to maintain skills and to meet QA requirements.

We have purchased and installed a PC-based computer-aided imaging system which enhances imaging and measurement capabilities of our TEM and optical microscopes. We are actively pursuing the purchase of a new scanning electron microscope (SEM) to which the imaging system will also interface. These computer-assisted analyses are environmentally friendly and extend and enhance the researcher's ability to see relationships between process and properties of metallurgicals, ceramics, biologicals, and just about any other prospective samples.

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RADIOACTIVE MATERIALS ANALYSIS

J. L. Botts

The Radioactive Materials Analytical Laboratory (RMAL), Building 2026, performs analyses on intermediate and high-level radioactive materials that require the use of gloveboxes, C-zone hoods and hot cells. During this year the group analyzed some 3,600 samples performing 11,500 determinations.

As during several previous years, the characterization of mixed radioactive/hazardous waste continued to be the principal activity of the group. These characterizations included the analysis of the waste for radionuclide and chemical content, as well as determining some physical properties. These measurements are provided to determine and classify the waste as RCRA, TRU, or mixed and to evaluate methods for treatment and disposal of the waste. Whenever possible EPA-approved procedures are used. Modifications of these procedures are necessary at times due to high radioactivity levels, high salt content, and matrix interferences. Typically most waste samples are characterized for gross beta/gamma, gross alpha, anions, cations, and

RCRA metals.

The RMAL facility is the primary source of analytical services for a number of programs at ORNL, including the Federal Facilities Agreement Program, Waste Operations, Remedial Action, and others. Recently we aided in characterizing materials for closure of the ORNL Building 3001 canal and in the characterization of transuranic mixed waste from Nuclear Fuel Services, Inc. in Erwin, Tennessee.

The processing of palladium isotopes as well as other medical isotopes continued this year. These isotopes have short half-lives, and all processing must be completed and delivery made within 24 hours. Due to a severe shortage of processing hot cell capability at ORNL, the RMAL hot cells are very much in demand for work of this nature.

The hazard screening for RMAL has been completed utilizing the facility's existing level of activity and radionuclide inventory. As presently operated the classification has been determined by the Plant Safety Evaluation Team to be low. Because of this classification the Operation Safety Requirements (OSR), under which the facility had been operating, have been downgraded to a Limiting Conditions Document (LCD). The original OSR will be retired and the new LCD will be the safety

documentation for the facility. Investigations are still under way to upgrade the facility to a moderate hazard classification because of its hot cell capability. This classification upgrade will require extensive modification in the heating and ventilation system.

Phase I of the Bethel Valley Low-Level Waste Project is nearing completion. This is a project to upgrade the liquid low-level waste collection and transfer system at ORNL. All underground transfer lines that transport radioactive solutions within the RMAL are being replaced with double wall piping as required by RCRA. The drain lines in hot cells 1-4 have been replaced as well as all the transfer lines in the laboratory. When Phase I is finished, we will again have the responsibility for decontaminating the remaining hot cells, the unloading cell, the decontamination cell, and the H&V filter pit. Completion of this decontamination is required before construction can conclude Phase II of this project, targeted for early 1994.

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Support to the Robotics and Process Systems Division

The analytical laboratory located in Building 7602 continues to function as the service laboratory for the Robotics and Process Systems Division. One of the major efforts requiring extensive analytical services was the AVLIS Uranium Enrichment Program. Extensive analysis of uranium solutions by ICP required the removal of the uranium by extraction prior to the ICP analysis. Many other chemical analyses and physical measurements were performed as required to support this work.

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SPECIAL PROJECTS

T. R. Mueller

New Apparatus for High-Temperature/High-Pressure Sample Dissolution

For several years, a sealed tube dissolution technique with nitric and hydrochloric acids has been used to dissolve iridium metal and alloys prior to analysis for trace elements. The technique works well but produces quantities of hydrogen which sometime explode when the sealed tube is opened with a torch. Because of the safety hazards associated with the sealed tube, we have procured a commercial high temperature/high pressure apparatus (Anton Parr, KG) for dissolution of samples that are difficult to dissolve.

The new apparatus operates under computer control. The rate of heating and duration of processing at pressure and temperature can be adjusted through keyboard modifications to the run-time computer program. A printed and graphical report of the actual temperature profile during the processing may be produced.

With this apparatus, we were able to dissolve samples of iridium in the range of

0.1 to 0.3 g in about two hours. The cool-down cycle is also about two hours in duration. The pressurized chamber can accommodate up to six samples. With weighing, other sample preparation and post-dissolution handling and clean-up, it is possible to process one loading in about eight hours. This represents a reduction of about 8 to 16 hours with respect to the sealed tube method as normally practiced. In addition to the iridium samples, we have used the apparatus to dissolve samples of oil and soil with good results.

*J. H. Stewart, Jr., T. R. Mueller,
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Computer Programs for Mercury Determination by Cold Vapor Atomic Absorption Spectroscopy

We have continued to support programs developed for use with cold vapor atomic absorption spectroscopy. The programs, HGMAN, MANREP, and HGRTSPIK were reported previously. The programs have been modified slightly to meet our needs with new types of samples and additional

reporting requirements. The modified versions are available for distribution. In addition to providing formats for supervisory review and local files, they generate data in the format required for direct entry into the division's data base, AnaLIS.

T. R. Mueller

**Support of Remediation Efforts
on Fume Hood Systems
Contaminated with Perchloric Acid**

In the previous Annual Report, we presented work with methylene blue (MB) as a method for the detection of perchlorates. That work was done in preparation for the full-scale evaluation of the extent of contamination by perchlorates in fume hood systems throughout ORNL.

A committee was established to determine the number of hoods at ORNL that could be identified as having significant levels of contamination by perchlorates. The first task for the committee was to establish a definition for significant. For lack of a better criterion, the committee chose the value used by the National Fire Protection Association NFPA45. This value is rather arbitrary, but, by comparison with

quantitation studies with MB, we were able to assign a value of about 750 ppm to the acceptable concentration obtained in a fixed volume of wash solution. The committee chose 500 ppm as the level at which decontamination would be required before maintenance could be performed or normal work could proceed. All hoods with concentrations of perchlorate greater than 500 ppm in the wash solutions were shut down until decontamination could be performed.

Our preliminary work with MB was quantitated and the range of applicability of the method established. Two additional methods for determination of perchlorates were investigated; namely, the use of an ion-specific electrode and ion chromatography. The types and levels of interferences by various surfactants were determined.

The MB method was found to be useful as a screening technique. It could be used both as a field and laboratory method. Its use was thought to be most applicable to systems where radioactive species were found to be present. Although the method gives reproducible results for perchlorate concentrations as low as 10 ppm in the laboratory, field use or use with samples from hood systems was not practical below 500 ppm. The upper limit is about

15,000 ppm, where the color intensity makes it difficult to use qualitatively. Used according to the procedure in the previous report, it can yield both qualitative and quantitative results in one test. The method is insensitive to pH between 2 and 13, the range over which it was tested.

We have found the ion-specific electrode to be useable in the field and in the laboratory. A battery-operated meter, purchased from the Orion Corp., worked very well. Ammonium sulfate was used as a buffer. The electrode responds with a change of 0.057V/decade in perchlorate concentration. It can be used in the range 1 to 10,000 ppm, wherein a plot of EMF vs. log of the concentration of perchlorate is linear.

A study of interferences by metals, anions, and surfactants was undertaken. None of the metals found in our hoods interfered at levels up to 10,000 times that of perchlorate. Most common anions had no effect; but a slight decrease in potential is observed with oxalate, and a slight increase in potential is noted for benzoate. These latter effects are trivial since they correspond to only a few ppm perchlorate.

Because most surfaces to be sampled are covered with a layer of hydrocarbons, it is desirable to penetrate this layer by the use of

detergents, both for sampling and dismantling activities. Nonionic, anionic, and cationic surfactants were investigated. Anionic materials showed the greatest interferences. The other materials had only minor effect on the electrode potentials measured. For survey use, the presence of anionic materials can be tolerated at the 50 ppm level, since the potentials are shifted in the "fail-safe" (i.e., higher apparent perchlorate) direction.

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Common Laboratory Practices -- LIMS Cost-Benefit Analysis Team

A team was selected to aid the Common Lab Practices Committee, which is assisting the Energy Systems' analytical chemistry laboratories by developing proposals to provide consistency across the laboratories. This team's charter was to perform a cost-benefit analysis for the pursuit of a Laboratory Information Management System (LIMS) to be used by all Energy Systems analytical laboratories.

Specific tasks identified were:

1) determine the current cost of operating LIMS, 2) estimate cost of operating an Energy Systems-wide LIMS, and 3) develop a cost-benefit analysis for presentation to the Analytical Managers Council and the Performance Management Council (PMC).

The team report was presented to the PMC on August 31, 1992. The team was asked to continue with implementation of the submitted plan.

T. R. Mueller

instruments in the ACD at ORNL. Such other items as the number of analyses performed by each instrument per year, the status of interfaces to databases, and an analysis of the feasibility of automatic data acquisition were addressed. After presenting its report to the AMC, the committee was asked to remain active in order to implement some of its recommendations.

T. R. Mueller

Laboratory Instrument Data Interface Survey Committee (LIDIS)

A committee was appointed by the Analytical Managers Council (AMC) to inventory the software used to interface laboratory instruments to computer data systems at the five Energy Systems site laboratories. Many tasks were necessarily addressed by the committee in order to satisfy the intent of this charter. One of the tasks was the collection of a list of instruments at each analytical laboratory. This list now resides in a composite database and locally in a database representing

3. ORGANIC CHEMISTRY

M. R. Guerin

This section is responsible for a diverse program of analytical research, methods development, and analytical services. Research is directed toward development of advanced spectroscopic and separation techniques for identifying and quantifying trace organics in complex matrices. Trapped ion techniques, including Fourier transform mass spectrometry (FTMS) and ion trap mass spectrometry (ITMS), continue to receive major attention in both our fundamental and applied research areas. Laser desorption FTMS techniques have been used to elucidate the structure of oligonucleotides modified by exposure to chemicals and radiation and to investigate the formation, modification and properties of fullerenes.

Methodologies have been developed employing ITMS for the trace detection of volatile and semivolatile organics in a wide variety of media, including water, soil, air, urine, milk, foods, and others. Advances have been made in ion trap instrumentation as well, including the design and construction of an instrument which is about one-sixth the size of a commercial ITMS and requires significantly less power. Advances have also been made in fundamental studies of high concentration, nonlinear, and preparative chromatography and investigations of gas-solid adsorption. Specific applications of these advanced techniques have addressed the separation of enantiomers, fullerenes, and other compounds. Separation methods are also being developed for isolating trace compounds from complex mixtures, including isolation of potent carcinogens from combustion mixtures with high performance liquid chromatography and isolation of target compounds from environmental matrices with solid phase extraction. Work has also continued on the development and application of sample extraction, purification and analysis methods for radioactive mixed wastes.

Field sampling and analysis techniques have continued to be areas of special expertise in the section. This year we have combined novel sampling, separations, and spectroscopic detection

techniques for both in-field measurements and enhanced off-site analysis. This work has included development of unique sampling systems, deployment of advanced analytical instrumentation in the field, and provision of special analytical support for environmental studies at DOE's Hanford and Savannah River sites. In addition, a number of commercially available test kits that use immunoassay methods to screen for PCBs and mercury in soil were rigorously evaluated for field use. Environmental compliance and survey services are provided in support of ORNL and other DOE installations and for work-for-others programs. Specialty services involving chromatographic, spectroscopic, and other techniques are also provided in support of life sciences, environmental, and physical sciences research programs at ORNL.

ORGANIC SPECTROSCOPY

M. V. Buchanan

The principal goal of this group is to develop spectroscopic techniques for the unambiguous identification and quantitative measurement of trace organics. Research areas currently being emphasized are the development of advanced analytical capabilities for the detailed structural characterization of normal and modified biomolecules, rapid detection and quantification of trace organics in environmental and physiological matrices, and the investigation of fullerene and fullerene derivatives as new materials. Trapped ion mass spectrometry continues to

be the major focus of our research, including Fourier transform mass spectrometry (FTMS) and quadrupole ion trap mass spectrometry. As part of this research, specific emphasis is placed on the enhancement of the fundamental analytical capabilities of mass spectrometry, including ionization techniques, gas phase ion chemistry, and advanced instrumentation, with the transformation of these developments into practical techniques and instrumentation which may be employed in analytical laboratories.

Structural Characterization of Normal and Modified DNA with FTMS

Matrix assisted laser desorption ionization (MALDI) is now extensively used with the FTMS for the generation of molecular ions from modified and normal nucleotides, nucleosides, and small oligonucleotides. Continued emphasis is placed on the development of gas phase processes for the detailed structural characterization and isomeric differentiation of these molecules using the unique capabilities of the FTMS. It has been determined that gas phase hydrogen/deuterium exchange reactions provide a useful method for locating the site of adduct substitution on modified nucleosides, permitting the differentiation of isomers. For example, the number of H/D exchanges between methylated guanosines and deuterium oxide is dependent on the site of methyl attachment to the guanosines, which changes the number of acidic hydrogens present on the nucleoside. Whereas 8-methyl guanosine exchanges up to three hydrogens with deuterium oxide, 1-methyl guanosine exchanges only two hydrogen atoms. The rate of H/D exchange is also strongly influenced by the resonance

structures of the methylated guanosines. By comparing possible resonance structures for each protonated methyl guanosine isomer with experimental data about the number and rate of H/D exchanges, it has been possible to propose a reaction mechanism involving a concerted proton abstraction/deuterium cation donation.

Selective cationization of nucleosides was also explored as another means of determining the site of alkyl substitution. For these experiments, inorganic salts, such as barium chloride, were mixed with the analyte prior to laser desorption. For barium chloride, the resulting MALDI spectra consisted mainly of $(M + Ba - H)^+$ rather than the protonated molecules, $(M + H)^+$, typically observed. Although collision-induced dissociation (CID) of the protonated ions is virtually the same for all methyl guanosine isomers, CID of the bariated ions resulted in fragment ions which could be used to unambiguously differentiate the various isomers. A number of other gas phase ion-molecule reactions which may be diagnostic for differentiation of DNA adducts are also under investigation. For example, vinyl ethers and alkyl borates are being examined for their utility to selectively react with phosphate ester bonds in order to

determine oligonucleotide sequences.

Collaborative research to characterize DNA materials modified by exposure to chemicals and radiation has also continued with several researchers, including Dr. Jean Cadet (Grenoble, France), Godwin Mubaguo (Virginia State University), and Hiroko Yoshida (Health and Safety Research Division). A number of far-UV radiation damaged nucleic acid products have been examined by FTMS in collaboration with Dr. Cadet. These products are a series of isomers which could be differentiated by CID techniques. Dr. Mubaguo has synthesized a number of compounds which may be quite useful as matrices for the MALDI experiments at 355 nm. An ORNL Seed Money project with Dr. Yoshida involved the use of FTMS for the direct examination of X-ray radiation products of nucleotides. Picomole quantities of radiation products could be structurally identified with MALDI-FTMS using 266-nm radiation and a nicotinic acid matrix. This technique eliminated the need to hydrolyze and derivatize the modified molecules prior to analysis and provided a means of directly identifying products of nucleosides, nucleotides and oligonucleotides. In some of the studies, high performance liquid chromatography

(HPLC) was used to purify and collect fractions of the radiation products prior to examination by FTMS. In one experiment, a degassed aqueous solution of the dinucleotide TpT was irradiated with 5,000 Gy (^{60}Co gamma rays) and then examined with HPLC and FTMS. The major radiation damage was simple bond cleavages to yield free thymine and thymidine. An HPLC fraction containing many minor peaks was examined by MALDI FTMS and found to contain a number of hydroxylated products, including hydroxymethyluracil and thymine glycol.

A new data system is currently being installed on the FTMS that includes two SUN SPARC work stations, an Odyssey tower, and software purchased from EXTREL FTMS. The experimental sequences, SWIFT waveforms, and instrument operation are implemented in a UNIX open windows environment. Data acquisition and SWIFT waveform generation can be completed in a fraction of the time previously required on the outdated Nicolet 1280 computer. The capabilities of this new computer system will allow us to create very intricate experimental sequences and enhance current capabilities in ion manipulation. In addition, having two work

stations will greatly help the throughput on the instrument because one station may be used to collect data, while the other can be used for off-line data analysis and plotting.

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Program

Construction of a MALDI Time Of Flight Mass Spectrometer

A time of flight (TOF) mass spectrometer has been constructed for use with matrix assisted laser desorption ionization (MALDI) studies. This instrument will be used to carry out fundamental studies of the MALDI process by combining conventional time of flight detection with direct observation of the MALDI plume. The spectrometer uses a short-pulse nitrogen laser for desorption and ionization, a ± 30 kV acceleration region, a 1.7 meter flight tube, and a dual microchannel plate detector. The vacuum chamber is evacuated with a 300 L/s

turbomolecular pump backed by a molecular drag pump. Initially, data will be collected using a digital oscilloscope and downloaded to a personal computer for data analysis. Software is being written for computer control of the oscilloscope, data transfer and mass spectral data analysis.

Construction of the instrument has been completed and initial checks of instrument operation have been successful. Initial testing of the instrument will involve the analysis of a series of proteins covering a molecular weight range of 5,000 to > 60,000 daltons using conditions that have been successfully implemented on the FTMS in our laboratory and other TOF systems. Once instrument operation has been demonstrated, experiments will focus on the desorption/ionization of oligonucleotides. Experiments will involve empirical evaluations of new matrices for oligonucleotide analysis and fundamental studies using model systems to address questions related to the ionization mechanisms under MALDI conditions. The fundamental studies will employ detection of both ionic and optical signals, with the optical signals providing an additional dimension of information regarding the physical and chemical environment of the

laser plume. The instrument will also be used to examine small oligonucleotides currently studied by MALDI FTMS to ascertain whether the upper mass limitations of current MALDI FTMS measurements are due to problems in ion formation or ion trapping.

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Characterization of Fullerenes

Research has continued in the examination of the formation, modification, and properties of fullerenes C_n where $n = 60-500$, in particular focussing on buckyball, C_{60} . These diverse studies are funded by a Laboratory Director's Research and Development grant and involve close collaboration with Bob Compton (Health and Safety Research Division). In addition, this research includes a number of other ORNL research divisions (Solid State, Metals and Ceramics, Chemistry), as well as the University of Tennessee (UT) Department of

Chemistry.

Fourier transform mass spectrometry (FTMS) was used to not only detect and identify modified fullerenes but was also used to probe the properties of these new species. For example, charge exchange reactions were used to bracket the electron affinities of both $C_{60}F_{46}$ and $C_{70}F_{54}$. These experiments involve examination of the charge transfer between the fluorinated fullerenes and a variety of reagents which differ in electron affinity, ranging from p-benzoquinone (EA = 1.89 eV) to chlorine (EA = 3.6 eV). The electron affinities of the fluorinated species were found to be substantially higher (> 1 eV) than the parent fullerenes, implying that the addition of substituents can dramatically alter the electronic properties of fullerenes. This result is somewhat surprising because theoretical calculations indicate that the electron affinities of highly-substituted fullerenes such as $C_{60}F_{60}$ should be quite low.

In an effort to investigate the hydrogenation of fullerenes, we exposed a solid sample of C_{60} to a hydrogen rf discharge plasma. FTMS examination revealed that hydrogenated fullerenes, $C_{60}H_x$, were not generated by this experiment; however, larger fullerenes $(C_{60})_n$ were

observed, implying that coalescence (i.e., C_{60} ---> C_{120} , C_{180} , C_{240} , etc.) was occurring under these reaction conditions. This coalescence process is thought to be induced by low energy electron bombardment of the fullerene material. Experiments are under way to elucidate the formation mechanism and the structures of these larger fullerenes.

Studies have also focused on investigating the chemical reactivity of fullerenes in solution. In particular, the redox chemistry of fullerenes was examined by monitoring the reaction of alkali metals (K, Na, Li) with C_{60} , C_{70} in toluene solutions. Under these conditions, the fullerenes are electrochemically reduced and precipitated from the toluene solution. For example, addition of sodium metal to a toluene solution of C_{60} results in a color change of the solution from the characteristic purple to clear in a couple of days. This color change is accompanied by formation of a black insoluble residue, indicating the loss of fullerene from solution. No C_{60} was found in the black precipitate, implying that these redox conditions were sufficient to destroy the fullerene. Experiments are under way to determine whether the fullerene is electrochemically reduced to the point where it becomes reactive with the toluene solvent

and is destroyed.

Collaborative work with Mous Diack and Georges Guiochon (ORNL Analytical Chemistry Division and UT Department of Chemistry) has resulted in the development of techniques for the extraction and separation of fullerenes from soot. This research involved the development of both HPLC and FTMS techniques for fullerene purification and characterization. FTMS examination of HPLC fractions indicated that good separation could be achieved for C_{60} and C_{70} ; however, HPLC fractions of larger fullerenes also contained other impurities (possibly polycyclic aromatic hydrocarbons) which had been extracted from the fullerene soot.

Finally, a collaboration with Peter Buseck and Semeon Tsipursky, Arizona State University Geology Department, led to the first detection of naturally occurring fullerenes. These compounds were detected in a Shungite rock from Russia using electron microscopy and FTMS and the results were published in *Science*. A variety of meteorites were also examined, but none were found to contain fullerenes. These studies required careful control of the laser desorption conditions used to generate the mass spectra to insure that the compounds

indeed originated from the sample and were not generated by the laser desorption process.

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Fundamental Studies of Electrospray Ionization

An electrospray ionization source which was constructed last year has been employed to examine the chemical and physical phenomena which occur during the electrospray process. These studies will allow us to fully define the analytical utility of electrospray for application to a variety of biomolecules of interest for our research program. Reports from our laboratory and others have shown that the electrospray response of compounds can be quite variable, depending upon the composition of the analyte solution. These differences in response could have profound limitations on the analytical utility of this very promising ionization technique. In these studies, we

are specifically interested in exploring the parameters that control or contribute to the electrospray response of an analyte. Initial studies have shown that decreasing the surface tension of the solution improves the electrospray sensitivity. This has been confirmed by monitoring the intensity of *n*-hexyltrimethylammonium bromide in solutions of decreasing surface tension. Similarly, the roles of analyte surface activity and solvation have been investigated. Electrospray analysis of a mixture of *n*-alkyltrimethylammonium bromides (C_6 through C_{18}) demonstrates a correlation between observed signal intensity and molecular weight. In this homologous series, the largest cations are known to have the highest surface concentrations. The effect of ion solvation has been examined with a group of tetraalkylammonium bromides. Increasing the size of the alkyl group reduces the ion-solvent interactions and results in an enhancement of the electrospray response.

Amino acids have been used as model compounds to verify some of these surface concentration effects for biomolecules. These compounds have the general structure $NH_2CH(R)COOH$, in which the group *R* can be acidic, basic, hydrophilic or hydrophobic. Thus, amino acids provide a set of similar

compounds where the interactions among a number of parameters can be investigated. Electrospray studies of twelve amino acids reveal correlation between their electrospray response and degree of hydrophobicity, which in turn correlates with solvation. The results thus provide additional confirmation of the role of ion solvation in electrospray. In most instances, the gas phase basicity of an analyte is related to its solution basicity through its solvation enthalpy, especially if entropic contributions are minimal. Therefore, both gas phase and solution basicities are being addressed in our current investigations. Our investigations to date demonstrate that many factors contribute to the electrospray process and affect the general analytical utility of this technique. Clearly, a more thorough understanding of these factors is necessary before the full potential of this ionization technique can be realized.

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Environmental Ion Trap Mass Spectrometry

Progress has continued in the development of direct sampling ion trap mass spectrometry (DSITMS) for the rapid analysis of organic pollutants in environmental samples. Improvements have been made in the sample introduction devices used with this instrumentation, including the development of smaller and more reliable sample introduction modules for direct air monitoring, thermal desorption, and water/soil purge analysis. These modules have been standardized for use with all of our ion trap mass spectrometer systems which are equipped with the direct sampling interface. Additional progress in the DSITMS hardware has primarily been in the area of field instrumentation. Significant improvements have been made in the instrument modification to the Finnigan MAT ITS-40 to make it easier to transport and use in the field. Especially important has been the replacement of the oil-filled rotary vacuum pumps with a combination molecular drag/diaphragm pump. This has resulted in a reduction in power consumption from approximately 1500 watts to 550 watts and a weight reduction of approximately

20 kg. Furthermore, by eliminating the oil-filled pumps from the mass spectrometer, the background is considerably less contaminated which is important for trace analytical work. During 1992, field deployments of the DSITMS were conducted at the Savannah River Laboratory and Portsmouth, Ohio. Additionally, a fieldable ion trap was delivered to the Hanford Site for use at their tank farm. Laboratory-based ion traps at ORNL were used to respond to local problems and were also used for the analysis of a number of water samples collected at Portsmouth.

Considerable progress has been made in data generation for the analysis of volatile organics in water. A laboratory-based ITMS has been used to generate the data necessary for preparation of a regulatory method. The technique employs our multiplexed data acquisition software, which allows collection of both electron ionization and chemical ionization spectra in a single analysis. These data are generated according to a standard procedure using appropriate QA and QC measures to assure validity. Careful studies are being performed to establish the method detection limits (MDL) and the certified reporting limits (CRL) for all 34 volatile organic compounds on the EPA Target

Compound List. At the present time, over half of the compounds have been completed and the MDL's are 5 ppb or better. Pilot studies suggest that DSITMS will also be applicable to the determination of many semivolatile organics. Results for polychlorinated biphenyls and selected pesticides are especially promising.

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Advanced Ion Trap Instrumentation

The success of direct sampling ion trap mass spectrometry (DSITMS) for environmental analysis suggested that the technology might be extended to the determination of "threat"-chemicals (e.g., military chemical agents, explosives chemicals, drugs). The concept is to develop instrumentation (now termed a Multi-Threat Analyzer) applicable to multiple-threat chemicals in multiple-media. The nature of the chemicals and scenarios for its deployment require more sophisticated instrumentation than is required for common environmental applications.

A Multi-Threat Analyzer (MTA) has been constructed; it is currently undergoing performance testing and is being used for methods development. This instrument incorporates all of the features of a full-sized laboratory-based ion trap mass spectrometer in a package which is 47 cm wide and 85 cm tall. In general, the 2-drawer filing cabinet-sized MTA represents several major accomplishments in component down-sizing and overall power usage. Most significantly, the redesign of the rf generator represents an important milestone in reaching the ultimate goal of developing a man-portable

MTA instrument. The new rf generator operates at half the frequency of commercially available ion traps. This factor alone reduces the rf voltage from 7,500 volts to 1,800 volts while still maintaining the same mass range. Further, the physical size of the rf coil has been reduced by approximately 95% and the total rf power consumption has been reduced to 1/16th of that required for the commercial instruments. Overall, these design changes have resulted in reductions in power requirements to less than 1,000 watts total, making this instrument feasible for transportable operation. Performance of the new rf generator has been outstanding and has shown excellent frequency and voltage stability over time. Other significantly downsized components include the programmable dc voltage supply which is used for selective ion storage and the high voltage power supplies used for biasing the conversion dynodes on the ion detector. The vacuum chamber has also undergone a major size reduction, and the pumping system has been modified for low power consumption and smaller size through the use of a ceramic bearing turbo pump and a molecular drag pump. No oil filled pumps are used in the system which helps reduce background contamination.

Specific capabilities of this instrument include both electron impact and chemical ionization, selective ion storage, axial modulation ion detection, and tandem mass spectrometry (MS/MS). Additionally, this instrument is equipped with prototype electronics for improved mass resolution and for negative ion detection. The sample inlet system at the present is the ORNL designed direct sampling interface and associated modules for the analysis of air, liquids, and sorbent tubes. Provisions for coupling the instrument with a glow discharge source have also been included in the instrument design to facilitate the analysis of low volatility compounds such as explosives. A new design for a glow discharge source has been completed and construction will begin shortly.

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Methods and Instrumentation for the Rapid Detection of Chemical Agents and Agent Precursors

Specialty instrumentation has been designed and constructed here for the trace level detection of chemical agents in air as part of a U.S. Army program to destroy chemical munitions. During November 1991, training was provided to personnel from a new subcontractor to the Army who will be conducting analyses at the Chemical Agents Munitions Disposal Systems (CAMDS) facility in Tooele, Utah, on the operation of the automated thermal desorption system developed at ORNL. The thermal desorption unit was interfaced with a gas chromatograph which was equipped with a flame photometric detector and the entire system was checked and cleaned. Analytical results obtained by CAMDS personnel for chemical agents GB and HD were well within the necessary requirements in terms of both sensitivity and reproducibility. In addition, it was clearly demonstrated that the automated thermal desorber provides considerable improvement in terms of analysis time and overall reduction in sample handling requirements.

During the week of August 24, 1992, personnel at the analytical laboratory of the Tooele Army Depot were trained in the operation of the Finnigan ITMS ion trap mass spectrometer for the analysis of chemical warfare agents. The training was conducted by M. B. Wise and G. B. Hurst; a total of five laboratory personnel attended the training sessions including three people from the CAMDS laboratory and two people from a contractor-operated laboratory. The scope of the training was intended to provide first-time users with sufficient information to enable them to perform all necessary operating tasks on their own. This included information on daily performance checks of the instrument, manual tuning, writing and editing scan functions, data acquisition, using the data reduction software, calibration, quantification, and advanced instrument programming. Laboratory training included instrument tuning, writing and optimizing scan functions, and data acquisition using chemical warfare (CW) agent standards.

Work was also initiated on the development of methods for the detection of precursors of chemical agents for use in treaty verification. As part of this work, baseline data are being collected for a number of targeted compounds and will

include gas chromatographic retention indices, electron impact and chemical ionization mass spectra obtained with a quadrupole GC/MS, and MS/MS spectra using an ITMS. Some of the target compounds are very polar and will require derivatization prior to analysis by mass spectrometry, consequently on-column derivatization techniques are being developed for these compounds.

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Rapid Analysis of Drugs in Physiological Fluids

A new analytical approach for the rapid isolation and detection of phenothiazine, an anthelmintic drug, in milk was developed as part of a program for the Food and Drug Administration. The method is based on introduction of the sample into an ITMS with little or no sample preparation so that the total analysis time was kept to a minimum. Isobutane was used as a chemical ionization reagent to selectively ionize this nitrogen-containing drug to form

predominately $(M + H)^+$ ions with m/z 200. Collision induced dissociation was used to form characteristic product ions, providing an additional level of selectivity. Initial studies using matrix spikes were designed to evaluate whether the milk samples could be directly injected onto a sorbent material, such a glass wool, and thermally desorbed into the ITMS with no sample preparation. This approach was successful, but repeated analyses resulted in an accumulation of material in the transfer line into the ITMS, indicating the need for some type of sample clean-up steps. After evaluating several rapid clean-up procedures, it was found that small C_{18} solid phase extraction microcolumn disks provided a convenient means of achieving the required low ppb detection limits while keeping the overall sample analysis times to a minimum. In this method, 1 to 100 μL of milk are extracted through one of these discs contained in a disposable 10 mL syringe assembly. After elution of the milk, the disc is washed with 500 μL of water, removed from the syringe assembly and inserted into a glass desorption tube. This tube is then placed in the thermal desorption unit of the ITMS and analyzed. Detection limits for this method were 10 ppb with a total sample preparation and analysis time of 10 minutes.

This technique was then evaluated with milk from a cow that had been dosed with 10 g phenothiazine per 45 kg of body weight in a test conducted by the sponsor. After receipt of the first set of dosed milk samples, a calibration curve was prepared from fortified milk samples containing 0 to 5000 ppb of the drug using the solid phase extraction/desorption ITMS method. The dosed milk samples were analyzed, including samples from milkings conducted from 8 to 96 hours post dosage and two controls. The calibration plot was linear from 5 to 5000 ppb, with a detection limit (95% confident limit) of 10 ppb. Samples from 8 to 56 hours post dosage were found to contain phenothiazine, while both controls and samples from 72 hours to 96 hours post dosage were determined to contain the drug at levels below the method detection limits. A dose response curve showed an exponential decrease in concentration of phenothiazine as a function of time, with the concentration at 56 hours corresponding to 30 ppb. According to the sponsor, this corresponds to what is typically observed in these animal dosing studies.

Work has also continued on the development of techniques for the rapid determination of nicotine and cotinine in

urine as part of an ongoing National Institute of Cancer program. In this method, no sample clean-up is required, and a 1 μ L aliquot of raw urine is injected onto a Tenax sorbent trap and thermally desorbed into the ITMS. Selectivity is achieved using isobutane chemical ionization and MS/MS detection. Both nicotine and cotinine are detected at concentrations of 100 ppb in urine and calibration plots are linear over at least three orders of magnitude, with reproducibility on the order of 5 to 15%. This range of linearity easily encompasses the levels of nicotine and cotinine found in the urine of active smokers, allowing smokers and nonsmokers to be easily distinguished. To achieve even lower detection limits, which will allow an evaluation of exposure of nonsmokers to environmental tobacco smoke, rapid sample preparation steps are being evaluated. We are working with a commercial vendor (who developed the microcolumn solid phase extraction discs used in the FDA milk studies) to identify a suitable solid phase for nicotine and cotinine. A primary secondary amine (PSA) phase was evaluated by placing the small disc directly in 3a glass desorption tube and spiking 1 to 10 μ L of spiked raw urine onto the disc. The sample was then thermally desorbed

directly from the disc into the ITMS. This method reduced the detection limit for nicotine to about 10 ppb, which is at the high end of nicotine levels for nonsmokers exposed to environmental tobacco smoke. Methods are currently being investigated to further reduce detection limits and make the technology more broadly applicable for the analysis of nicotine, cotinine, and other nicotine metabolites in the urine of nonsmokers.

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Special Spectroscopic Studies

Our group continues to provide special spectroscopic support to programs within our section and to other researchers at ORNL. Combined gas chromatography/mass spectrometry (GC/MS) has been used in a wide range of studies. One large program involved the characterization of vapor samples taken from an underground waste storage tank on the Hanford reservation. Samples were collected on sorbent traps and analyzed by thermal desorption into a GC/MS. Tentative identification of the

components was based on electron ionization spectra and confirmation of molecular weights was obtained with CH₄ chemical ionization (CI). Hydrocarbons, mainly alkanes and alkenes containing 5 to 15 carbons, were the most abundant components. Oxygenated hydrocarbons, such as C₁₆ to C₁₈ alkanic acids and C₅ to C₁₁ alkanones, were also identified.

In studies conducted by the Special Projects group, a group of chromatographic peaks were observed using a nitrogen/phosphorus GC detector. Both EI and CH₄ CI spectra indicated that nitrogen was present in these compounds. However, these compounds gave no response under NH₃ CI conditions, suggesting that these compounds were not amines. Further inspection of the EI spectra suggested that these compounds did not contain fragments corresponding to nitro- or nitroso-containing functionalities. Instead, it was thought that these compounds were C₅-C₈ alkyl nitriles. These assignments were then confirmed by matching their GC retention times with those obtained from authentic standards.

GC/MS with negative ion chemical ionization was also employed to screen a large number of samples for the presence of polychlorinated biphenyls in environmental samples, in support of the Organic Analysis

group. Additional studies were conducted with researchers in a number of other divisions, including Health and Safety Research, Environmental Sciences, Chemistry, and Chemical Technology. In this latter case, the work performed resulted in the successful funding of a Seed Money project in collaboration with Eli Greenbaum. A number of specialized spectroscopic studies were also conducted with the FTMS for researchers in Health and Safety Research, Biology, Metals and Ceramics, Solid State, and other divisions.

C. Y. Ma, S. M. Smith, R. L. Hettich

SEPARATIONS AND SYNTHESIS

W. H. Griest

The general responsibility of this group is the development and application of organic separations and synthesis methods. High performance liquid chromatographic (HPLC) separation methods are being developed to isolate trace amounts of dibenzo(a,l)pyrene from complex combustion-generated matrices for the National Cancer Institute. Solid phase extraction methods are being developed for the preparation of environmental samples for analysis of chemical warfare agent decomposition products and regulated pollutants for the U.S. Army. Sub-parts per trillion detection limits are required for some constituents. Other work for the Army included the development and demonstration of prototype visual indicators for detecting nitroesters and moisture in munitions.

Development and application of analytical methodology for radioactive mixed waste continue as major specialties of the group. The ALARA (As Low As Reasonably Achievable) principle has guided the adaptation of EPA and other sample extraction, purification, and analysis methods

for the DOE. A notable accomplishment this year was the development of an HPLC method for the direct determination of EPA Toxicity Characteristic Leaching Procedure (TCLP) acidic semivolatile compounds. A small service effort in the preparation of radioactive mixed wastes for organic analysis supports waste management and environmental remediation programs within and outside ORNL.

Solid Phase Extraction

Methodology

Solid phase extraction (SPE) techniques have been extensively utilized in projects for developing analytical methods for regulatory pollutants and chemical warfare agent hydrolysis products in water or solid waste. The EPA method for preparation of water samples for analysis of herbicides requires alkaline hydrolysis, acidification and solvent extraction, drying and concentration of this extract, and then derivatization before analysis using gas chromatography with electron capture detection (GC/ECD). Our combined SPE-HPLC method is much more rapid and efficient and does not generate as much hazardous waste or use the highly toxic

diazomethane. The SPE method involves drawing 1L of acidified water through 47 mm octadecylsilane (C_{18}) extraction disks and eluting the collected components with methanol. After concentration, the methanol is analyzed using reverse phase HPLC with UV absorbance detection (see later section on direct analyses). 2,4,5-T (a herbicide) is used as a surrogate standard for the determination of 2,4,-D and Silvex (herbicides). Application of this method to a State of Tennessee Certification Sample yielded a 2,4,5-T recovery of 87%, and 2,4,-D and Silvex results of 45 and 13.4 ppb, respectively, which were within 10% of the certified values. Several pond water samples were subjected to this method and herbicides were not detected. 2,4,5-T recoveries were > 90%, except for one sample which contained highly visible levels of algae. For this sample the extraction time was long and the recovery was 50%.

The same SPE technique with C_{18} extraction disks but employing GC/ECD analysis also has been found effective for recovering PCBs from water and aqueous mixed waste samples. Recoveries of Aroclors-1221 and 1260 at 25 ppb in water were 99% and 63% respectively, and for the surrogate standards tetrachloro-m-xylene

(TCMX) and decachlorobiphenyl (DCBP) at 3 and 10 ppb (respectively) were 107% and 109%. The C_8 and C_{18} extraction disks performed equally well and both were more efficient and exhibited much less of a blank to GC/ECD than did conventional packed column SPE. The radioactivity carried over into the extract from mixed wastes is being determined but is not expected to be significant.

An anion exchange SPE method is being adapted for the extraction of methylphosphonic acid, ethylmethylphosphonic acid, and isopropylmethylphosphonic acid from groundwater at 5-10 ppb concentrations. These compounds are hydrolysis products of chemical warfare agents and their presence signifies groundwater or soil contamination by the agents. Conditions are being optimized for the extraction of phosphonic acids from water using an aminopropyl silane SPE column. The 100 ng sorbent column was found optimal for 50 mL sample volumes, providing an efficient compromise between capacity and volume of eluting solvent required. Primary aminopropylsilane columns (Varian, Sunnyvale, Calif.) were more efficient than columns of the same functionality obtained from Baker (Phillipsburg, N. J.), suggesting subtle

differences in the packing chemistry; both were superior to secondary or quaternary amine phases. The collected phosphoric acids are eluted from the SPE columns using 1.5 mL of 0.1 M trimethylphenylammonium hydroxide, a reagent which forms methyl esters of the acids when the eluate is injected into the hot (300°C) inlet of a GC. The derivatization reaction is not quantitative and "ghosting" is observed at low levels equivalent to ca. 2 ppb. Method optimization is not yet complete at the 5-10 ppb level, but at 50 ppb recoveries are greater than 60% and are quantitative at 100 ppb.

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Ultra Trace Level and Complex Isolation Problems

A novel solid phase sample introduction method coupled with combined reverse and normal phase semipreparative scale HPLC has been developed and applied to the isolation of a dibenzo(a,l)pyrene enriched subfraction from crude aromatic fractions from coal and plant combustion particulates. The crude fractions were prepared by

extensive solvent partitioning and adsorption chromatography on alumina (see last year's report). They are sparingly soluble in common HPLC mobile phases and thus cannot be readily injected in solution. Rather, they are evaporated onto C₁₈-silica, and the coated silica is dry-packed into an HPLC guard column upstream of an C₁₈-silica semipreparative scale column. The system is then flushed using a step gradient ranging from reverse phase (water/methanol, 90/10, v/v) to normal phase (methanol/acetonitrile/methylene chloride, 10/50/40) compositions. Analytical scale reverse phase HPLC shows high resolution subfractionation with very little compositional overlap among subfractions. A six-ring polycyclic aromatic hydrocarbon (PAH) fraction corresponding to less than 0.005% of the original material is obtained from the HPLC subfractionation. Although this represents considerable purification, dibenzo(a,l)pyrene could not be identified because of its very low concentrations and co-eluting compounds which are thought to be alkylated PAH. Therefore the identification and determination of dibenzo(a,l)pyrene will require further purification via size exclusion or other chromatography prior to analytical HPLC.

Methodology is being developed for the ultratrace-level determination of nitrosodimethyl amine, nitrosoethylmethyl amine, and nitrosodiethyl amine in groundwater with detection limits of 0.7 ng/L. Two extraction approaches are being developed: conventional solvent extraction and purge and trap. Although these nitrosamines are fairly volatile, their high water-solubility prevents them from being purged efficiently from water unless they are salted-out. With saturated sodium chloride, purge/trap recoveries of 9-11% are achieved at a nitrosamine concentration of 100 μ g/L, but with potassium carbonate at 60% of saturation, recoveries are 40 to 60%. Although the waste from this preparation mode is not RCRA hazardous, the method would require considerable salt (77g/100 mL) for a routine analytical operation. Therefore, the solvent extraction option is being expedited at the present. Continuous solvent extraction after SW-846 method 3520 was found to be much more efficient than any of the SPE methods tested, which included partition, ion exchange, and complexation. Up to 1 L of water is continuously extracted with methylene chloride at alkaline pH for 18 hrs and the solvent is concentrated to 0.8 mL. Injection of a few μ L into a GC

equipped with a nitrogen-phosphorus detector does not meet the very low detection limits required. Therefore a solid phase sorbent method for introducing a much larger volume of the extract into the GC is being developed. We have found that up to 100 μ L of methylene chloride can be evaporated into traps packed with carbonaceous sorbents and the nitrosamines injected into the GC by thermal desorption of the trap. At least 80% recoveries (evaporation plus desorption) were achieved over the range of 1-5 ng per nitrosamine, and at 0.5-1 ng recoveries were 60% or greater. The conditions for placing and evaporating the extract in the sorbent tubes are being optimized and we will need to achieve good recoveries at the 0.1 ng level to meet detection limit requirements.

As part of a project to adapt EPA SW-846 methods to radioactive mixed waste analysis, a PCB extraction and purification method has been adapted and evaluated for glove box or hot cell use. Ca. 0.5g samples of waste sludge are spiked with TCMX and DCBP surrogate standards at concentrations of 0.3 and 1.0 ppm, respectively. A single 30 min. extraction is performed in an ultrasonic bath with 5 mL of hexane, and 4 mL of the extract are washed with 2 mL of

concentrated sulfuric acid. The latter is back-extracted once with hexane and the combined hexane layers are concentrated to 4 mL for GC/ECD analysis. This clean-up method is much more effective than the EPA protocol Fluorosil method, and also achieves a 10^6 reduction in radioactivity levels in the extract. Aroclor 1221 and 1260 recoveries from 5 ppm spikes in surrogate waste sludges ranged from 80-110% with precision of 7-17%. Surrogate standard recoveries were 61-80% for TCMX and 80-90% for DCBP. Recoveries of PCBs are slightly lower but still within acceptable limits for extracts which require multiple washes.

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Analytical Separation and Quantitation

EPA SW-846 methodology for sample preparation and analysis of the Toxicity Characteristic Leaching Procedure (TCLP) acidic semivolatile organic compounds in aqueous wastes or TCLP leachates of solid samples requires solvent extraction, drying,

concentration, derivatization, and GC/ECD. These multiple operations make the procedure costly, slow to perform, and increase the variability of the analytical results. Also, the acetate in the TCLP leaching fluid interferes with the derivatization. In our project to adapt SW-846 methods for radioactive mixed waste analysis, we have developed a direct HPLC analysis method which requires very little sample preparation and which considerably reduces operator exposure to radioactive samples. The method utilizes a polymeric reverse phase column, a binary gradient of 0.1 M acetic acid (in acetonitrile/water) and acetonitrile, and ultraviolet absorbance detection at 280 and 235 nm. Samples are only filtered (and acidified, if alkaline) and 25 μ L are injected for HPLC analysis. The eight TCLP acidic semivolatile organics are determined in a 20 minute run with detection limits below the TCLP regulatory limits. The phenols and herbicides are routinely quantified at 280 nm, and if needed, the herbicides also can be measured at 235 nm. The herbicide 2,4,5-T is used as a surrogate standard. Compound identifications from the retention times on the primary column are confirmed by the UV spectra recorded using the diode array detector, or by retention time

on a secondary confirmatory column. At the present, a C18-silica column is being used for confirmation, but additional columns with different selectivities are being tested to improve the confidence of the confirmatory separation.

The method performance has been evaluated by matrix spiking two standard sample matrices, TCLP extraction fluid No. 2 (simulation of a TCLP leachate) and 5 M sodium nitrate (a surrogate for nuclear storage tank liquid waste), at two concentrations which were at or below the TCLP regulatory limits. Recoveries from the TCLP extraction fluid were 87% or better. Recoveries from the sodium nitrate were much lower, and appeared to decrease with time of sample storage, suggesting that the TCLP acidic extractable organics may have limited stability in high nitrate content nuclear wastes. Recoveries of the 2,4,5-T surrogate standard for 61 TCLP leachates analyzed over a 12-month period were excellent and had very good reproducibility ($96.7 \pm 14.8 \%$). This method has been extended to the determination of other herbicides in special analytical services. Tebuthiuron and trifluralin were determined in two rainwater run-off samples for another DOE site. The detection limits for direct

analysis were 0.32 and 0.21 $\mu\text{g/mL}$, respectively.

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W. H. Griest*

Fate of Composted Explosives

As described in the last Annual Report, we have demonstrated that composting can considerably reduce the explosives content and toxicity of soil contaminated with explosives. One question remaining, however, is the fate of the biotransformed explosives. To gain insight into this issue, another Army contractor provided us with compost which had been spiked with carbon-14 labelled trinitrotoluene ($^{14}\text{C-TNT}$) and composted in a 90-day field composting experiment. We ultrasonically extracted the compost four times with acetonitrile and measured the extracted ^{14}C -activity by liquid scintillation counting to estimate the free TNT and its biotransformation products. Next, the extracted compost was hydrolyzed eight times using alcoholic potassium hydroxide, and the hydrolysate was counted for ^{14}C -activity to determine bound biotransformation products, and finally, the

residue was combusted, and the liberated ^{14}C -carbon dioxide was collected and counted to estimate nonhydrolyzable bound biotransformation products.

In compost samples collected as the start (day 0) and completion of composting (day 90), 75% of the ^{14}C -activity initially added to the compost was found in the hydrolyzable bound fraction, indicating that the TNT had been transformed rapidly to a product which could resist solvent extraction. Most likely, this product is a metabolite of TNT which is covalently bound to either some soil component or to the bacteria. The rapid initial biotransformation at day 0 suggests that the ^{14}C -TNT spike sprayed onto the compost was much more available to the bacteria than was the native TNT in the contaminated soil. The free (or solvent extractable) ^{14}C -activity decreased from 26% at day 0 to 1.2% at day 90, indicating that additional biotransformation occurred during composting. The nonhydrolyzable bound ^{14}C -activity remained about the same from day 0 (3.5%) to day 90 (4.7%). It may represent a transformation product which was physically inaccessible to the alkaline reagent, or a product resistant to alkaline hydrolysis, such as one bound by a heterocyclic ring linkage. The ^{14}C -activity

balance was excellent at day 0 ($103.5 \pm 8.7\%$), which shows that the methodology was valid. At day 90, $80.5 \pm 3.0\%$ of the ^{14}C -activity was accounted for. No ^{14}C -activity was detected in the compost surrounding the spiked sample, which suggests that the unaccounted activity represents TNT which was completely mineralized to carbon dioxide, water, and ammonia by the composting.

The results suggest that TNT is not completely mineralized by composting, but rather is bound to the compost in a form which can be hydrolyzed. This is in agreement with previous laboratory-scale composting studies, but none of the previous studies tested for hydrolyzable/nonhydrolyzable products. This observation suggests that the environmental availability and identities of the biotransformation products should be studied to determine the long-term behavior and acceptability of composting for remediating explosives-contaminated soil.

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Predictive Surveillance of Munitions Performance and Safety

As described in the previous Annual Report, we have been developing technologies for the nondestructive testing of combustible cartridge case (ccc) munitions for nitroester and moisture content. Nitroester migration into the ccc from the propellant weakens a critical adhesive joint in the case wall while moisture reduces the case wall hardness and affects the combustion efficiency of the ccc upon firing. Methods are needed for the rapid, nondestructive evaluation of ccc munitions for these two components. Two technologies are being developed: visual indicators which are attached to the exterior of a round and which change color in response to the buildup of these compounds in the ccc, and portable instruments for more quantitative measurements. The former would allow an instant use/no use determination in the field by gun crews, while the latter is more suited for quantitative testing in the field or in ammunition storage depots by quality assurance specialists in ammunition surveillance (called QUASIS in the Army). It also could be incorporated into automated ammunition handling systems.

Prototype visual indicators have been developed and demonstrated in laboratory experiments using cellulose test squares spiked with known amounts of nitroglycerin (a propellant nitroester) or water. For nitroesters, a modified Griess reagent system has been devised for solid state reaction. The dry reagents are applied in a thin layer to glass fiber paper and this reagent strip is then sealed on the surface of a spiked cellulose test square using plastic tape. The color of the indicator strip changes from white to magenta over the course of a few days in the presence of nitroglycerin at low percentage concentrations. The intensity of the color is proportional to the nitroglycerin content of the test square. Cupric chloride was selected for the moisture indicator. Both impregnated glass fiber paper and thin pellets of cupric chloride change color from brown to blue-green in response to moisture, but the latter configuration appears more useful because of its lesser sensitivity. Moisture concentrations of 6-8% require ca. 1-3 weeks for color change. At their present state of development, the indicator performance in laboratory tests suggests that they would be more suitable for temporary, one-time tests of munitions for short periods of time rather than for permanent installation on the

rounds and continuous indication. Further work must address questions of indicator stability and lifetime, sensitivity range, potential sources of interferences, and adaptation to and response calibration with actual munitions.

Two instrumental techniques have been tested for their ability to determine moisture and nitroesters in ccc material. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was not able to detect nitroglycerin spiked into nitrocellulose coupons, but that could be a result of the similar IR spectra of nitroglycerin and cellulose nitrate and the low concentration of nitroglycerin spiked. Moisture did cause small, but poorly reproducible changes in the IR spectra of nitrocellulose. The DRIFT technique was not encouraging in these scoping experiments, and other IR techniques such as attenuated total reflectance may perform better. Electrical capacitance also was tested, and was found to have considerable promise for moisture detection. Capacitance measurements at low frequencies readily detected changes in ccc moisture. An inexpensive battery powered commercial device for determinations of moisture in building materials was obtained for testing. The Army is now funding the

optimization and further testing of this device.

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Radioactive Mixed Waste Analysis

The Organic Chemistry section has maintained a capability for the analysis of organic compounds in radioactive mixed waste (RMW). Low level radioactivity samples containing less than 3700 Bq (0.1 μ Ci) of Class 1 radiotoxicity nuclides per sample can be prepared and analyzed in the nonzoned Organic Analysis group (OAG) laboratories in Building 4500S. Samples with greater activity are prepared in the Separations and Synthesis group contamination zone laboratory in the Radioactive Materials Analytical Laboratory (Building 2026), and if the extracts are sufficiently decontaminated, they are transferred to the OAG for instrumental analysis. This year, two nuclear waste tank characterization campaigns and a

contaminated ground water treatment study were the main clients of these services. Also served were several infrequent or one-time requests such as for PCBs in radioactive sediment from environmental compliance monitoring.

A major factor hindering optimum analytical performance and preventing the meeting of all regulatory analytical requirements is the continued lack of dedicated organic analytical instrumentation (primarily GC/MS) for contamination zone laboratories. As a result of this deficiency, volatile organic analyses are no longer offered, unless the samples are low enough in radioactivity to permit their analysis in nonzoned laboratories. Other analyses will be phased out if their performance cannot meet customer requirements or if their sample load cannot justify their continued maintenance.

In contrast, RMW analytical methods development has been a major activity this year. In a project for the DOE Office of Technology Development, Laboratory Management Division, EPA SW-846 and other methods are adapted to glove box and hot cell use with RMW, with the ALARA principle as the guiding factor in this adaptation. Method performance is

evaluated with standard surrogate samples and documented in protocols prepared for the DOE Analytical Methods Compendium. Other laboratories are assisted in adopting the technology. This project addresses organic as well as inorganic and radiochemical analysis. The latter two are conducted by collaborators in the Inorganic and Radiochemistry section. Sample preparation and analysis methods developed this year for characterization of regulatory organics in RMW are detailed in the previous sections of this group's report, and inorganic and radiochemical methods are described in the TRU group report.

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SPECIAL PROJECTS

R. A. Jenkins

This group performs research and development and provides specialty services in the areas of airborne contaminants and of field analytical technologies. These activities are based on expertise in air sampling, off-site support, and specialty instrumentation developed as a result of earlier studies of tobacco smoke and other aerosols. A characteristic of this work is that it requires combining sampling, separations, spectroscopy, and instrumentation capabilities of the section and division to achieve its objectives. Initiatives in sampling and in field analytical technologies in this period combined with a major involvement in the Department of Energy Office of Technology Development program are establishing the group as the focal point for research in field screening and for off-site specialty support.

Contamination of Building Materials by Chemical Agents

It has recently been recognized that a need exists to better define the manner in which chemical warfare agents interact with building materials. The information is needed to choose effective means of sampling and treatment to characterize and decontaminate structures. We have employed the agent simulants diisopropylmethyl phosphonate (DIMP), dimethylmethyl phosphonate (DMMP), and chloroethylethyl sulfide (CEES) to study the rates of permeation and evaporation of agents contaminating several porous building materials.

Cylindrical coupons of test material were placed in a permeation rate cell designed here specifically for this application. The design allows the three regions (face, back, lateral) of the specimen to be isolated and individually sampled. Simulants were spiked on one side of the coupon while mounted in the test cell, and air samples drawn through all three spaces of the cell were collected on sorbent media-containing tubes. The tubes were analyzed by thermal desorption gas chromatography, using sulfur or phosphorus specific detection.

The resulting data show that the simulant permeation through wood is nearly always in the lateral direction, with the wood grain. CEES penetrates much more rapidly than the DIMP or the DMMP, with permeation times of less than one hour, compared with a range of 7 - 20 hours for DIMP, and 30 - >120 hours for DMMP. Decontamination of the wood surfaces with large amounts of HTH slurry was not completely effective if the DIMP or DMMP was allowed to contact the wood for a few hours prior to decontamination. For gypsum wall board, all simulants permeated through to the side opposite to that spiked in a matter of a few hours. CEES permeated more rapidly (less than one hour) than the other simulants. Maximum breakthrough airspace concentrations ranged from a low of $150 \mu\text{g}/\text{m}^3$, to a high of nearly $300,000 \mu\text{g}/\text{m}^3$. Permeation into the lateral space was also substantial, but the time required for the permeation and the airspace concentrations were highly variable, even for a particular simulant.

We find that there is substantial sample to sample variation in the individual coupons of the porous media which have been tested. This suggests that for definitive results with a particular medium, large numbers of

individual coupons may have to be tested. Overall, if the actual agents behave comparably to that of the simulants, the data suggest that permeation into porous building materials is relatively rapid, and that decontamination of wood with HTH, if delayed for any significant length of time, is not likely to be effective, unless the decontamination mixtures can penetrate the media as effectively as the agents themselves.

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Hanford Underground Waste Storage Tank Study

One of the underground storage tanks at DOE's Hanford Site periodically releases noxious vapors, especially during low pressure meteorological events. On selected occasions, there have been incidents of worker exposure. In early February, we were directed by DOE's Office of Technology Development to provide technical and experimental design assistance to the effort

to characterize the exhausted species. Samples of the filtered tank headspace vapors collected on sorbent media have been received periodically throughout the year. Initial analysis of Depot Area Air Monitoring System (DAAMS) tubes indicated that at the sampling rates being employed, there was considerable breakthrough of hydrocarbons, making the tubes very difficult to analyze. Analysis of one of the tubes revealed one relatively high volatility phosphorus containing compound, albeit at fairly low concentrations. Gas chromatography/mass spectrometry (GC/MS) analysis of a few of the tubes yielded no characteristic ion fragments of phosphonates ($m/z = 97$) that can be confidently ascribed to phosphonates. Later GC/flame photometric detection of an additional suite of DAAMS tube samples exhibited no phosphonates, or other phosphorus containing compounds in the vapor emanating from Tank 241-C-103. However, data from single sorbent traps have indicated the presence of small quantities of tributyl phosphate, as well as at least one and perhaps two unknown species which contain phosphorus. Evidence to date suggests that one of these two unknowns also contains sulfur. From additional analyses of multi-sorbent traps, we have confidently identified

a homologous series of cyano-substituted alkanes in the tank vapors. Additional tentatively identified compounds include a series of alkanes and alkenes (referred to by others as normal petroleum hydrocarbons), as well as heavier alkanolic acids (straight or branched chain fatty acids). In mid-September, Tank 103-C was declared an Unresolved Safety Question, due to concerns about tank vapor flammability, delaying the acquisition of additional samples until after the beginning of the new calendar year.

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Carbonaceous Multisorbent Traps for Air Sampling

We have been investigating the use of carbonaceous multisorbent traps for a number of field applications. These traps are filled with sequentially loaded beds of commercially available graphitized carbon blacks and carbon molecular sieves. The traps have a number of potential advantages over earlier systems, including desorption at much higher temperatures, which enhances

analytical efficiency, and fewer chemical artifacts. Of particular interest to us have been triple sorbent traps, containing Carbotrap C, Carbotrap, and Carbosieve S III because they promise to provide an effective method for trapping a wide range of airborne organic contaminants. The sorbents are relatively hydrophobic, have no surface ions or active functional groups, and are not subject to degradation by common solvents.

Recent investigations with traps used to collect moderately volatile compounds, such as benzene and toluene, under ambient humidity conditions have indicated that only a small fraction of the target analytes are released during thermal desorption. The problem appears to be linked to the most adsorptive sorbent, Carbosieve S III, and our desorption process. Our experiments have shown a strange phenomenon: the moderately volatile compounds will not be released if Carbosieve S III is next to Carbotrap in the stainless steel trap, or if it is in a separate trap that is joined to a Carbotrap-filled trap during desorption. However, if the Carbosieve S III portion of the trap is removed before desorption is performed, all compounds are chromatographed. Until this difficulty can be resolved, we have been using double sorbent

traps (only Carbotrap and Carbotrap C) which efficiently trap moderate to high boiling compounds, such as trichloroethylene, perchloroethylene, and m-xylene, with recoveries at +90%. For the low boiling compounds, a separate Carbosieve S III trap is used. However, we are continuing to investigate the functionality of these triple sorbent traps which are capable of becoming an important sampling tool in many of our projects.

A. B. Hoffman, C. E. Higgins

Field Methods Evaluation

A project for the Laboratory Management Division of DOE's Office of Technology Development involving the development and validation of fieldable analytical methods has continued. The ultimate goal is reduction in costs and reporting times associated with laboratory-based analyses. Important aspects of this work are its emphasis on those contaminants and matrices of critical importance to the DOE complex, and the rapid deployment of methods through the use of commercially available technologies. Because of the

breadth of the project, it is being conducted in parallel to and in collaboration with Los Alamos National Laboratory. Each laboratory is focusing on those areas in which it maintains particular expertise. During the past year, commercially available field test kits for PCBs, mercury, lead and nitrate were evaluated here with reference to accuracy, precision, cost-effectiveness, specificity, and ease of use under field settings. PCBs and mercury, in soils, were analyzed by immunoassay. Ionic lead and nitrate, in water, were measured using chemical test strips. Except for lead, each analyte was measured in both spiked and naturally contaminated samples. Twenty to 40 samples per day can be analyzed with the immunoassays and even more with the strip tests. The sensitivity of the immunoassays is in the 2-5 ppm range. Nitrate was consistently detected at ≥ 5 ppm, lead ion at ≥ 20 ppm. Results obtained using these methods compared favorably with those obtained by standard laboratory methods. In addition to being useful as field screening methods, these kits can be used in the laboratory to sort out negative samples and/or to define proper dilutions for positive samples requiring further analysis. Standardized protocols for their use have

been submitted for inclusion in the DOE Methods Compendium.

L. C. Waters, R. R. Smith,

R. A. Jenkins

Arrayed Sampler for Subsurface Volatile Organics

There is a need for subsurface sampling in the vadose zone for a broad range of volatile organic compounds (VOCs) at contaminated sites, either during site characterization or remediation. One approach to the determination of a broad range of VOCs is to collect them on sorbent cartridges and subject them to analysis using sensitive, high resolution technology. An important activity this year has been the field testing and demonstration of an arrayed, multisorbent sampler for in-situ collection of volatile species at depths up to 40 meters in the vadose zone. The sampler consists of an array of six traps each packed with sequential beds of sorbent materials. One end of each trap can be opened to a screened space. The sampler can be lowered into a 10 cm diameter screened borehole and controlled from the surface. Air samples of nearly any

volume and/or time duration can be passed through the traps and the volatile organics retained. The arrayed sampler is then returned to the surface and the traps analyzed. Inflatable packers can be used to isolate the geologic zone being sampled, if appropriate.

The system was successfully deployed and demonstrated at the Savannah River Integrated Demonstration Project site in January and March, 1992. In the latter trial, the system was mated with the direct sampling ion trap mass spectrometer, in order to provide near real-time analysis of soil gas concentrations in defined subsurface regions. Numerous vadose zone samples were collected. Data acquired during the sampling yielded a wide range of apparent soil gas concentrations. Results from these initial field trials indicate that the sampler functions as expected. It is clearly capable of being deployed by one operator to depths of over 30 meters, and is adequately rugged in its current configuration. Soil gas samples as small as 15 mL can be concentrated on the multisorbent traps, and can be returned to the surface for analysis, with quantitative results.

Several modifications have been made to the sampler to improve its operation in deep

vadose zone wells. These modifications include expansion of the spacing of the packers to permit isolation of 60 cm long screened intervals, addition of a water sensor alarm system, independent operation of the packer cuffs, and stabilization of the flow meter readout at low flows. We expect to field test the modified sampler during 1993.

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**Instrumentation and Controls Division*

ORGANIC ANALYSIS

M. P. Maskarinec

The Organic Analysis group performs quantitative determinations of organic compounds in a wide variety of sample matrices, and some qualitative analyses on unusual matrices. Virtually all of these matrices are environmental in origin, (or are affected by environmental regulations) and can be roughly divided into routine environmental analyses and compliance analyses. Most methods used are taken directly from published regulatory protocols such as those promulgated by the EPA. Increasingly, the results generated must be of litigation quality. The group supports Laboratory programs as well as similar external and work-for-others programs. The group currently consists of eighteen full-time staff members, as well as supplemental staff from the Separations and Synthesis group, a decrease of two since last year, with no new hires expected before the end of calendar year 1993.

The primary missions of the group are supported by four interdependent efforts: 1) sample receipt and tracking; 2) sample preparation and gas chromatographic

screening analysis; 3) gas chromatographic/electron capture detection (pesticides and PCBs) and gas chromatography/mass spectrometric analysis; 4) reporting and quality control. Task leaders are designated for various support duties, including method implementation, nonroutine maintenance, work scheduling, and training. The receiving and reporting function is under the control of the group leader. In some of these areas, both staff and equipment capabilities have been expanded and/or upgraded during the year. We have continued to maintain our drinking water certification for the analysis of volatile organic compounds by acceptable performance on the EPA water supply series quality control samples as required by the State of Tennessee. In addition, we have applied for and received State certification for the analysis of samples collected during underground storage tank investigations. A significant effort has also been directed at maintaining performance on the monthly performance evaluation samples provided by the Analytical Products Group (APG).

Sample Receipt and Tracking

The efforts of the group are highly dependent on sample handling and tracking. Our sample tracking/chain-of-custody procedures have been in place for well over three years, and the efforts during this period have been primarily directed at refinement of the process. A staff member has been designated as full-time sample custodian, and has been given the responsibility of assuring that all programmatic deadlines are met. This is a very important duty, particularly at a time when more and more of the data generated are being reviewed for use in litigation. Refinements have been made primarily in the area of receipt of radioactive samples. Because most of our samples cannot be screened completely by standard health physics procedures, we have acquired our own survey meters, developed an SOP for screening radioactivity in samples, and established a process for acceptance of samples or delivery to Building 2026 for initial preparation. In addition, a formalized system has been initiated for the purpose of expediting sample return. This includes a designated storage area and a customer sample return logbook.

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Sample Preparation

No major changes have occurred in the sample preparation laboratory since the last annual report. However, the staff has been upgraded through experience, additional training, and collaboration with outside preparation experts. We have continued to refine the implementation of the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311). Since the time of promulgation, several issues which were not resolved or which led to difficulties in implementation have been resolved. The major hurdles have been mainly logistical, e.g., the difficulty in simple cleaning of apparatus after use. We have installed a restaurant-type sink, with deep basins and spray nozzles, to allow the efficient cleaning of apparatus without excessive labor on the part of the analyst.

A major effort during 1992 was directed at improving the recovery and overall accuracy of tissue preparation methods. With the help of Joann Treece of Paducah, several major improvements were made in the overall process of tissue preparation. The primary focus was on the initial homogenization of the samples, a step to which we had paid very little attention. A commercial grinder was acquired which

allowed more complete homogenization than our previous process of chopping and cutting. Fish tissue ground in such a manner with the addition of sodium sulfate prior to grinding, and the subsequent freezing of the sample, produces a matrix of sandy consistency, which is very easy to work with in the subsequent extraction step. In addition, we have set up an automated Soxhlet extraction system (Organomation, Inc.) to take advantage of the superior performance of this technique with respect to tissue extraction. This equipment will allow extraction of multiple samples in a reliable, reproducible manner. We expect to perform all future extractions of tissue samples in this manner.

With respect to the preparation of oil samples, we have implemented a florisil column clean-up prior to analysis to eliminate interferences. This has allowed us to reduce the number of false positives and to obtain better accuracy for this matrix.

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Gas Chromatography

The gas chromatography (GC) laboratory has been divided into two separate efforts. The first includes all compliance analysis for PCBs and pesticides. The second involves GC analysis for other purposes, such as screening waste samples, providing analysis of Toxicity Characteristic Leaching Procedure (TCLP) extracts for phenols, and performing analysis of total petroleum hydrocarbons and BTX (benzene, toluene, xylene). The pesticide laboratory has been upgraded with three new instruments, all Hewlett Packard (HP) 5890s with dual electron capture detectors (ECDs). The lab also contains one older GC with dual ECDs. One of the HP instruments is equipped with dual autosamplers to allow increased throughput for waste oil characterization. The other two instruments have dual column and single injection, to allow simultaneous confirmation. In a second laboratory, three instruments are configured for flame ionization detector (FID) analyses. Each of the two laboratories contains a state of the art chromatographic data system. In a third separate laboratory, two automated purge and trap samplers are coupled with gas chromatographs for the analysis of volatiles

for screening and also for gasoline range organics. All systems have capillary capability (either narrow bore or megabore). Many of these older chromatographs have considerable downtime, due to the age of the instrument and also to the increased numbers of highly contaminated samples. However, by using the older instruments for FID work, and performing most of the ECD work on the newer instruments, the life of the older instruments has been significantly extended. The HP data system acquired with the new instruments has the capability of handling all of the instrument control and preliminary data reduction requirements. This system is to be networked with the GC/MS data system for the automated generation of Contract Laboratory Program (CLP) forms.

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Gas Chromatography/ Mass Spectrometry

The GC/MS laboratory performs routine analysis primarily on environmental samples. The effort is divided between the analysis of volatiles and the analysis of extractables. Currently, three staff members are assigned to the laboratory which is concerned with the analysis of volatiles, with two other staff members assigned to the analysis of extractables. Four instruments are available for the analysis of volatiles, and two for semivolatile analysis. All instruments are maintained on vendor service contracts, which has allowed the instruments to be operated with minimal downtime. Two VOA GC/MS systems were purchased during 1991 and have been operated virtually continuously during 1992. One of the instruments has been dedicated to the analysis of groundwater by method 8240, and also occasionally for the 524.2 drinking water method.

The second of the newer instruments has been devoted to the analysis of TCLP extracts. Again a capillary column is used for this purpose. By adjusting all parameters, analysis of the TCLP volatiles extract has been extended to include most of the

base/neutrals, including pyridine. Acceptable calibration curves have been generated for these compounds, and this has removed the need for a separate GC/MS analysis of the semivolatile fraction of the TCLP extract. Parameters which were found to be crucial include the purge flow, the purge temperature, the trap material, and the desorption temperature. The result of these studies has been a much improved measurement system.

A new purge and trap equipped with a water management system was added which we hope will reduce the problem of carryover of water to the capillary column. This has its primary effect on the gases and early eluting analytes. The PTA-30 w/s autosampler is now being used primarily for soil samples. This is because the instrument lends itself well to the analysis of discrete samples, which previous work has shown to be the most representative sampling method. The instrument can be made to run unattended for increased laboratory sample throughput, reduced operator time and lower cost per analysis, although there are physical problems with the configuration of the trap and desorption. In addition, the unit possesses the capability of adding the surrogates and internal standards to the sample, improving analytical accuracy. We

intended that this unit would be dedicated to the analysis of relatively clean water and soil samples, and that has been its primary use to date.

In the analysis of semivolatile organics, the primary modifications to the systems have been the addition of new electronic pressure control devices on the injector ports. When fully operational, these devices are expected to dramatically improve the chromatography of the late-eluting peaks, and to decrease the analytical run time. In addition, instruments previously committed to semivolatile analysis of TCLP extracts are now used for the more regular analysis of NPDES and RCRA water samples.

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Reporting and Quality Control

Significant effort during the past year was devoted to improving the quality of the work of the group. As in previous years, much of this effort was driven by the results of external audits. Additional certification was obtained from the State of Tennessee for performing analysis of samples resulting

from underground storage tank remediation. This certification is a result of satisfactory performance on external samples for volatiles, pesticides, and herbicides. The HPLC method for herbicides was used, and the results were found to be acceptable. This was a big step in gaining approval for this promising methodology. In addition, we have continued to participate in the performance evaluation program administered commercially by the Analytical Products Group. Our scores have been quite consistent, and we have had very few outlier results over the last year. These materials are similar in nature to the EPA performance evaluation materials, with the exception that the results are transmitted to the laboratory promptly, allowing for immediate corrective actions.

One of the major problems, in terms of QA, has been an inadequate system of data review. This has been partly due to staff limitations and partly due to a lack of formality in the review process. As a result, several steps have been initiated to prevent reoccurrence. Where the group leader was previously reviewing all results prior to and after reporting to AnaLIS, task leaders have been assigned the job of reviewing data prior to reporting, and the group leader is now

reviewing data only at the final stages. We have found that this intermediate review greatly reduces the opportunity for error. In addition, we have developed and implemented a QC checksheet for use by the analysts. This checksheet brings the level of data review down to the individual responsible for the generation of the data. This has had two major impacts. First, the analysts have become much more aware of the specific QC requirements of the methods. Second, since the checksheet is delivered with the data report, there has been an improvement in customer satisfaction. Work still remains to be done: SOP's need updating, new methods must be implemented, and more data must be electronically reviewed. However, a significant amount of progress has been made.

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ORNL/UT RESEARCH PROGRAM

G. A. Guiochon

The ORNL/UT Distinguished Scientist Research Program is a joint venture of the Laboratory and The University of Tennessee. It is designed to attract distinguished scientists to contribute to both institutions through their specialty expertise and their ability to attract highly qualified predoctoral and postdoctoral students. The Analytical Chemistry Division hosts a program focusing on research in chemical separations. Research on high concentration, non-linear and preparative chromatography and on gas-solid adsorption has continued in this period.

Maximum Production Rates and Optimum Operating/Design Parameters in Overloaded Elution and Displacement Chromatography

A theoretical study to optimize experimental conditions to achieve a maximum production rate in overloaded elution and displacement chromatography has been completed. This study is based on the use of the equilibrium-dispersive model of chromatography and the competitive

Langmuir isotherms to calculate individual band profiles in elution and displacement, and of a Simplex algorithm to optimize the production rate of either component of a binary mixture. The operating parameters (sample size, mobile phase velocity, and the displacer concentration in the displacement mode), and the column design parameters (column length and average particle diameter) were optimized simultaneously. Binary mixtures of relative concentrations 3:1 and 1:3 were considered over a number of separation factors between 1.2 and 1.8.

One of our major results is that, in either mode of chromatography, the maximum production rate is achieved at very low values of the retention factors, k' , much lower than those used in current practice. In all cases, unless k' greatly exceeds that optimum value, the production rate is higher in overloaded elution than in displacement chromatography. This is particularly true for the extraction of a minor component which is not eluted first.

A. Felinger, G. A. Guiochon*

*UT Postdoctoral Program

Various Strategies for Mixed Zone Recycling in Preparative Chromatography

Preparative chromatography is becoming an increasingly popular technique for the production of purified products in the pharmaceutical industry. The process is still new and many improvements and refinements are possible. One procedure often advocated is the injection of large size samples, collection of the purified products contained at both ends of the interfering bands of the elution chromatogram, and recycling of the central, mixed zone. Various strategies combining this band shaving with the injection of fresh feedstock have been described in the literature. Using methods previously developed, we have optimized the experimental conditions for these methods for maximum production rate or for minimum amount of solvent used per unit mass of purified product produced. We have calculated the production rates achieved for products of a given purity, the cost in terms of amount of solvent required, and the concentration of the collected fractions.

A comparison of the results achieved shows that, surprisingly, recycling methods improve production rate and costs by relatively low margins, usually between 10

and 30%. This improvement is achieved at the cost of a more complicated operating scheme, and requires complex computer control of the unit. Further investigations are in progress, as well as experimental studies on the implementation of the recycling methods.

F. Charton, G. A. Guiochon*

*UT Predoctoral Program

The Change of Pressure Drop During Large-Scale Chromatography of Viscous Samples

The variation of the inlet pressure during the injection and the elution of a band of a viscous compound, or pressure drop profile, was calculated for overloaded elution chromatography, assuming a significant difference between the viscosities of the solvent and the pure solute. The viscosity of the mixture was calculated using the Grunberg-Nissan equation. By means of numerical integration of the mass-balance equation, the concentration profile along the length of the column was calculated. Then, using the instantaneous concentration profiles to derive the local viscosity, hence

the local pressure gradient, the pressure drop was determined by integrating the local pressure gradient along the column.

The change of pressure drop calculated is significant only when the concentration of the injected sample is very high. If a dilute sample is injected, even large sample volumes will not really change the pressure drop. The maximum pressure drop observed in each case is practically independent of the adsorption isotherm. The only determining factors are the solute concentration in the sample, the amount of the sample injected, and the solute viscosity.

A. Felinger, G. A. Guiochon*

*UT Postdoctoral Program

Prediction of a Protein Band Profile in Preparative Reversed Phase Gradient Elution Chromatography

The overloaded band profiles of Lysozyme in reversed phase preparative chromatography were recorded on a C18 chemically bonded silica column, with acetonitrile/water as the mobile phase. These experiments were carried out under isocratic conditions at 31.6, 31.9 and 32.2%

acetonitrile (ACN) for loading factors up to 43% of the column saturation capacity and under linear-solvent-strength gradient-elution with gradient slopes of 0.5 and 1% ACN/min, for loading factors up to 11.3%. The adsorption isotherms of Lysozyme were measured for the same solvent compositions and found to be accurately accounted for by a Langmuir isotherm model.

Using a Craig model implementation of the equilibrium-dispersive model of chromatography, the band profiles of Lysozyme were calculated. An excellent agreement was observed between these calculated profiles and the experimental profiles recorded at loading factors below 5%. By contrast, band profiles calculated using a Langmuir isotherm failed to describe the experimental bands. At column loadings exceeding 8%, a slight but systematic deviation takes place between calculated and experimental profiles. This is most probably due to the considerable concentration effect of the gradient, making the band experience phase equilibrium in a concentration range which greatly exceeds the one where the isotherm data have been measured.

M. Z. El Fallah, G. A. Guiochon*

*UT Postdoctoral Program

**Optimization of the
Experimental Conditions for
Maximum Production Rate of
Purified Enantiomers
in Chromatography**

The optimum experimental conditions (sample size, mobile phase flow velocity and composition) are calculated for maximum production rate of either one of two enantiomers contained in feeds of different compositions (1/1, 1/10 and 10/1). The products are obtained at 99% purity. The calculations use the equilibrium-dispersive model of chromatography and the equilibrium isotherms determined experimentally from the rear, diffuse boundary of overloaded elution profiles. The production rate measured experimentally under the optimum conditions agrees within 4% of the calculated values. There is an optimum value for the retention factor which is higher than predicted by a model assuming constant separation factor, because both separation factor and retention decrease with increasing organic solvent concentration in the mobile phase.

Optimum experimental conditions are predicted for the maximum production rate of (i) D- or L-alanine, purified to a 99%

purity from a racemic mixture of their N-benzoyl derivatives and (ii) (R)- or (S)-2-phenylbutyric acid also purified to a 99% purity from their racemic mixture by preparative chromatography on ionically immobilized bovine serum albumin, using phosphate buffers with an adjustable concentration of 1-propanol. The experimental production rates and recovery yields measured under these conditions are in excellent agreement with the calculated values. These results validate the approach used for optimization of preparative liquid chromatography.

*S. C. Jacobson**, *A. Felinger***,
G. A. Guiochon

*UT Predoctoral Program

**UT Postdoctoral Program

**Estimation of the Number
of Enantioselective Sites
of Bovine Serum Albumin
Using Frontal Chromatography**

On a column packed with bovine serum albumin (BSA) immobilized covalently to silica, the adsorption isotherms of the enantiomers of mandelic acid, tryptophan, 2-phenylbutyric acid and N-benzoylalanine are measured using a buffered mobile phase. Knowing the amount of BSA immobilized on the column (36 mg), the ratio of the number of enantiomer molecules needed to saturate the enantioselective retention mechanism to the number of BSA molecules is determined. The mean of the set of eight enantiomers is 0.28. These data confirm that at most one enantioselective site exists for each BSA molecule for the kind of enantiomers studied. This explains the low saturation capacity of the stationary phase and the low production rate which can be achieved in preparative chromatography.

S. C. Jacobson, G. A. Guiochon*

*UT Predoctoral Program

**Modeling of the Adsorption Behavior
and the Chromatographic Band Profiles
of Enantiomers on Immobilized
Cellulose Esters**

The single component and the competitive adsorption isotherms of the two enantiomers are measured by frontal analysis. The experimental data do not fit the Langmuir model, but are well accounted for by a bilangmuir model. This model assumes the existence of two types of adsorption sites on the adsorbent surface. A first type corresponds to all the non-selective interactions between the enantiomers and the stationary phase. The coefficients of this first term are the same for both enantiomers. The second type of sites corresponds to the enantio-selective interactions which are responsible for the separation of the two enantiomers. As these interactions are essentially due to the formation of a labile complex between the enantiomer and some groups at the surface of the stationary phase, the number of adsorption sites is the same for both enantiomers, only the free energies of interaction differ. Accordingly, the energy coefficient of the corresponding Langmuir terms are different, but the saturation capacity is the same for both enantiomers.

Thus, although the bilangmuir model has four parameters for a compound, the model requires only five parameters for the two enantiomers.

As a demonstration of the validity of this modeling approach, the competitive bilangmuir isotherm model built using the parameters of the single component bilangmuir model for the two enantiomers accounts very well for the experimental data obtained for the competitive isotherms. Furthermore, the individual elution profiles of the two compounds are in excellent agreement with the profiles calculated with the equilibrium-dispersive model of chromatography, using the competitive bilangmuir isotherm.

The results obtained with methyl mandelate on cellulose tri(4-methyl benzoate) coated silica are quite different from those obtained with Tröger's base on cellulose triacetate. In this latter case, the equilibrium isotherm of the lesser retained enantiomer was well accounted for by the Langmuir model, while the isotherm of the more retained enantiomer followed the quadratic model, and exhibited an inflection point. Further investigations are in progress to attempt a better understanding of the separation mechanism of enantiomers on

cellulose-based stationary phases.

F. Charton, G. A. Guiochon*

*UT Predoctoral Program

Contribution to the Isolation and Characterization of Buckminsterfullerenes

Buckminsterfullerenes are extracted from samples of the soot generated by the high energy electric arc discharge between two graphite electrodes and supplied by R. N. Compton of the Health and Safety Research Division. A rapid and quantitative procedure based on ultra-sonic extraction was developed. It permits the rapid evaluation of adjustments made in the synthesis process by relating them to the mass of the fractions obtained. Production yields measured as the proportion of total fullerenes extracted from the soot samples are of the order of 4 to 5% in most cases, 10% in the best case.

Purified samples of C_{60} , C_{70} and C_{84} are obtained by high performance liquid chromatography, using chemically bonded

C18 silica as stationary phase and n-hexane as the mobile phase. The purified fullerenes were identified by laser desorption Fourier transform mass spectrometry and verified by UV-visible spectroscopy. The results are consistent with those previously reported.

We have studied the separation of the buckminsterfullerenes C_{60} and C_{70} by liquid chromatography on different systems. First considered were classical adsorption systems involving normal phase (with silica as stationary phase), non-aqueous reversed phase (with C_{18} silica), and non-polar adsorption (on graphitized carbon black). Mobile phases of different compositions, but all based on hydrocarbons as the main solvent, were used. Then, we studied systems based on the use of charge transfer complexation as the retention mechanism, and used dinitro-benzoyl-phenyl-glycine (NBPG) and R-(-)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid (TAPA), also with hydrocarbon mobile phases of different compositions.

While we found that the adsorption of the fullerenes on all the other phase systems studied is exothermic, we observed that their interactions with the charge transfer phases exhibit an unusual endothermic behavior. The retention times of C_{60} and C_{70} on these

phases increase with increasing temperature. The adsorption enthalpy and entropy derived from the Van't Hoff plots confirm this rare temperature dependence. The adsorption enthalpy is positive and the adsorption entropy strongly negative.

M. Diack, G. A. Guiochon*

*UT Postdoctoral Program

Accuracy of Adsorption Isotherm Determinations

The conventional ECP (elution by characteristic point) method of isotherm determination is based on the solution of the ideal model of chromatography for the diffuse band fronts (usually the rear of a band). The ideal model assumes that the column efficiency is infinite. It predicts that the retention time of a concentration on the diffuse part of the band profile is linearly related to the slope of the isotherm. A simple integration procedure permits the determination of the isotherm from the profile recorded for a large size sample of a pure compound. A model error comes from the fact that actual columns have a finite

efficiency, and accordingly the band profiles are more dispersed than predicted by the model. This introduces a systematic error which has never been studied.

Using previous theoretical results, we are studying the magnitude of this systematic error and trying to develop some appropriate corrections. The effect is especially important at low concentrations where the deviation between the measured and the true isotherms may become important when the column efficiency is moderate.

*H. Guan**, *B. J. Stanley***,

G. A. Guiochon

*UT Predoctoral Program

**UT Postdoctoral Program

Comparative Study of Various Methods for the Determination of Adsorption Energy Distribution Functions

The gas-solid equilibrium isotherm of 1-chlorobutane vapor was measured on three different alumina samples. These samples were high performance grade alpha-alumina powder for ceramics. They were rated as

good, medium, and bad from their firing performance. The isotherms were measured by applying the ECP (elution by characteristic point) method to the band profiles obtained upon injection of large size samples of the vapor on an open tubular column whose inner wall was previously coated with a layer of the powder.

These isotherms were fitted to the Generalized Freundlich Isotherm, and excellent agreement was obtained upon optimization of the coefficients by a non-linear procedure. Adsorption energy distribution functions were derived from these isotherms using the Sips method, Hobson method, and the condensation approximation method. These functions are compared together. They are also compared with the adsorption energy distributions derived directly from the adsorption isotherms, using the last two methods, without assuming any isotherm model. The Hobson method gives good results in the low to medium pressure range, but deviates from the exact solution in the high pressure range. The condensation approximation method does not give an accurate adsorption energy distribution.

Two programs based on the Adamson and Ling and on the House and Jaycock

HILDA methods, respectively, are shown to give adsorption energy distributions which are in excellent agreement with those obtained from the analytical solutions in the particular cases when such analytical solutions exist. These methods require no assumption regarding the adsorption energy distribution. They use raw or smoothed isotherm data, but without needing any isotherm model. It is shown, however, that isotherm data should be measured over a wide range of adsorbate partial pressures, extending to near the saturation capacity. While lacking accurate low pressure data will result in an inaccurate energy distribution in the high energy range, lacking these high pressure data may result in an entirely wrong energy distribution.

*S. Golshan-Shirazi**, *B. J. Stanley***,

G. A. Guiochon

*University of Tennessee

**UT Postdoctoral Program

4. OPERATIONS

W. R. Laing

This year the division was the recipient of 20 reviews, appraisals and audits by external evaluators. Corrective actions are being tracked on an internal database with evidence packages to verify completion. Training has been given to staff on quality control practices. The division's quality control program showed a quality level of 97.6% where 95% was expected. Double-blind spiked solutions had an average spike recovery of 93%. Over 1500 ampules of quality control solutions were distributed to inspectors in the Nuclear Regulatory Commission (NRC) Water Quality Program.

Environmental Protection monitored satellite accumulation areas and 90-day accumulation areas. A waste minimization plan was written and PCB-containing transformers were tracked. Clean-up of legacy contamination continues.

The division's Safety Program increased its visibility and maintained its effectiveness. There has not been a lost workday case since June 1972. A division-wide clean-up was conducted in the Fall and quarterly safety inspections continued.

The Analytical Improvement Council provided advice on delegation of authority, outlined procedures for voicing concerns, and conducted a follow-up communication survey. An employee handbook is being prepared.

The division used courses from ORNL, Energy Systems, consultants, academic institutions and manufacturers to meet training needs. Our first expert system training module was developed this year to meet a requirement for training on environmental regulations. The Transuranium Analytical Laboratory has begun a regimented program to meet the training requirement for non-reactor nuclear facilities. Division staff received over 2000 hours of training this year, an average of 13 hours per person.

The Radiation Control Officer monitored the activities of the division to provide a safe workplace for personnel. Participation on an ALARA Working Committee provided insight on means for reducing radiation exposure. Twelve occurrence reports were filed this year with most of these related to contamination incidents. A new procedure for occurrence reporting has been written.

QUALITY ASSURANCE/ QUALITY CONTROL

**J. L. Miranda, L. C. Satterfield,
J. L. Wagner***

During the past year the division was subjected to 20 reviews, appraisals and audits by external evaluators. A significant amount of time was spent participating in these, and also developing the associated corrective action plans. The actual tally of resultant corrective actions will not be determined until the division receives feedback on the plans from the evaluation teams. Factors addressed in the corrective action plans that might affect the tally included findings that overlapped within an evaluation or with other evaluations and findings that were not referenced to requirements.

One of the more significant evaluations was the Environmental, Safety and Health (ES&H) appraisal of the ACD. It was part

of an Oak Ridge National Laboratory effort to appraise the implementation and effectiveness of the management systems in each division for ES&H self-assessment, conduct of operations, and assurance of environmental compliance. It also included root cause analysis, corrective action tracking and closure, trending, and lessons learned. Addressing the recommendations of the team will help the division improve its implementation of DOE Order 5482.1B, the source of the appraisal criteria.

In the wake of the ES&H appraisal, self-assessment teams were organized to focus on three areas for improvement within the division: research and development interfaces, the division quality control (QC) program, and the protocols for ion chromatography systems. Self-assessment surveillances were also planned.

The division completed a number of other quality improvement activities over the year. One priority was the quality of

environmental data. The division contracted a course on quality assurance fundamentals tailored to the analytical laboratory. Most of the participants in the course were analysts involved in environmental compliance work. This course was followed by training on how to improve processes by making better use of the control charts provided by the QC program. This will be followed in 1993 by a computer-based training package on the analysis requirements associated with different environmental regulations.

Other significant quality improvement activities were piloted by the Transuranium and Activation Analysis group. This group developed a more efficient format for

procedure writing, a more streamlined and better documented approach to procedure reviews, and the first group QA plan to begin fully implementing DOE Order 5700.6C, "Quality Assurance".

Ninety-six quality control solutions were distributed by the QC laboratory to five ACD groups in 1992. Results were compared to the make-up value $\pm$ two sigma. Ninety-five percent of the results should fall within this bracket. The performance of the laboratories is shown in the table below.

Overall in ACD, 8953 external control results were reported in AnaLIS, with an overall ACD quality level of 97.6%.

Table 4.1. Quality Control Results

Group	No. of Results	Quality Level ¹
Inorganic Analysis	3787	98.5%
Radioactive Materials Analysis	1758	96.5%
Transuranium and Activation Analysis	1690	97.2%
Low-Level Radiochemical Analysis	431	93.3%
Organic Analysis	1287	98.1%

¹ Quality Level = No. of Results within Limits / Total No. of Results * 100

All results that fell outside of the two sigma limits and did not have a special cause assigned to them were investigated. A Pareto Chart was constructed to determine the most frequent failure cause. The most frequent cause was entering a control under the wrong procedure name and/or wrong batch code. Other special causes include mistakenly entering wrong values, instrument problems, and calculation errors. Actions were taken to reduce these types of errors.

In 1992, the quality control group also provided researchers with control solutions to be used in their work. Approximately 30 spiked solutions were prepared for the Organic Spectroscopy group.

Training sessions during group meetings have been held to help educate the analysts concerning how to enter results into AnaLIS, how to construct their own control charts, how to use QC data to gain process knowledge, trend analysis, and to emphasize the importance of total quality management and continuous improvement. These training sessions will continue throughout 1993. Monthly proficiency environmental testing samples were purchased from Analytical Products Group (APG) for both the organic and inorganic laboratories. All analytical

chemistry laboratories operated by Martin Marietta Energy Systems participate in this monthly program. The organic analysis laboratory submitted nearly 700 results during 1992; 98.0% were acceptable. The inorganic laboratory reported over 900 results; 98.1% of them were acceptable. Acceptable to APG means that the data submitted were less than 1.97 deviations from the mean value.

The double-blind spiking program continued; control samples were prepared by the QC personnel and submitted to ACD by the customer alongside routine environmental samples. A total of 62 samples spiked with PCBs, metals, organics, and/or radioisotopes was submitted during the year, resulting in 141 analyses. Eight unspiked blank solutions were also submitted. The annual average recovery of spiked material was 92.8%. All analyzed blank samples showed no spiked compounds.

In 1992, 8953 external control results were reported as compared to the 3990 results reported in 1991, an increase of 125%. Acceptable results increased slightly from 96.7% in 1991 to 97.6% in 1992. The organic laboratory increased its activity in the APG Proficiency Environmental Testing (PET) program from 1991 to 1992 by 40%

and the inorganic laboratory increased its involvement in the program by 12.5%.

The ACD Quality Control group continued activities relating to the quality control project contracted with the Nuclear Regulatory Commission. The project supports the evaluation of nonradiological water chemistry at nuclear power reactors by providing standards for licensee analysis, analyzing split samples from primary and secondary coolant systems of the reactors, assisting the regional inspectors with technical questions pertaining to the standards, and monitoring the statistical evaluation of all analytical data.

In 1992, all of the standards were certified and certificates of analysis were developed. Instructions and reporting forms were constructed and, after a field test, were revised based on comments from the inspectors involved in the field test. Over 1500 standards ampules were shipped to requesting inspectors in all four regions. ORNL has received 13 split water samples and results for 100 standards on the standards report forms.

Throughout 1993, the QC group plans to continue distributing standards, proceed with the collection of standards results, enter standards results into a database so that a

multitude of statistical tests can be performed on them, analyze split samples and draw conclusions from all information obtained to help assist the NRC inspectors in evaluating the adequacy of the licensees' chemistry measurements.

*Office of Quality Programs and Inspection

ENVIRONMENTAL PROTECTION

C. A. Biggs

Environmental issues at ORNL have been an area of high visibility this year. All of the Waste Storage Areas in the division are inspected by ORNL personnel from the Office of Environmental Compliance and Documentation (OECD) each month. This includes RCRA Satellite Accumulation Areas, RCRA 90-day Storage Areas, and Toxic Substances Control Act (TSCA) Storage Areas. Some of ACD's areas are RCRA/TSCA storage areas. These are inspected monthly with an RCRA emphasis and also with a TSCA emphasis. There has been a push to educate all ACD personnel concerning environmental regulations and how they are being interpreted in particular

situations. This will be an ongoing emphasis for ACD.

During 1992, ACD has taken the following steps to determine problem areas and look at baseline assessments for our waste streams:

1. ACD Waste Minimization Plan. This addressed all waste streams within the division. Clean-up continued in several areas so a true baseline may not be recognized this year.
2. Drain Survey. All drains within the division were examined to determine where they were being routed. This was done by recent blueprints, where available, and dye testing. We still have a few labs in 4500N that will require dye testing. This should be completed in 1993.
3. Surveys for PCB Materials. There were several calls to identify equipment that might contain PCB oils. Two areas were identified: one transformer in 4500N and several PCB light ballasts at 2026. The light ballasts have all been replaced with non-PCB light ballasts. The transformer is still in operation and will be inspected annually to ensure that it continues to meet all TSCA requirements.
4. Comprehensive Surveys for Rad Contamination. A program was begun with health physics personnel to do a comprehensive survey of ACD laboratories that will identify any legacy rad contamination. This is a slow process and will be an ongoing project for several years.

Overall, the division is continuing to emphasize environmental issues. This requires an awareness of where we are today, what problem areas might exist, and where we should be at this time next year. We expect to see these issues improved over the next year.

SAFETY PROGRAM

S. D. Wright

An Environmental, Safety and Health Action Plan was implemented as a guide toward better safety in the Analytical Chemistry Division during 1992. The division experienced four (4) first aid cases against three (3) during the same period last year. Increased awareness of safety has been emphasized in all our safety meetings as a result of the above incidents.

The division has not experienced a lost workday case since June 1972.

Notable achievements this report period:

1. Safety meetings held - 24; total attendance - 550.
2. Several ES&H appraisals were conducted. Deficiencies were documented and corrective actions taken.
3. Spring Clean-up Week activities in May included fire training at Buildings 2026 and 4500N.
4. Special seminars relating to environmental safety and health were given.
5. Monthly safety meetings at Building 2026 were continued.
6. Operation safety summaries for ACD laboratory operations were documented.

This has been a time of increased activity in areas of many ES&H audits, investigations, and inspections. ACD personnel have made significant advances toward a safer working environment. These include better housekeeping, safer laboratory practices, and a much-improved attitude in general about personal safety.

The division continues to maintain a high level of safety awareness and accident prevention.

ANALYTICAL IMPROVEMENT COUNCIL

C. E. Higgins

The orientation manual for new Analytical Chemistry Division employees, started by the Orientation Committee of the Analytical Improvement Council (AIC), has been expanded in scope to serve as an employees' manual for all ACD members who desire it. Hard copies also will be available in all section offices, and written material may also be made available on VAX.

In response to the DOE Panel's suggestion that ACD should have a formal method for the delegation of authority, AIC formulated a six-point method. The main point, to prevent confusion about who is in charge during the absence of the supervisor, would require the supervisor to appoint an interim leader, preferably in writing, and to notify the employees affected.

AIC also wrote a procedure for raising environmental, safety, and health concerns, starting within the division but including Martin Marietta Hot Line numbers. It is being included in the employees' manual.

AIC has recommended that typed purchase orders be sent to the requestors

before they are submitted for authorized signatures. This helps prevent mistakes caused by typo's.

Members of AIC participate in the "adopt-a-shelf" program at the Central Research Library by periodically arranging loose (unbound) journal editions chronologically.

The 1992 Employee Communication Survey was reviewed by AIC. A marked increase in ACD's favorable responses occurred in this survey compared with the 1989 survey. Of the 118 questions common to both surveys, the vast majority (84%) showed an increase in favorable response this year. Only 15% of the responses showed a decrease (1% unchanged), and the decrease averaged only 5% per response compared to an average increase of 11% in the favorable responses. ACD's favorable responses averaged 58% compared to 53% for both ORNL and Energy Systems. However, the fraction of division personnel responding was only about half that for ORNL and Energy Systems, so AIC sponsored a second communications survey using questions from the original survey and tailored to ACD. Over half of the division members responded to the second survey. A very large number (80%) of the questions received very favorable responses, and the average of the

favorable responses increased to 65%. Of the few questions receiving unfavorable responses, two dealt with communication (not being apprised of changes affecting the employee before they are made, and not receiving feedback from the immediate supervisor concerning job performance). Other unfavorable responses concerned procedures and policies which did not help get the job done, and inadequate work space. On the whole, however, the responses were overwhelmingly positive. AIC has attempted to help by offering suggestions in areas wherein the division has the potential to create further improvement.

TRAINING PROGRAM

T. R. Mueller

The past year has seen a considerably increased emphasis on training activities in ACD. Training direction and extent is driven by laws, orders, directives and policies. The ACD training effort is organized with a training manager whose function it is to maintain oversight of the Training Program, and with a coordinator who is charged with the task of implementing that program.

The training needs of individuals must be established. These needs must be met with the appropriate courses of instruction and training. A Training Needs Overview (TNO) program has been implemented at ORNL and serves to assist in identifying and scheduling training. The division draws on several sources for curricula that satisfy the needs. Some courses are taught by locally trained staff, some are provided through contracts with commercial vendors or through academic institutions, and some training is obtained from manufacturers of equipment in use in the division.

To meet the varied needs, it is necessary to locate sources of supply and schedule attendance for training. A database, TRAIN, was developed and is maintained for this

purpose. With this database it is possible to verify training for an individual, to prompt for required retraining with appropriate anticipation, and to provide summary reports that are useful in tracking the individual for compliance with training requirements or for monitoring the division-wide training effort.

Self-paced, computer-based training is finding wider acceptance as an instructional technique. The coordinator has been trained to administer some of this training. He has also been trained and serves as a presenter for classroom training.

Site-specific, job-specific, and on-the-job training are components of the ACD training program. Accredited training also is required for ACD personnel who work in the Radiochemical Engineering Development Center. This is provided through liaison with the Chemical Technology Division.

Many laboratory instruments now have computers associated with them. Often, an operator must be conversant not only with the analytical procedure, but also with the functions of the computer, in order to configure an instrument for proper measurement and report generation. Personnel are afforded the opportunity to enroll in computer language courses and to attend vendor training schools to acquire and maintain necessary skills needed for routine

or research activities.

ACD staff received 2050 hours of required training in calendar year 1992. Twenty people were involved in other education courses. Most of the latter courses were related to development of computing skills or data systems access. New employees at the Laboratory now receive three days of orientation, one of which is spent in the division.

RADIATION CONTROL

L. Robinson

Demands placed on the Radiation Control Officer (RCO) continued to increase in 1992. A new degree of "formality" and administration is being expected of the position. For example, a two-day training program was developed specifically for RCOs, and a Laboratory-wide procedure is being written to more clearly define the duties and responsibilities of RCOs.

During 1992 the RCO served on the ALARA Working Committee for the Laboratory, reviewed several procedures for radiological safety in the division, reviewed operations at most of the ACD laboratories involved with radioactive materials or

sources, and provided ACD managers and staff with information pertaining to changes in ORNL's health physics practices and procedures.

The demands of the Occurrence Reporting system are somewhat unpredictable. Due to the time constraints on reporting occurrences, it is often necessary for this function to take priority over all other activities. The division has had a number of reportable incidents with which the RCO has had to become involved. A total of twelve reportable incidents occurred in the last twelve months. Ten of these incidents involved personnel or property contamination. A two-day training course in root cause analysis was successfully taken to aid in the analysis of occurrences. A new division level procedure for occurrence reporting has been written.

5. EDUCATION PROGRAMS

The division maintains liaison with the academic community through a number of joint programs. These include hosting fellowship holders from ORAU, co-op students from The University of Tennessee (UT), special undergraduates from the Great Lakes Colleges Association and a program with Historically Black Colleges and Universities. In addition, graduate programs are maintained with UT.

Doug Goeringer served as Student and Faculty Programs Coordinator during 1992.

OAK RIDGE ASSOCIATED UNIVERSITIES

Postgraduate Research Program. David M. Chambers completed his research on explosives detection projects.

Bobette Nourse completed her work with Michelle Buchanan on a DOE-sponsored project to identify DNA adducts with mass spectrometry.

Michael D. Barnes continued working on new techniques for ultrasensitive detection of organic and biological molecules with Mike Ramsey.

Kevin Hart continued his appointment to pursue further research and development projects in mass spectrometry.

Jun Xu continued work with Lester Hulet in slow positron research.

S. Habibi-Goudarzi began research on fundamentals of collision activation and collision-induced dissociation in the Organic Mass Spectrometry group.

Roland Hergenroder began research on proof-of-principle demonstrations of microchip liquid chromatography in the Optical Spectroscopy group.

Lance Koutny began his appointment in the Optical Spectroscopy group with Mike Ramsey on proof-of-principle demonstrations of microchip liquid chromatography.

Mo Yang initiated his research on optical spectroscopy of trapped molecular ions and ion mobility spectrometry at atmospheric pressure in the Optical Spectroscopy group.

Stephen Jacobson was awarded the Alexander Hollaender Distinguished Postdoctoral Fellowship to conduct research with Mike Ramsey on proof-of-principle demonstrations of microchip liquid chromatography.

Environmental Restoration and Waste Management Fellowship. Rhys H. Thomas worked with Robert Hettich on the investigation of the stabilities and reactivities of fullerenes with compounds of environmental interest.

Professional Internship Program. Patrick Limbach (Ohio State University) continued his research with Michelle Buchanan in developing a new means of injecting ions into a Fourier transform mass spectrometer.

Matthew Miller (University of Wisconsin) conducted research with Mike Ramsey in ultrasensitive detection using lasers.

Research Participant Program. Daniel J. Van Dalsem (University of Kentucky) conducted research with Frank Dyer to improve the neutron activation analysis methodology for the determination of aluminum, calcium, and manganese in biological tissues.

Gregory Kerchner (Harvard University) investigated novel gel substrates for the capillary gel electrophoretic separations of biopolymers, especially short-chain oligonucleotides and proteins.

Faculty Research Participation Program. Kin C. Ng (California State University) worked with Mike Ramsey to develop high-resolution, ultrasensitive laser spectroscopic techniques.

Elizabeth Stemmler continued her collaborative research with Michelle Buchanan in gas-phase ion chemistry and isomeric differentiation using mass spectrometry.

Lori Wang (University of Tennessee) worked to develop a software program to extract data from the AnaLIS database.

Eddie Wang (University of Tennessee, Chattanooga) worked with Bob Shaw on diamond film synthesis.

J. M. E. Quirke (Florida International University) worked with Gary Van Berkel on electrospray ionization mass spectrometry and mass spectrometric analysis of porphyrins.

SEED Program. Omayra Padilla DeJesus (University Gardens High School, Puerto Rico) studied organic ion imaging by SIMS with Peter Todd.

Ivelisse Hernandez Santiago (Jose S. Alegria School, Puerto Rico) worked with Michelle Buchanan in sample preparation for environmental analysis.

UNIVERSITY OF TENNESSEE

Distinguished Scientist Program. Georges Guiochon is continuing his work through the ORNL/UT Distinguished Scientist Program. He maintains research groups at both UTK and ORNL. During 1992, postdoctoral researchers at ORNL included M. Diack, A. Fellingner, and B. J. Stanley; predoctoral students were F. Charton and H. Guan. M. Z. El Fallah, S. Jacobson, and E. O. Murphy completed their appointments in 1992.

Postgraduate Research Program. L. R. Riciputi continued his research in the use of stable isotopes with the CAMECA ion microprobe with Warner Christie.

Changming Jin conducted research with Bob Hettich on the development of Fourier transform mass spectrometry for the structural characterization of normal and modified fullerenes.

Lawrence Taylor completed collaborative research in trace element analysis by neutron activation analysis with Frank Dyer.

Sheng Dai continued his appointment with Jack Young to develop analytical sensors to be used in the electrolytic production of magnesium metal from molten chloride salt solutions.

J. E. Coffield assisted Jack Young with molten salt preparation and electrochemical studies.

Predoctoral Research. M. R. Troutman continued research with Gary Glish on instrument development and application.

Laboratory Graduate Participation Program. Mona Shahgholi continued her research with Michelle Buchanan and Robert Hettich in the Organic Chemistry Section.

Eric R. Stubblefield worked with Mike Ramsey's group on the document tagging project.

CO-OP PROGRAM

Douglas L. Theobald, University of Tennessee, continued his co-op assignment with Michelle Buchanan in the Organic Spectroscopy Group.

HISTORICALLY BLACK COLLEGES AND UNIVERSITIES

Troy J. Stewart (Alcorn State University) worked with Joe Stewart on microwave digestion for ICP/MS samples.

W. K. Adeniyi (North Carolina A&T University) worked with Ted Mueller on a study of various methods for dissolving low solubility materials in liquid solvents.

GREAT LAKES COLLEGES ASSOCIATION

Marcie J. Shapiro (DePauw University) conducted research with Bill Whitten on laser techniques for ultra trace analysis.

Andrea L. Ondracek (Albion College) worked with Larry Robinson on elemental analysis and neutron flux characterization of HFIR pneumatic tubes.

6. SUPPLEMENTARY ACTIVITIES

Supplementary activities in ACD follow a two-way path. From outside the Laboratory come the Advisory Committee, consultants, and seminar speakers. From within, the division members participate in professional societies and special technical assignments. Awards and patents often follow such activities.

ADVISORY COMMITTEE

The 1992 Advisory Committee was composed of:

D. D. Bly, retired, E. I. du Pont de Nemours, Wilmington, Delaware
I. H. Warner, Emory University, Atlanta, Georgia
E. S. Yeung, Iowa State University, Ames, Iowa
W. D. Ehmann, University of Kentucky, Lexington, Kentucky
R. A. Hites, Indiana University, Bloomington, Indiana

CONSULTANTS

The following experts served on a short-term consulting basis this year.

George M. Alber, Ohio State University, Columbus, Ohio
Stephen Arnold, Polytechnic University of New York, New York
Michael Blades, University of British Columbia, Vancouver, British Columbia
J. Thomas Brenna, Cornell University, Ithaca, New York
Richard M. Caprioli, University of Texas Medical School, Houston, Texas

Peter Carr, University of Minnesota, Minneapolis, Minnesota
 Peter C. Chen, University of Wisconsin, Madison, Wisconsin
 Changming Jin, Rice University, Houston, Texas
 Murray Johnston, University of Delaware, Newark, Delaware
 Fred L. King, West Virginia University, Morgantown, West Virginia
 Lance B. Koutny, Iowa State University, Ames, Iowa
 Sheldon Landsberger, University of Illinois, Urbana, Illinois
 Daniel J. McGraw, University of New Mexico, Albuquerque, New Mexico
 Richard K. Marcus, Clemson University, Clemson, South Carolina
 Allen P. Mills, Jr., AT&T Bell Laboratories, Murray Hill, New Jersey
 Lloyd M. Smith, University of Wisconsin, Madison, Wisconsin

The following experts served on a long-term basis this year.

G. M. Begun, Retired, Martin Marietta Energy Systems, Oak Ridge
 J. A. Carter, Retired, Martin Marietta Energy Systems, Oak Ridge
 K. D. Cook, University of Tennessee, Knoxville
 A. L. Harrod, Retired, Martin Marietta Energy Systems, Oak Ridge
 W. M. Holland, University of Tennessee, Knoxville
 R. E. Jones, Retired, Martin Marietta Energy Systems, Oak Ridge
 W. S. Lyon, Retired, Martin Marietta Energy Systems, Oak Ridge
 Gleb Mamantov, University of Tennessee, Knoxville
 A. G. Marshall, Ohio State University, Columbus, Ohio
 H. S. McKown, Retired, Martin Marietta Energy Systems, Oak Ridge
 B. Philpot, Retired, Martin Marietta Energy Systems, Oak Ridge
 R. L. Walker, Retired, Martin Marietta Energy Systems, Oak Ridge

33rd ORNL/DOE CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

The 33rd Annual Conference was held in Gatlinburg at the Park Vista Hotel, October 6-8, 1992. Attendance was 375, with representatives from foreign countries, academia, industrial institutions, DOE contractors, and other government agencies. There were 28 exhibits. Major topics included management and technical developments in environmental restoration programs, separations of organics, inorganics and radionuclides, plasma source mass spectrometry, automation, organic mass spectrometry, environmental monitoring and laboratory management.

S. D. Wright and A. L. Harrod were Arrangements Chairmen, W. R. Laing was Technical Program Chairman, and C. C. Overbey was Treasurer. D. S. Blazier and C. L. Gaudreau were conference secretaries. Other conference committee members were D. C. Duckworth, D. D. Jackson (LANL), R. A. Jenkins, L. N. Klatt, R. T. Short, W. D. Shults, and C. R. Yonker (DOE).

SEMINAR PROGRAM

The ACD Seminar Committee was chaired by Greg Hurst this year. Other members were Ted Mueller, Jack Young, Gary Van Berkel, Frank Dyer, and Rose Ramsey.

<u>Speaker</u>	<u>Title of Talk</u>	<u>Date</u>
Changming Jin Rice U. Houston, Tex.	"Generation and Structural Characterization of Fullerenes"	1/6/92
Peter C. Chen U. of Wisconsin Madison, Wis.	"Infrared Four Wave Mixing Spectroscopy"	1/23/92
Lance B. Koutny Iowa State U. Ames, Iowa	"Ultraviolet Absorption Imaging and Automated Analysis of DNA in Gel Electrophoresis"	2/28/92
Michael Blades U. of British Columbia Vancouver, B.C.	"New Optical and Mass Spectrometric Methods for Trace Element Analysis"	4/23/92

<u>Speaker</u>	<u>Title of Talk</u>	<u>Date</u>
Daniel J. McGraw U. of New Mexico Albuquerque, N. Mex.	"New Kinds of Mirrors, Lenses and Spatial Filters and Their Application in Spectroscopy"	5/27/92
Murray Johnston U. of Delaware Newark, Del.	"Lasers and Mass Spectrometry"	7/10/92
George M. Alber Ohio State U. Columbus, Ohio	"The Theory and Instrumentation for Precise Mass Measurement by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry"	7/17/92
Fred L. King West Virginia U. Morgantown, W. Va.	"The Characterization and Analytical Application of Modulated Glow Discharge"	8/3/92
Lloyd M. Smith U. of Wisconsin Madison, Wis.	"Automated DNA Sequencing: A Look for the Future"	9/4/92
Sheldon Landsberger U. of Illinois Urbana, Ill.	"Recent Advances and Future Development in the Application of Nuclear Analytical Methods to Air Pollution Studies"	9/29/92
Allen P. Mills AT&T Bell Labs Murray Hill, N. J.	"Basic Physics and Materials Analysis Experiments with Pulsed and Muon Beams"	10/12/92
Richard M. Caprioli U. of Texas Medical School Houston, Tex.	"Integrating Fast Atom Bombardment, Electrospray and Laser Desorption Mass Spectrometry into the Biotechnology Laboratory"	10/29/92
Peter Carr U. of Minnesota Minneapolis, Minn.	"Zirconia: A Nearly Indestructible Support for Analytical and Preparative High Performance Liquid Chromatography"	11/4/92

AWARDS AND HONORS

Mike Ramsey has been appointed to the Advisory Board of *Analytical Chemistry* beginning January 1993.

Mike Ramsey was selected by the Bowling Green State University Department of Chemistry as their Alumnus of the Year.

Gary Glish was awarded the Analytical Chemistry Division Distinguished Service Award for his contributions to ACD and ORNL.

Dub Shults has been appointed to the Board of Advisors for the College of Liberal Arts and Sciences, The University of Tennessee.

Doug Theobald, UT co-op student in the Organic Chemistry section, received the Calvin Buchler Scholarship and the Analytical Chemistry Award from the Analytical Chemistry Division of the American Chemical Society.

Energy Systems Awards Night

Darrell Wright received an Administrative Support Award at the annual Energy Systems Awards Night ceremony.

ADDITIONAL PROFESSIONAL ACTIVITIES

K. G. Asano

Secretary

East Tennessee Mass Spectrometry Discussion Group

C. M. Barshick

Member

ASMS Elemental Interest Group

VG9000 Users Group

C. A. Biggs

ACD Coordinator

Environmental Protection

ACD Representative

Waste Minimization

S. J. Bobrowski

Member

Analytical Improvement Council

Treasurer-Elect

ACS East Tennessee Section

Chairman

ACD Orientation Committee

M. V. Buchanan

North American Editor

Biological Mass Spectrometry

Editorial Board

Analytical Chemistry

Organic Mass Spectrometry

Advisory Board

National Science Foundation Biological Centers Program

Member

Energy Systems Advisory Committee for Values

ORNL Values Committee

ORNL AA/EEO Strategic Plan Implementation
Committee

S. D. Cates

Member

Analytical Improvement Council

ACD Representative

Staffing Contact

Occurrence Reporting

D. C. Duckworth

Member

ASMS Elemental Interest Group

VG9000 Users Group

F. F. Dyer

Member

ACD Seminar Committee

N. M. Ferguson

ACD Representative

Energy Systems Environmental Analysis Committee

G. L. Glish

Associate Editor

Journal of the American Society for Mass Spectrometry

Consultant

Finnigan MAT, San Jose, Calif.

Member

ORAU Traveling Lecture Program

D. E. Goeringer

ACD Coordinator

Student and Faculty Programs

Member

Energy Systems Ph.D. Recruiting Team

C. C. Granger

Member

Analytical Improvement Council

W. H. Griest

Consultant

DOE SBIR Review

Electric Power Research Institute

Environmental Protection Agency IERL/TSO

Center for Indoor Air Research

DOE Office of Technology Development (Underground
Storage Tank Characterization)**M. R. Guerin**

Consultant

DOE and NCI SBIR Reviews

PHS Office of Smoking and Health Additives

G. A. Guiochon

Associate Editor

Analytical Chemistry

Advisory Board

*Journal of Chromatography**Chromatographia**Journal of Liquid Chromatography**Journal of Chromatographic Sciences*

President

8th International Symposium on Preparative
Chromatography, PREP '93, Washington, D. C.

Member

Scientific Committees of PREP '92, Nancy, France;
HPLC '92, Baltimore; HPLC '93, Hamburg, Germany;
HPLC '94, MinneapolisHPLC Permanent Committee of the International
Symposia on Column Liquid ChromatographyACS Board, Chromatography Subdivision, ACS Division
of Analytical ChemistryNational Science Foundation Division of Chemistry
Triennial Oversight Review Committee

G. A. Guiochon (cont.)

Consultant

NSF Department of Chemistry proposal reviews

DOE OBES proposal reviews

ACS Petroleum Research Fund proposal reviews

NASA proposal reviews

S. H. Harmon

Member

Analytical Improvement Council

R. L. Hettich

Member

ORAU Traveling Lecture Program

East Tennessee ACS Section Nominating Committee

Treasurer

East Tennessee Mass Spectrometry Discussion Group

C. E. Higgins

Coordinator

Performance Improvement Program

Chairman

Analytical Improvement Council

G. B. Hurst

Member

Analytical Improvement Council

ACD Safety Committee

East Tennessee ACS Chemistry Olympiad Committee

Chairman

ACD Seminar Committee

R. H. Ilgner

Secretary

East Tennessee Mass Spectrometry Discussion Group

R. A. Jenkins

Editorial Board	<i>The Journal of Smoking Related Disorders</i>
Consultant	Federal Trade Commission, Standardized Smoking Practices
	National Institute on Drug Abuse SBIR Reviews
Member	Department of Defense Program Manager/Rocky Mountain Arsenal Expert Panel on Structures Sampling and Analysis
Chairman	Savannah River Integrated Demonstration Project Monitoring Technical Support Group

J. M. Keller

Site Representative	Energy Systems Multi-Plant Analytical Committee
ACD Coordinator	Emergency Samples

W. R. Laing

Chairman	ASTM Committee C-26, Nuclear Fuel Cycle
ACD Coordinator	Energy Conservation
	Quality Assurance
	Total Quality Management
ACD Representative	ACD Technical Support Recruiting
Fellow	American Society for Testing and Materials
Technical Program Chairman	ORNL/DOE Conference on Analytical Chemistry in Energy Technology
Member	ASTM Committee D-33, Protective Coatings
	ASTM Committee D-34, Waste Management
	ISO Technical Committee 85, Subcommittee 5
	ORNL Pregrievance Committee

E. H. McBay

Member

Analytical Improvement Council

S. A. McLuckey

Chairman

East Tennessee Mass Spectrometry Discussion Group

Consultant

National Institutes of Health SBIR Review

Member

DOE SBIR Review

ASMS Program Review Board

Organizer

Symposium on Electrospray Ionization, ACS Meeting,
Washington, 1992**J. M. McMahon**

Coordinator

Y-12 Safety

M. P. Maskarinec

Member

EPA Working Group on Improvement of Tentatively
Identified Compound (TIC) Identification

ASTM Committee D-34

T. L. Mims

Member

Analytical Improvement Council

J. L. Miranda

ACD Coordinator

Quality Control

ACD Representative

Energy Systems QA/QC Training Team

T. R. Mueller

ORNL Representative

5-plant LIDIS Committee

5-plant LIMS Committee

ACD Representative

ORNL User Advisory Committee for Computing Technology

ORNL Perchloric Acid Committee

ORNL Training Accreditation Committee

Classification Officer

ACD Coordinator

Training

ACD Presenter

Ethics Awareness

"Coaching - The Key to Team Success"

Member

ACD Seminar Committee

C. D. Parks

Member

Analytical Improvement Council

J. C. Price

ACD Representative

Classification Officer

J. M. Ramsey

Editorial Advisory Board

Progress in Analytical Spectroscopy

Advisory Board

Analytical Chemistry

Member

Energy Systems Publication Award Selection Committee

DOE/ISA Laboratory Advisory Group for Effluent Research (LAGER)

Award Selection Committee, ACS Division of Analytical Chemistry

J. M. Ramsey (cont.)

Member	ORNL Laser Safety Committee
	Program Advisory Committee, ACS Division of Analytical Chemistry
	ORAU Traveling Lecture Program
ACD Coordinator	Laser Safety

R. S. Ramsey

Consultant	National Cancer Institute SBIR Reviews
	Center for Indoor Air Research
Member	ACD Seminar Committee

L. Robinson

President	Oak Ridge Chapter, NAACP
Treasurer	East Tennessee Chapter, National Association of Black Chemists and Chemical Engineers
Member	ASTM Task Group on Nuclear Methods of Chemical Analysis
ACD Coordinator	Radiation Control
	Occurrence Reporting
	Minority Educational Institution Representative

T. M. Rosseel

Past President	American Vacuum Society, Tennessee Valley Chapter
Member	ORNL Proposal Review Committee

R. W. Shaw

ACD Representative

Ph.D. Recruiting

Member

Analytical Improvement Council

W. D. Shults

Past Chairman

East Tennessee Section, American Chemical Society

Past Chairman

Education Committee, ACS Division of Analytical Chemistry

Advisory Committee

Chemistry and Laser Science Division, Los Alamos National Laboratory

Review Committee

Analytical Chemistry

Member

Board of Visitors, Chemistry Department, The University of Tennessee, Knoxville

Board of Advisors, College of Liberal Arts and Sciences, The University of Tennessee, Knoxville

Energy Systems Analytical Managers Council

DOE Analytical Managers Group

D. H. Smith

Member

ASMS Isotope Ratio Interest Group

R. R. Smith

Member

ACD Safety Committee

J. R. Stokely

Member

DOE Future Analytical Support Task Team

ACD Coordinator

BS/MS Recruiting

P. J. Todd

Consultant

National Institutes of Health, General Medicine

National Institute of Mental Health

Coordinator

ACD Awards

B. A. Tomkins

Member

ACD Seminar Committee

P. M. Trentham

ACD Representative

Affirmative Action

R. E. Valiga

ACD Representative

Carcinogen Control Program at Y-12

Environmental Protection Officer at Y-12

RCRA Satellite Waste Storage Areas Operator at Y-12

Coordinator

Generator Certification Officer, TRU Waste at Y-12

Generator Certification Officer, Low-Level Waste at Y-12

Hazardous Materials Inventory System at Y-12

G. J. Van Berkel

Member

ACD Seminar Committee

M. B. Wisc

Coordinator

ASMS Environmental Interest Group

S. D. Wright

Arrangements Chairman	ORNL/DOE Conference on Analytical Chemistry in Energy Technology
ACD Coordinator	Safety and Housekeeping
	Computer Systems Security
	Chemical Inventory

J. P. Young

Fellow	American Association for the Advancement of Science
Organizer	Symposium on Radiation and Society, ACS Meeting, San Francisco, April 1992
Chairman-Elect	ACS East Tennessee Section
ACD Representative	ORNL Graduate Fellow Selection Panel
ACD Coordinator	Technology Utilization
Member	Program Advisory Committee, ACS Division of Nuclear Chemistry and Technology
	Chemistry Olympiad Committee, ACS East Tennessee Section
	ACD Seminar Committee

7. PRESENTATION OF RESEARCH RESULTS

As in past years, the division has actively responded to the evolving priorities of the ORNL research effort by changing the emphasis of some of its own programs or instituting new studies. Subjects of major concern include nuclear and nonnuclear energy, new instrumentation and its application, and environmental problems such as monitoring and clean-up at ORNL and elsewhere. The multidisciplinary approach required in many such problems is indicated by the number of papers and talks coauthored by members of other ORNL divisions and outside organizations. Such persons are designated by an asterisk.

PUBLICATIONS

BOOKS AND PROCEEDINGS

<u>Author</u>	<u>Author(s), Title, Where Published</u>
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- Guerin, M. R.; Wise, M. B.; Thompson, C. V.; Buchanan, M. V., "Rapid Characterization and Monitoring by Direct Sampling Ion Trap Mass Spectrometry", *Spectrum '92: Nuclear & Hazardous Waste Management Proceedings*, Boise, Idaho, August 23-27, 1992, p. 1556.
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- Duckworth, D. C. Marcus, R. K.*; Cable, P. R.*; Duckworth, D. C.; Buchanan, M. V.; Pochkowski, J. M.*; Weller, R. R.*, "Sampling Radio Frequency Glow Discharge With a Fourier Transform/Ion Cyclotron Resonance Mass Spectrometer", *Proceedings of the 40th ASMS Conference on Mass Spectrometry and Allied Topics*, Washington, D. C., May 31-June 5, 1992, p. 1029.
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- McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Ion-Molecule Reactions of Multiply Charged Ions Derived from Electrospray", *Book of Abstracts, 12th Annual Conference on Mass Spectrometry*, Amsterdam, August 26-31, 1991, p. 188.
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Glish, G. L.

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- Walker, R. L. Bostick, D. T.; Vick, D. O.; May, M. P.; Walker, R. L., *The Isolation of Lutetium from Gadolinium Contained in Purex Process Solutions*, ORNL/TM-12000, September 1992.
- Young, J. P. Young, J. P.; Mamantov, G., *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-1925, February 1992.
- Young, J. P.; Mamantov, G., *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-2080, May 1992.
- Young, J. P.; Mamantov, G., *In-Line Sensors for Electrolytic Magnesium Cells - Annual Progress Report for Period Ending August 1992*, ORNL/M-2291, August 1992.
- Young, J. P.; Mamantov, G., *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-2482, November 1992.

ORAL PRESENTATIONS

As in previous years, staff members have made presentations at local, national, and international meetings. The papers covered a wide variety of subjects, reflecting the division's broad spectrum of activities.

<u>Speaker</u>	<u>Author(s), Title, Where Presented</u>
Asano, K. G.	Asano, K. G.; Lykens, J. S.; McLuckey, S. A.; Glish, G. L., "Comparison of Electron Ionization and Chemical Ionization Sensitivities with the ITS40 and the TSQ 700", 40th American Society for Mass Spectrometry (ASMS) Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
Barnes, M. D.	Barnes, M. D.; Whitten, W. B.; Ramsey, J. M.; Arnold, S.*, "Cavity-Enhanced Spontaneous Emission Rates for Rhodamine 6-G in Levitated Microdroplets", U. S. Army Chemical Research Development Engineering Center Conference on Obscuration and Aerosol Research, Aberdeen Proving Ground, Md., June 22-26, 1992 (invited).
	Barnes, M. D.; Ng, K.*; Whitten, W. B.; Arnold, S.*; Ramsey, J. M., "Digital Molecular Detection in Levitated Microdroplets", 1992 Optical Society of America Annual Meeting and 8th Interdisciplinary Laser Science Conference, Albuquerque, N. M., September 20-25, 1992 (invited).
	Barnes, M. D.; Whitten, W. B.; Ramsey, J. M.; Arnold, S.*, "Cavity-Enhanced Rhodamine 6-G Spontaneous Emission Rates in Levitated Microdroplets", DOE Workshop on Laser Technology in Chemical Measurement, Santa Fe, October 19-21, 1992.

- Barshick, C. M. Watson, C.*; Barshick, C. M.; Eyler, J. R.*; Wronka, J.*; Laukien, F.*, "Glow Discharge Ionization on a High Mass Resolution External Ion Source Fourier Transform Ion Cyclotron Resonance Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Barshick, C. M.; Smith, D. H., "The Application of Solution Residue Sample Preparation to Environmental Waste Remediation", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Barshick, C. M.; Duckworth, D. C.; Smith, D. H., "Direct Solids Analysis by Glow Discharge Mass Spectrometry: Problems and Perspectives", DOE SUBWOG 12C Meeting, Gatlinburg, October 8-9, 1992 (invited).
- Barshick, S. A. Rossi (Barshick), S. A.; Johnson, J. V.*; Yost, R. A.*, "Fundamentals of Short-Column GC/MS/MS and Applications to Anabolic Steroid Screening", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Barshick, S. A.; Buchanan, M. V.; Wise, M. B.; Guerin, M. R., "Screening Methods for Drugs in Physiological Fluids Using Thermal Desorption Ion Trap Mass Spectrometry", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Bray, A. M. Bray, A. M.; Keller, J. M., "Clean-up of Regulatory Samples for ICP and GFAA", DOE/ORO Multi-Site Analytical Chemistry Meeting, ORNL, March 31, 1992 (invited).
- Buchanan, M. V. Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Hurst, G. B.; Guerin, M. R., "Chemical Analysis Using the Quadrupole Ion Trap: Environmental and Physiological Applications", 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992.

- Buchanan, M. V. Buchanan, M. V., "Bioanalytical Ion Trap Mass Spectrometry", Analytical Chemistry Division Information Meeting, March 18, 1992 (invited).
- Buchanan, M. V.; Caton, J. E.; Waters, L. C.; Hettich, R. L.; Hurst, G. B.; Xu, J., "Trace Detection of Drugs in Milk and Meat Using Direct Sampling ITMS", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Wise, M. B.; Buchanan, M. V.; Thompson, C. V.; Guerin, M. R., "Environmental Field Measurements with an Ion Trap Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992 (invited).
- Buchanan, M. B.; Hettich, R. L.; Nourse, B. D., "Characterization of DNA Adducts with Fourier Transform Mass Spectrometry", 204th American Chemical Society National Meeting, Washington, D. C., August 23-28, 1992 (invited).
- Buchanan, M. V.; Rossi, S. A.; Wise, M. B.; Thompson, C. V.; Merriweather, R., "Rapid Analysis Using Direct Sampling Ion Trap Mass Spectrometry", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.
- Chambers, D. M. Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Novel Improvements to Matrix-Assisted Laser Desorption Ion Trap Mass Spectrometry", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992.
- Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Fundamental Investigations with a New Atmospheric Sampling Glow Discharge Ionization Source", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

- Chambers, D. M. Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Instrumental Aspects of Matrix-Assisted Laser Desorption in a Quadrupole Ion Trap Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Matrix-Assisted Laser Desorption in an Ion Trap Mass Spectrometer for Analysis of Biological Molecules", Eastern Analytical Symposium, Somerset, N. J., November 18, 1992 (invited).
- Christie, W. H. Christie, W. H.; Riciputi, L. R.; Cole, D. R.*; Rosseel, T. M., "An Ion Microprobe Study of Small-Scale Chemical Variations that Occur in Certain Dolomitized Limestones", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Christie, W. H.; Riciputi, L. R.; Cole, D. R.; Rosseel, T. M., "An Ion Microprobe Study of Small-Scale Chemical Variations that Occur in Certain Dolomitized Limestones", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Dale, J. M. Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", Analytical Chemistry Division Information Meeting, March 18-20, 1992 (invited).
- Duckworth, D. C. Marcus, R. K.*; Duckworth, D. C.; Glish, G. L.; McLuckey, S. A.; Buchanan, M. V.; Wise, M. B.; Pochkowski, J. M.*; Weller, R. R.*, "Sampling Radio Frequency Glow Discharge Sources with Ion Trap and Fourier Transform/Ion Cyclotron Resonance Mass Spectrometers", 1992 Winter Conference on Plasma Spectrochemistry, San Diego, January 6-11, 1992.
- Duckworth, D. C.; Smith, D. H.; McLuckey, S. A.; Glish, G. L.; Buchanan, M. V.; Marcus, R. K.*; Weller, R. R.*; Pochkowski, J. M., "Inorganic Mass Spectrometry with Trapped Ions", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).

Duckworth, D. C.

Duckworth, D. C., "Advances in Inorganic Mass Spectrometry", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).

Duckworth, D. C.; Smith D. H.; McPherson, R. L.; Marcus, R. K.*, "Radio Frequency Powered Glow Discharge Mass Spectrometry Utilizing a 40.68 MHz Excitation Potential", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Marcus, R. K.*; Cable, P. R.*; Duckworth, D. C.; Buchanan, M. V.; Pochkowski, J. M.*; Weller, R. R.*, "Sampling Radio Frequency Glow Discharges with a Fourier Transform/Ion Cyclotron Resonance Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Weller, R. R.*; Pochkowski, J. M.*; Duckworth, D. C.; Marcus, R. K.*; Buchanan, M. V., "RF-GD/FTMS: An FTMS System with a Lensless External Ion Source for High Resolution Elemental Mass Spectrometry", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Duckworth, D. C., "Design and Characterization of a Radio Frequency Powered Glow Discharge Source for the VG9000", 3rd International Conference on Plasma Source Mass Spectrometry, University of Durham, Durham, United Kingdom, September 13-18, 1992 (invited).

Duckworth, D. C.; Barshick, C. M.; McLuckey, S. A.; Glish, G. L., "Sampling Radio Frequency Powered Glow Discharges with a Quadrupole Ion Trap", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992 (invited).

Barshick, C. M.; Duckworth, D. C.; Smith, D. H., "Solution Residue Analysis Using Glow Discharge Mass Spectrometry", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.

- Duckworth, D. C. Duckworth, D. C.; Barshick, C. M.; Smith, D. H.; McLuckey, S. A., "Extending the Dynamic Range in Glow Discharge/Ion Trap Mass Spectrometry", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Dyer, F. F. Dyer, F. F.; Robinson, L.; Nichols, G. R.*, "A Search for Arsenic in Hair and Nail Remains of Former President Zachary Taylor by Neutron Activation Analysis", 2nd International Symposium on Nuclear Analytical Chemistry, Toronto, June 3-5, 1992.
- Dyer, F. F.; Robinson, L., "Neutron Activation Analysis as a Cost-Effective Alternative to Wet Chemistry", Institute of Nuclear Materials Management, Orlando, Fla., July 19-22, 1992.
- Combs, D. W.; Dyer, F. F.; Robinson, L., "The Use of Neutron Activation for the Remedial Investigation of East Fork Poplar Creek and a Comparative Estimation of Human Health Risks Between Methods", International Topical Meeting on Nuclear and Hazardous Wastes: Spectrum '92, Boise, Idaho, August 23-27, 1992.
- Giaquinto, J. Giaquinto, J., "Operation of the Spectro Flame ICP", DOE/ORO Multi-Site Analytical Chemistry Meeting, ORNL, March 31, 1992 (invited).
- Glish, G. L. Glish, G. L., "The Mass Spectrometer as a Gas Phase Laboratory", University of North Carolina Seminar, Chapel Hill, December 12, 1991 (invited).
- Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J.; Chambers, D. M., "Quadrupole Ion Traps: The Next Generation", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Glish, G. L., "Quadrupole Ion Traps: The Next Generation", Midwest Mass Spectrometry Discussion Group, St. Louis, March 26, 1992 (invited).
- Glish, G. L., "The Mass Spectrometer as a Gas Phase Chemical Laboratory", Southern Illinois University Seminar, Carbondale, Ill., March 27, 1992 (invited).

- Glish, G. L. Glish, G. L.; McLuckey, S. A., "High Performance Low Cost vs. Low Performance High Cost: A Tale of Two Mass Spectrometers", University of Delaware Seminar, Newark, Del., March 28, 1992 (invited).
- Glish, G. L., "Organic Mass Spectrometry Highlights", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).
- Glish, G. L.; McLuckey, S. A.; Duckworth, D. C.; Marcus, R. K., "RF-Glow Discharge Combined with a Quadrupole Ion Trap for Elemental Analysis", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Glish, G. L.; Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A., "Quadrupole Ion Trap Mass Spectrometry of Large Desorbed Ions". Desorption '92 Conference, Burg Waldeck, Germany, September 6-9, 1992 (invited).
- Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Hart, K. J., "Multiple Stages of Mass Spectrometry: Expanding the MS/MS Experiment", Joint ACS Middle Atlantic/ACS Southeast Regional Meeting, Arlington, Va., December 6-8, 1992.
- Goeringer, D. E. Goeringer, D. E.; Chambers, D. M.; McLuckey, S. A.; Glish, G. L., "Investigations of Matrix-Assisted Laser Desorption of Biomolecules in a Quadrupole Ion Trap", ASMS Conference on Mass Spectrometry, Sanibel Island, Fla., January 25-28, 1992.
- Goeringer, D. E., "Ion Trap Fundamentals", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).
- Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M.; McLuckey, S. A.; Glish, G. L., "Theoretical Basis of Resolution Enhancement in the Quadrupole Ion Trap", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

- Goeringer, D. E. Goeringer, D. E.; Chambers, D. M.; McLuckey, S. A.; Glish, G. L., "Matrix-Assisted Laser Desorption of Peptides Coupled with CID in a Quadrupole Ion Trap", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Goeringer, D. E.; Van Berkel, G. J., "On-Line GC-Tandem MS in the Quadrupole Ion Trap Via Random-Noise CID", 9th Asilomar Conference on Mass Spectrometry, Monterey, Calif., September 27-October 1, 1992 (invited).
- Goeringer, D. E.; Van Berkel, G. J., "Gas Chromatography-Tandem Mass Spectrometry Implemented on a Bench-Top Quadrupole Ion Trap-Based Instrument Using Random Noise to Effect Collision-Induced Dissociation", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Graudons, J. A. Graudons, J. A.; Dyer, F. F., "Neutron Activation Analysis of LWR Mixed-Bed Resins for ^{129}I ", 2nd International Symposium on Nuclear Analytical Chemistry, Toronto, June 3-5, 1992.
- Griest, W. H. Griest, W. H., "Radioactive Mixed Waste Characterization", Argonne National Laboratory, Chemical Technology Division Seminar, Argonne, Ill., February 20, 1992 (invited).
- Griest, W. H., "Oak Ridge National Laboratory Underground Nuclear Waste Storage Tank Characterization for the DOE National Tank Waste Characterization Workshop", DOE National Tank Waste Characterization Workshop, Hanford, Wash., June 25-27, 1992.
- Griest, W. H.; Stokely, J. R., "Characterization of Radioactive Mixed Wastes: The Scientific Perspective", Eighth Annual Waste Testing and Quality Assurance Symposium, Arlington, Va., July 14-17, 1992. (invited)

- Guerin, M. R. Guerin, M. R.; Wise, M. B.; Thompson, C. V.; Buchanan, M. V., "Rapid Characterization and Monitoring by Direct Sampling Ion Trap Mass Spectrometry", Spectrum '92: Nuclear & Hazardous Waste Management, Boise, Idaho, August 23-27, 1992.
- Guiochon, G. A. Guiochon, G., "Separation of Enantiomers and Proteins by Preparative Chromatography", Bob Jones University, Greenville, S. C., January 23, 1992 (invited).
- Guiochon, G.; Diack, M.; El Fallah, M. Z.; Jacobson, S. C.; Zhu, J.*, "Advances in Non-Linear Chromatography. Comparison Between Theoretical and Experimental Results", 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992 (invited).
- Guiochon, G.; Roles, J.*, "Study of the Surface Heterogeneity of Various Materials", 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992 (invited).
- El Fallah, M. Z.; Guiochon, G., "Modeling Preparative Gradient Elution Chromatography of Proteins", 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992 (invited).
- Jacobson, S. C.; Guiochon, G., "Experimental and Theoretical Band Profiles of Enantiomers Separated on Immobilized Bovin Serum Albumin at High Concentrations", 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992 (invited).
- Guiochon, G., "Theoretical Predictions and Experimental Measurements of Band Profiles and Production Rates in Liquid Chromatography", 65th Anniversary of Prof. Ernst Bayer, University of Tübingen, Germany, April 3, 1992 (invited).
- Golshan-Shirazi, S.*; Guiochon, G., "The Modeling of Preparative Liquid Chromatography", PREP '92, Nancy, France, April 6-8, 1992 (invited).

Guiochon, G. A. Compton, R. N.*; Hettich, R. L.; Ritchie, R. H.*; Britt, P.*; Pretzky, A. A.*; Frey, W. F.*; Tuinman, A. A.*; Adcock, J. L.*; Mukherjee, P.*; Diack, M.; Guiochon, G., "On the Generation, Separation, Physics, and Chemistry of Large Carbon Clusters", 181st Electrochemical Society Meeting, St. Louis, May 17-22, 1992 (invited).

Guiochon, G.; Diack, M.; El Fallah, M. Z.; Felinger, A.; Golshan-Shirazi, S.*; Katti, A. M.*; Jacobson, S. C.; Seidel-Morgenstern, A.*, "Competitive Isotherms, the Key to Understanding Separations in Preparative Chromatography", HPLC'92, 16th International Symposium on Column Liquid Chromatography, Baltimore, June 15-19, 1992 (invited).

Jacobson, S. C.; Golshan-Shirazi, S.*; Guiochon, G., "Retention Mechanisms of Enantiomers on Immobilized Proteins and Equilibrium Isotherms", 204th American Chemical Society National Meeting, Washington, D. C., August 23-28, 1992 (invited).

Guiochon, G., "Chromatography, Today and Tomorrow", 12th International Symposium on Microchemical Analysis, Cordoba, Spain, September 7-10, 1992 (invited).

Felinger, A.; Jacobson, S. C.; Guiochon, G., "Optimization of the Production Rate of a Chromatographic Column Operated in Overloaded Elution and Displacement Chromatography. Comparison of the Performance", 19th International Symposium on Chromatography, Aix-en-Provence, France, September 14-18, 1992 (invited).

Guiochon, G., "The Modeling of Liquid Chromatography. Ideal Model, Equilibrium-Dispersive Model, Kinetic Models", University of Orsay, France, September 22, 1992 (invited).

Guiochon, G.; Felinger, A.; Golshan-Shirazi, S.*; Jacobson, S., "Optimization of Preparative Chromatography Without Equations", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992 (invited).

Guiochon, G. A. Seidel-Morgenstern, A.*; Guiochon, G., "Adsorption Isotherms and Overloaded Elution Profiles for the Enantiomers of Tröger's Base on Microcrystalline Cellulose Triacetate", National Meeting of the American Institute of Chemical Engineers, Miami Beach, November 2-6, 1992 (invited).

Felinger, A.; Guiochon, G., "Optimization of the Production Rate of a Chromatographic Column Operated in Overloaded Elution and Displacement Comparison of the Performance", National Meeting of the American Institute of Chemical Engineers, Miami Beach, November 2-6, 1992 (invited).

Guiochon, G.; Diack, M.; El Fallah, M. Z.; Golshan-Shirazi, S.*; Jacobson, S. C.; Seidel-Morgenstern, A.*, "Competitive Isotherms, the Key to Understanding Separations in Preparative Chromatography", Eastern Analytical Symposium, Summit, N. J., November 16-20, 1992 (invited).

Hart, K. J. Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Reactions of Neutral Chemical Ionization Gases with Analyte Ions", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Determination of Product Ion Structures Derived from the Reaction of Phenylum and Substituted Phenylum Ions with Neutral Reagent Gases", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Effect of Experimental Parameters on Effective Ion Temperatures in a Quadrupole Ion Trap", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Hart, K. J.; Habibi-Goudarzi, S.; McLuckey, S. A., "Automated Interpretation of MS/MS Spectra of Multiply Charged Oligonucleotides", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).

- Hayes, S. M. Hayes, S. M.; MacDougall, C. S.; Ferguson, N. M., "TEM Analysis for Asbestos", 44th Martin Marietta-Westinghouse Six-Site Analytical Chemistry Meeting, Paducah, Ky., November 10, 1992.
- Hettich, R. L. Hettich, R. L.; Yoshida, H.*, "Matrix-Assisted Laser Desorption FTMS for the Characterization of Radiation-Induced Damage to DNA", ASMS Workshop on Lasers in Mass Spectrometry, Sanibel Island, Fla., January 25-28, 1992.
- Hettich, R. L.; Compton, R. N.*, "Characterization of Fullerene Growth and Doping by Laser Desorption FTMS", ASMS Workshop on Lasers in Mass Spectrometry, Sanibel Island, Fla., January 25-28, 1992.
- Hettich, R. L., "Development of Matrix-Assisted Laser Desorption FTMS for the Characterization of Modified Nucleotides and Oligonucleotides", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Hettich, R. L.; Buchanan, M. V.; Compton, R. N.*, "Laser Desorption FTMS for the Structural Characterization of Nucleic Acid Constituents and Fullerenes", 24th Central Regional Meeting of the ACS, Cincinnati, May 27-29, 1992 (invited).
- Hettich, R. L.; Compton, R. N.*, "Examination of Fullerene Growth and Doping by Laser Desorption FTMS", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Hettich, R. L.; Yoshida, Hiroko*, "Characterization of Radiation-Induced Damage to Nucleic Acid Constituents by Matrix-Assisted Laser Desorption FTMS", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Hettich, R. L.; Buchanan, M. V.; Compton, R. N.*, "Laser Desorption FTMS for the Structural Characterization of Nucleic Acid Constituents and Fullerenes", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Hettich, R. L.

Hettich, R. L.; Nourse, B. D.; Yoshida, H.*; Buchanan, M. V., "Matrix-Assisted Laser Desorption FTMS for Modified Nucleotides and Oligonucleotides", AAAS Science Innovation '92, San Francisco, July 21-25, 1992.

Hettich, R.; Yoshida, H.*, "Matrix-Assisted Laser Desorption FTMS for the Investigation of X-ray Induced Damage to Nucleic Acid Constituents", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.

Hettich, R. L.; Compton, R. N., "Characterization of Modified Fullerenes by Laser Desorption Fourier Transform Mass Spectrometry", Eastern Analytical Symposium, Somerset, N. J., November 18, 1992 (invited).

Hettich, R. L.; Jin, C.; Britt, P.*; Compton, R. N.*, "Structural Characterization of Fullerene-Based Materials by Laser Desorption Fourier Transform Mass Spectrometry", Materials Research Society, Boston, November 30-December 4, 1992.

Hulett, L. D.

Hulett, L. D., "The Interaction of Slow Positrons with Large Molecules and Surfaces", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).

Xu, Jun; Hulett, L. D.; Lewis, T. A.*, "The ORNL Slow Positron Facility and Quadratic-Potential Time-of-Flight Mass Spectrometer Instrumentation", Slow Positron Conference 5, Jackson Hole, Wyo., August 5-10, 1992.

Kossler, W. J.*; Hulett, L. D., "Preliminary Considerations of a Slow Positron Facility at CEBAF", 12th International Conference on Application of Accelerators in Research and Industry, Denton, Texas, November 2-5, 1992 (invited).

Xu, Jun; Hulett, L. D.; Lewis, T. A.*; Donohue, D. L., "Ionization Kinetics Measurements with a Combined Penning Trap - TOF Mass Spectrometer", 12th International Conference on Application of Accelerators in Research and Industry, Denton, Texas, November 2-5, 1992 (invited).

- Hurst, G. B. Hurst, G. B.; Hettich, R. L.; Wise, M. B.; Nodine, R. N.*; Buchanan, M. V.; Guerin, M. R., "Sensitive Detection of Targeted Volatile Organics by Direct-Sampling Ion Trap Mass Spectrometry", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Ilgner, R. H. Ilgner, R. H.; Biggs, C. A.; Scott, R. F.; Ma, C. Y.; Smith, S. M.; Maskarinec, M. P., "Sample Cleanup Techniques for Fish Tissue Extracts", Waste Testing & Quality Assurance Symposium, Arlington, Va., July 13-17, 1992.
- Jenkins, R. A. Jenkins, R. A.; Guerin, M. R., "Modern Tobacco Smoke Chemistry", Conference on Tobacco Smoking and Nutrition: Influence of Nutrition on Tobacco Associated Health Risks, Lexington, Ky., September 14-16, 1992.
- Guerin, M. R.; Jenkins, R. A., "Environmental Tobacco Smoke", Tobacco Chemists' Research Conference, Montreal, September 27-30, 1992 (invited).
- Jin, C. Jin, C.; Hettich, R. L., "Mass Spectrometry Studies of Fullerenes", Southeastern Section of the American Physical Society, Oak Ridge, November 12-14, 1992 (invited).
- Koutny, L. B. Koutny, L. B.; Hergenroder, R.; Jacobson, S. C.; Ramsey, J. M., "Microscale Chemical Instrumentation: Capillary Separations on a Chip", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- MacDougall, C. S. MacDougall, C. S.; Hayes, S. M.; Ferguson, N. M., "Everything You Always Wanted to Know About TEM/Asbestos but Were Afraid to Ask", Multi-Plant Committee Meeting, Oak Ridge, February 12, 1992.
- MacDougall, C. S.; Hayes, S. M.; Ferguson, N. M., "Computer-Aided Imaging", 44th Martin Marietta-Westinghouse Six-Site Analytical Chemistry Meeting, Paducah, Ky., November 10, 1992.

- McBay, E. H. McBay, E. H.; Smith, D. H.; McPherson, R. L., "Application of Gas Analysis Mass Spectrometry to Space Shuttle Launch Operations", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Swihart, G. H.*; McBay, E. H.; Smith, D. H.; Siefke, J. W.*, "The Kramer Deposit of Southern California - Preliminary Insights on the Origins of Zoned Lacustrine Evaporite Borate Deposits", Geological Society of America, Cincinnati, October 26-29, 1992.
- McLuckey, S. A. McLuckey, S. A.; Van Berkel, G. J.; Ramsey, R. S.; Glish, G. L., "Chemical Analysis Using the Quadrupole Ion Trap: Oligonucleotides", Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, March 9-13, 1992 (invited).
- McLuckey, S. A., "New Approaches to Mass(/Charge) Measurement: The Quadrupole Ion Trap", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992 (invited).
- McLuckey, S. A., "Fundamental Aspects of Gas-Phase Ions: Kinetics", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992 (invited).
- McLuckey, S. A.; Goeringer, D. E.; Glish, G. L., "Universal Collisional Activation in Ion Trap Mass Spectrometry", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- McLuckey, S. A.; Van Berkel, G. J.; Ramsey, R. S.; Glish, G. L., "Tandem Mass Spectrometry of Ions Derived from Nucleic Acids", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- McLuckey, S. A., "The Evolution of Analytical Mass Spectrometry at ORNL", Basic Energy Sciences Advisory Committee Review, ORNL, August 4, 1992.

- McLuckey, S. A. McLuckey, S. A.; Goeringer, D. E., "Explosives Detection by Tandem Mass Spectrometry", Physical Protection Technology Update, Albuquerque, N. M., August 12, 1992 (invited).
- McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L.; Ramsey, R. S., "Quadrupole Ion Trap Analysis of Multiply Charged Ions", 204th American Chemical Society National Meeting, Washington, D. C., August 23-28, 1992 (invited).
- McLuckey, S. A.; Van Berkel, G. J.; Ramsey, R. S.; Goeringer, D. E.; Glish, G. L., "Recent Advances in Biomolecule Analysis Using an Ion Trap Mass Spectrometer", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.
- McLuckey, S. A.; Goeringer, D. E.; Ramsey, J. M.; Wise, M. B.; Buchanan, M. V., "Ion Trap Mass Spectrometry for Vapor/Particle Detection", Contraband and Cargo Inspection Technology International Symposium, Washington, D. C., October 28-30, 1992.
- McLuckey, S. A., "On the Behavior of Stressed-out Biomolecules", East Tennessee Mass Spectrometry Discussion Group, Oak Ridge, December 10, 1992 (invited).
- Mamantov, G. Mamantov, G.; Dai, S.; Begun, G. M.; Young, J. P.; Coffield, J. E., "Development of Raman Spectroscopic Sensors for the Determination of Magnesium in a Molten Salt System", Electrochemical Society Symposium on Molten Salts, St. Louis, May 17-22, 1992.
- Mueller, T. R. Phillips, C. C.*; Bader, M.*; Haskew, M. W.*; Vick, D. O.*; Underwood W. S.*; Stewart, J. H.; Mueller, T. R.; Denton, D. L.; Moore, M. L.; Adeniyi, W. K.*, "Sampling and Analysis Procedures for Detection and Determination of Perchloric Acid Contamination in Laboratory Hoods", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).

- Nourse, B. D. Nourse, B. D.; Hettich, R. L.; Buchanan, M. V., "Methyl Guanine Isomer Differentiation Using Ion/Molecule Reactions and Collision Activated Dissociation in a Fourier Transform Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992 (invited).
- Nourse, B. D.; Hettich, R. L.; Buchanan, M. V., "Methyl Guanine Isomer Differentiation Using Fourier Transform Mass Spectrometry", Purdue University Seminar, West Lafayette, Ind., October 30, 1992 (invited).
- Ramsey, J. M. Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Laser Desorption from Single Microparticles in an Ion Trap Mass Spectrometer", ASMS Conference on Mass Spectrometry, Sanibel Island, Fla., January 25-28, 1992.
- Ramsey, J. M.; Whitten, W. B.; Arnold, S.*; Ng, K. C.*; "An Ultrasensitive Fluorescence Detector for Capillary Electrophoresis", 4th International Symposium on High Performance Capillary Electrophoresis (HPCE) '92, Amsterdam, February 9-13, 1992 (invited).
- Whitten, W. B.; Ramsey, J. M.; Ng, K. C.*; Arnold, S.*, "Digital Molecular Detection", Institute for Spectrochemistry and Applied Spectroscopy Seminar, Dortmund, Germany, February 18, 1992 (invited).
- Ramsey, J. M.; Whitten, W. B., "Digital Molecular Detection: The Analyst Learns to Count", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Ramsey, J. M., "Optical and Mass Spectrometry of Microparticles in the Electrodynamical Trap: Analysis of Picomoles to Yoctomoles", Clemson University Seminar, Clemson, S. C., March 27, 1992 (invited).
- Ramsey, J. M., "Digital Molecular Detection: The Chemist Learns to Count", Georgia Institute of Technology Seminar, Atlanta, April 2, 1992 (invited).

- Ramsey, J. M. Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Laser Ablation from Microparticles in an Ion Trap Mass Spectrometer", ACS Symposium on Laser Material Interactions, San Francisco, April 5-10, 1992 (invited).
- Ramsey, J. M., "Fluorescence Detection of Single Molecules in Solution", East Tennessee State University, Johnson City, Tenn., April 24, 1992 (invited).
- Ramsey, J. M., "Progress in Laser Spectroscopy", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).
- Dale, J. M.; Yang, M.; Whitten, W. B.; Ramsey, J. M., "Laser Desorption/Mass Spectrometry of Single Microparticles in an Ion Trap Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Barnes, M. D.; Ng, K.*; Whitten, W. B.; Arnold, S.*; Ramsey, J. M., "Laser Induced Fluorescence Spectroscopy of Microdroplets: Digital Molecular Detection", 45th Annual Summer Symposium on Analytical Chemistry, Logan, Utah, June 23-25, 1992 (invited).
- Dale, J. M.; Yang, M.; Whitten, W. B.; Ramsey, J. M., "Optical and Mass Spectroscopy of Single Microparticles Using the Electrodynamic Trap", 1992 Optical Society of America Annual Meeting and 8th Interdisciplinary Laser Science Conference, Albuquerque, N. M., September 20-25, 1992 (invited).
- Dale, J. M.; Yang, M.; Whitten, W. B.; Ramsey, J. M., "Laser-Based Measurements in the Electrodynamic Trap", 9th Asilomar Conference on Mass Spectrometry, Monterey, Calif., September 27-October 1, 1992 (invited).
- Barnes, M. D.; Whitten, W. B.; Ramsey, J. M.; Ng, K.; Arnold, S.*, "Digital Molecular Detection of Fluorescent Molecules in Microdroplets", DOE Workshop on Laser Technology in Chemical Measurement, Santa Fe, N. M., October 19-21, 1992.

Ramsey, J. M.

Ramsey, J. M., "Document Tagging Using Fluorescent Dichroic Fibers", American Express Company Presentation, New York, October 30, 1992 (invited).

Barnes, M. D.; Whitten, W. B.; Ng, K.; Arnold, S.*; Ramsey, J. M., "Digital Molecular Detection: The Chemist Learns to Count", Eastern Analytical Society Symposium, Somerset, N. J., November 18, 1992 (invited).

Ramsey, J. M., "The Ultimate Approach to Spectrochemical Analysis: Digital Molecular Detection", 2nd Symposium on Laser Spectroscopy, Merida, Venezuela, December 1-4, 1992 (invited).

Ramsey, J. M., "Microdroplets, Microparticles, and Microchips", 2nd Symposium on Laser Spectroscopy, Merida, Venezuela, December 1-4, 1992 (invited).

Barnes, M. D.; Whitten, W. B.; Ramsey, J. M.; Ng, K.*; Arnold, S.*, "Fluorescence Spectroscopy at the Limit: Detection of Single Molecules in Microdroplets", 2nd Symposium on Laser Spectroscopy, Merida, Venezuela, December 1-4, 1992 (invited).

Ramsey, J. M., "Fluorescence Spectroscopy at the Limit: Digital Molecular Detection", ORNL Executive Committee, December 15, 1992 (invited).

Ramsey, R. S.

Ramsey, R. S., "Measuring the Effects of UV-B Radiation: Separation and Detection Methodology", Centre d'Etudes Nucleaires de Grenoble Seminar, Grenoble, France, February 20, 1992 (invited).

Ramsey, R. S.; Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "The Analysis of Biomolecules by Microbore HPLC/Electrospray Ionization/Ion Trap Mass Spectrometry", Sixteenth International Symposium on Column Liquid Chromatography, Baltimore, June 14-19, 1992 (invited).

Ramsey, R. S.; Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "The Analysis of Biopolymers by HPLC/Electrospray Ionization/Ion Trap Mass Spectrometry", AAAS Science Innovation '92, San Francisco, July 21-25, 1992.

- Ramsey, R. S. Kerchner, G. A.*; Ramsey, R. S., "The Micellar Electrokinetic Capillary Chromatographic Separation of DNA Photoproducts", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Riciputi, L. R. Riciputi, L. R.; Cole, D. R.; Machel, H. G.*; Rosseel, T. M.; Christie, W. H., "The Ion Microprobe for Trace Element Analysis in Carbonates: Diagenesis in the Upper Devonian Nisku Formation, Western Canada Sedimentary Basin", Geological Society of America Annual Meeting, Cincinnati, November 2-6, 1992.
- Robinson, L. Robinson, L.; Dyer, F. F.; "The Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis", Chemistry Department, University of Kentucky, Lexington, January 24, 1992 (invited).
- Robinson, L.; Dyer, F. F., "A Search for Arsenic in Hair and Nail Remains of Former President Zachary Taylor by Neutron Activation Analysis (A Historical Prospective)", 19th Annual WATtec Conference, Knoxville, February 18-21, 1992 (invited).
- Robinson, L., "Accountability Measurements at ORNL", Energy Systems Five-Site Nondestructive Assay Measurements Meeting, K-25 Site, April 28-29, 1992 (invited).
- Robinson, L.; Dyer, F. F.; Combs, D. W.*; Wade, J. W.; Teasley, N. A.; Carlton, J. E.*; Ondracek, A. L.; Stokely, J. R., "The Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis", 2nd International Symposium on Nuclear Analytical Chemistry, Toronto, June 3-5, 1992 (invited).
- Robinson, L.; Dyer, F. F.; Carlton, J. E.*, "NAA and Multi-User Simulation Using a PC-Based MCA", American Nuclear Society, Boston, June 7-12, 1992 (invited).
- Robinson, L.; Dyer, F. F., "Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis", 8th Annual Waste Testing and Quality Assurance Symposium, Arlington, Va., July 13-17, 1992.

- Robinson, L. Robinson, L.; Dyer, F. F.; Combs, D. W.*; Wade, J. W.; Teasley, N. A.; Carlton, J. E.*; Ondracek, A. L.; Stokely, J. R., "The Determination of Hg and Other Trace Elements in Soil Using Neutron Activation Analysis", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Rosseel, T. M. Rosseel, T. M.; Riciputi, L. R.; Christie, W. H., "Digital-Imaging and Analysis with the Secondary Ion Microprobe", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Rosseel, T. M.; Riciputi, L. R.; Christie, W. H., "Secondary Ion Imaging and Analysis", DOE/BES Site Review, Oak Ridge, April 27-28, 1992 (invited).
- Rosseel, T. M.; Riciputi, L. R.; Christie, W. H.; Cole, D. R., "Digital-Imaging and Analysis with the Secondary Ion Microprobe", Fifth East Coast Workshop on Secondary Ion Mass Spectrometry, Somerset, Penn., May 20-22, 1992.
- Rosseel, T. M.; Christie, W. H., "Particle Search and Analysis Using Digital-Imaging SIMS", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Rosseel, T. M., "Secondary Ion Mass Spectrometry (SIMS)", Human Genome Dialog Group Meeting, Oak Ridge, August 12, 1992 (invited).
- Schenley, R. L. Schenley, R. L.; Sega, G. A.; Keller, J. M.; Tomkins, B. A.; Griest, W. H., "Methods for Regulatory Analyses of Radioactive Mixed Wastes", 47th Northwest Regional ACS Meeting, Missoula, Mont., June 17-19, 1992.
- Sega, G. A. Sega, G. A.; Schenley, R. L.; Griest, W. H., "Methods for Determination of PCBs in Radioactive Mixed Wastes", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Shaw, R. W. Shaw, R. W., "Tunable Lasers in Analytical Spectroscopy", Seminar for Directors of Industrial Research/Analytical Chemists, ORNL, February 20, 1992 (invited).

Shaw, R. W.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M., "Fundamental Studies of Chemical Vapor Deposition Materials Growth Processes", Analytical Chemistry Division Information Meeting, March 18-20, 1992 (invited).

Shaw, R. W.; Young, J. P.; Ramsey, J. M., "Resonance Ionization of Rubidium Using Sequential Diode Laser-Driven Transitions", 6th International Symposium on Resonance Ionization Spectroscopy and Its Applications, Santa Fe, N. M., May 24-29, 1992.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M., "Laser Spectroscopic Diagnostics for CVD Diamond Films", Gordon Research Conference on Diamonds, Plymouth State College, Plymouth, N. H., June 15-19, 1992.

Shaw, R. W., "Tunable Diode Lasers for Resonance Ionization Mass Spectrometry", North Carolina State University Seminar, Raleigh, N. C., September 14, 1992 (invited).

Shaw, R. W., "Laser Spectroscopic Diagnostics for CVD Diamond Growth", Industrial Diamond Association Conference, ORNL, September 17, 1992 (invited).

Shaw, R. W.; Young, J. P.; Ramsey, J. M., "Multiple Diode Laser Excited Rubidium RIMS", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).

Short, R. T.

Kruger, M. S.*; Cook, K. D.*; Short, R. T.; Todd, P. J., "Time Dependence and Surface Phenomena of Secondary Ion Emission from Solution", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

Short, R. T.; Todd, P. J.; Holland, W. M., "Organic Surface Analysis Using SIMS/MS Imaging", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).

- Stewart, J. H. Stewart, J. H., Jr.; Horwitz, E. P.*; Gouge P. S.; Hulmston, P.*, "Determination of Uranium and Transuranium Elements in Bioassay Fluids, Soils, and Air Filters by ICP-MS", 1992 Winter Conference on Plasma Spectrochemistry, San Diego, January 6-11, 1992 (invited).
- Stewart, J. H., Jr.; Mueller, T. R.; Moore, M. L.; Bader, M.*; Haskew, M. W.*; Phillips, C. C.*; Vick, D. O.*; Jerome, B. A.*, "The Determination of Perchlorates in Ventilation Systems", ACS Symposium on Industrial Hygiene Chemistry, San Francisco, April 5-10, 1992 (invited).
- Swafford, A. M. Swafford, A. M.; Keller, J. M., "Clean-Up of Regulatory Samples for ICP/ICP-MS", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Swafford, A. M.; Robinson, L.; Dyer, F. F., "Neutron Activation Analysis of Uranium and Gross Fissile Content by Delayed Neutron Counting", ORO/DOE Multi-Site Analytical Chemistry Meeting, Paducah, Ky., November 10, 1992 (invited).
- Thompson, C. V. Thompson, C. V.; Wise, M. B.; Blalock, A. V.*, "Development of a Real-Time Air Monitoring Interface for the ITS-40 Ion Trap Mass Spectrometer", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992 (invited).
- Todd, P. J. Todd, P. J., "Organic Ion Imaging", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Todd, P. J., "Organic Ion Imaging", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).
- Todd, P. J.; Short, R. T.; Grimm, C. C.; Holland, W. M., "Organic Ion Imaging", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.

- Todd, P. J. Todd, P. J.; Short, R. T., "Applications of an Imaging SIMS-MS/MS Microprobe to Complex Organic Systems", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.
- Van Berkel, G. J. Van Berkel, G. J.; Ramsey, R. S.; McLuckey, S. A.; Glish, G. L.; Goeringer, D. E., "Electrospray Ionization/Ion Trap Mass Spectrometry", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Van Berkel, G. J., "Fundamentals and Applications of Electrospray", DOE/BES Site Review, ORNL, April 27-28, 1992 (invited).
- Van Berkel, G. J.; Ramsey, R. S.; McLuckey, S. A.; Glish, G. L., "Microbore HPLC/Electrospray Ionization/Ion Trap Mass Spectrometry of Biomolecules", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Radical Cation Formation in Electrospray Ionization", 40th ASMS Conference on Mass Spectrometry and Allied Topics, Washington, D. C., May 31-June 5, 1992.
- Van Berkel, G. J.; Ramsey, R. S., "Geoporphyrin Analysis Using Electrospray Ionization-Mass Spectrometry", Porphyrin Geochemistry Symposium, 204th American Chemical Society National Meeting, Washington, D. C., August 23-28, 1992 (invited).
- Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Expanding the Understanding and Utility of Electrospray Ionization-Mass Spectrometry", 204th American Chemical Society National Meeting, Washington, D. C., August 23-28, 1992.
- Van Berkel, G. J., "Analysis of Electrospray Derived Ions Using a Quadrupole Ion Trap Mass Spectrometer", '92 International Conference on Biological Mass Spectrometry, Kyoto, Japan, September 20-24, 1992 (invited).

- Van Berkel, G. J. Van Berkel, G. J.; Quirke, J. M. E.*, "Development of Methodology to Expand the Range of Compound Types Amenable to Electrospray Ionization-Mass Spectrometry", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Wade, J. W. Wade, J. W.; Morton, S. J.; Stewart, J. H., "Determination of Neptunium-237 in Urine by ICP-MS", First National Conference on Inductively Coupled Plasma Mass Spectrometry, Philadelphia, September 19-20, 1992.
- Whitten, W. B. Whitten, W. B.; Ramsey, J. M.; Arnold, S.*, "Room Temperature Persistent Spectral Hole Burning", Computer Systems Policy Project Materials Track Meeting, Albuquerque, N. M., April 15-16, 1992 (invited).
- Whitten, W. B.; Ramsey, J. M.; Bronk, B. V.*, "Microparticle-Based Fluorescence Immunoassay", U.S. Army CRDEC Conference on Obscuration and Aerosol Research, Aberdeen Proving Ground, Md., June 22-26, 1992 (invited).
- Wise, M. B. Wise, M. B., "Fieldable Ion Trap Instrumentation for the Rapid Analysis of Volatile Organic Compounds in the Environment", Analytical Chemistry Division Information Meeting, March 18-19, 1992 (invited).
- Yang, M. Yang, M.; Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Optical Spectroscopy of Molecular Ions in a Quadrupole Ion Trap", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).
- Young, J. P. Young, J. P.; Mamantov, G.; Dai, Sheng; Coffield, J. E., "In-Line Analytical Sensor Development for Dow Chemical Company Electrolytic Magnesium Cells; A CRADA Project", Analytical Chemistry Division Information Meeting, March 18-20, 1992 (invited).
- Young, J. P.; Shaw, R. W., "A Miniature Carbon Furnace for Mass Spectrometry", 6th International Symposium on Resonance Ionization Spectroscopy and Its Applications, Santa Fe, N. M., May 24-29, 1992.

Young, J. P.

Dai, S.; Coffield, J. E.; Begun, G. M.; Mamantov, G.; Young, J. P., "Applications of Raman Spectroscopy to Molten Salt Systems", Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Philadelphia, September 20-25, 1992.

Dai, Sheng; Begun, G. M.; Young, J. P.; Coffield, J. E.; Mamantov, G., "Fused Silica General Purpose Spectroscopic Probe", 33rd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 6-8, 1992 (invited).

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Analytical Chemistry	Anal Chim Acta	Biomed Environ Mass Spectrom	Energy & Fuels	Environ Science & Technology	Int J Mass Spectrometry	J Am Chemical Society	J Am Soc Mass Spectrometry	J Chromatography	J Physical Chemistry	Organic Mass Spectrometry	Proposals	Other	Total
Barshick, C. M.													1	1
Buchanan, M. V.	5			3							3	7		18
El Fallah, M. Z.	2								3				2	7
Goeringer, D. E.	1								1				1	3
Griest, W. H.	4				1							4		9
Guerin, M. R.					1								4	5
Guiochon, G.	148 ^a					1			15	3		10	7	184
Hettich, R. L.					1									1
Laing, W. R.													28	28
MacDougall, C. S.													1	1
McLuckey, S. A.	3	2	1			6	11	3				7	2	35
Mueller, T. R.												2		2
Ramsey, J. M.	3											51	1	55
Ramsey, R. S.	1								1			2		4

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Analytical Chemistry	Anal Chim Acta	Biomed Environ Mass Spectrom	Energy & Fuels	Environ Science & Technology	Int J Mass Spectrometry	J Am Chemical Society	J Am Soc Mass Spectrometry	J Chromatography	J Physical Chemistry	Organic Mass Spectrometry	Proposals	Other	Total
Riciputi, L. R.												3	3	6
Robinson, L.													1	1
Rosseel, T. M.												9		9
Shaw, R. W.	1											4		5
Todd, P. J.		1						3	2		1	2		9
Tomkins, B. A.	2				1								1	4
Van Berkel, G. J.					2			1					1	4
Wade, J. W.													1	1
Whitten, W. B.	1	1										4	2	8
Wise, M. B.					1									1
TOTALS	171	4	1	3	7	7	11	7	22	3	4	105	56	401

^aAs Associate Editor

SUMMARY OF ANALYTICAL SERVICE WORK

ORGANIZATION	Number of Results Reported By			TOTAL
	Analytical Spectroscopy	Inorganic and Radiochemistry	Organic Chemistry ^a	
<hr/>				
<u>ORNL Unit</u>				
Analytical Chemistry		2,865	3,540	6,405
Central Management		216	8,280	8,496
Chemical Technology	1,978	20,725	14,100	36,803
Chemistry		1,028	2,760	3,788
Energy		1,445	2,280	3,725
Engineering		732	1,680	2,412
Engineering Physics & Mathematics	20	33	780	833
Engineering Technology	8	139		147
Environmental Compliance and Documentation		38,856	41,250	80,106
Environmental Sciences		10,990	5,010	16,000
Finance and Business Management		312	180	492
Fusion Energy		2		2
Health and Safety Research	12	751		763
Instrumentation and Controls		100	690	790
Laboratory Protection		147	420	567
Metals and Ceramics	2,808	4,635	9,840	17,283
Physics	32	572	1,350	1,954
Plant and Equipment		8,655	29,820	38,475
Quality		95	360	455
Research Reactors	8	1,664	4,260	5,932
Robotics and Process Systems	1600	2,000	240	3,840
Solid State		235	330	565
Waste Management and Remedial Action		53,091	10,770	63,861
<u>Others</u>				
K-25	324	1,526	7,590	9,440
Paducah		3,758	18,660	22,418
Y-12	1,146	2,940	3,660	7,746
Central Environmental Restoration		31,479	20,940	52,419
Miscellaneous	92	766	2,460	3,318
Work for Others		221		221
TOTAL	8,028	191,978	191,490	391,496

^aOrganic analysis records consist of samples analyzed. Number of results reported was obtained by multiplying samples analyzed by average number of results reported per samples (30).

FY 1992 DIVISIONAL MANPOWER AND FINANCIAL SUMMARY

<u>Source</u>	<u>\$K</u>	<u>PY</u>
DOE Programs		
Energy Research		
Basic Energy Sciences	2,151	11.6
Biological and Environmental Research	306	0.9
OERWM - Env. Restoration & WM-Def.	1,759	10.4
Nuclear Safeguards and Security	284	1.7
OERWM - Env. Restoration & WM-Nondef.	714	5.5
Industrial Energy Conservation	152	0.7
Fossil Energy Strategic Petroleum Reserve	<u>5</u>	<u>0.0</u>
Total DOE Programs	5,371	30.9
Work for Others - Federal Agencies		
Department of Defense	932	4.8
Nuclear Regulatory Commission	110	0.5
National Cancer Institute	248	1.5
National Institutes of Health	256	0.9
Federal Aviation Administration	333	1.7
NASA	107	0.7
Other Energy Systems Installations	692	5.5
Miscellaneous	<u>205</u>	<u>1.5</u>
Total WFO - Federal Agencies	2,883	17.1
Work for Others - Nonfederal Agencies		
Full Cost Recovery Customers		
Protective Coating/Uranium Ore Testing	4	0.0
University of California - Davis	10	0.0
Miscellaneous Cash Billed	<u>10</u>	<u>0.0</u>
Total Program 11	24	0.0
Indirect Staff/Nonchargers		5.8
Total DOE Programmatic, Federal and Nonfederal Agencies	8,278	48.1
Support/Services (does NOT include overhead)		
Other ORNL Divisions	6,575	72.1
Other Clients	2,853	31.3
Intra-divisional Charges	<u>908</u>	<u> </u>
Subtotal	10,336	103.4
Indirect Staff/Nonchargers		5.3
Total Support/Services	10,336	103.4
TOTAL FINANCIAL PLANS	17,706*	151.6

*Total ACD cost excludes intra-division charges.

GLOSSARY

ACD	-	Analytical Chemistry Division
ACS	-	American Chemical Society
AES	-	Atomic emission spectroscopy
AGC	-	Automatic gain control
AIC	-	Analytical Improvement Council
ALARA	-	As low as reasonably achievable
AMC	-	Analytical Managers Council
AnaLIS	-	Data management system for sample logging and data reporting
ARC	-	Automatic reaction control
ASGDI	-	Atmospheric sampling glow discharge ionization
ASMS	-	American Society for Mass Spectrometry
ASTM	-	American Society for Testing and Materials
BES	-	Basic Energy Sciences
BSA	-	Bovine serum albumin
BSCP	-	Background Soil Characterization Project
CA	-	Collisional activation
CAMDS	-	Chemical Agents Munitions Disposal System facility, Tooele, Utah
ccc	-	Combustible cartridge case
CI	-	Chemical ionization
CID	-	Collision-induced dissociation
CLP	-	Contract Laboratory Program
CR	-	Counting room
CRADA	-	Cooperative Research and Development Agreement
CRDEC	-	Chemical Research and Development Engineering Center
CRL	-	Certified reporting limits
CVD	-	Chemical vapor deposition
CW	-	Chemical warfare
CZE	-	Capillary zone electrophoresis
DAAMS	-	Depot Area Air Monitoring System
DNC	-	Delayed neutron counting
DOE	-	Department of Energy
DRIFT	-	Diffuse reflectance Fourier transform infrared spectroscopy
DSITMS	-	Direct sampling ion trap mass spectrometry
ECD	-	Electron capture detector
ECP	-	Elution by characteristic point
EFPC	-	East Fork Poplar Creek

EI	-	Electron ionization
EPA	-	Environmental Protection Agency
ESI	-	Electrospray ionization
ESI/ITMS	-	Electrospray ionization with ion trap mass spectrometry
ES/MS	-	Electrospray ionization mass spectrometry
FAB	-	Fast atom bombardment
FACSS	-	Federation of Analytical Chemistry and Spectroscopy Societies
FD	-	Field desorption
FID	-	Flame ionization detection
FTMS	-	Fourier transform mass spectrometry
FWHM	-	Full width at half maximum
GC/ECD	-	Gas chromatography with electron capture detection
GC/MS	-	Gas chromatography/mass spectrometry
GD/MS	-	Glow discharge mass spectrometry
HFIR	-	High Flux Isotope Reactor
HPLC	-	High performance liquid chromatography
ICP	-	Inductively coupled plasma
ICR	-	Irradiation control room
IMMA	-	Ion microprobe mass analyzer
ITD	-	Ion trap detector
ITMS	-	Ion trap mass spectrometer
LCD	-	Limiting conditions document
LIDIS	-	Laboratory Instrument Data Interface Survey (Committee)
LIMS	-	Laboratory Information Management System
LLRAG	-	Low-Level Radiochemical Analysis Group
MALDI	-	Matrix assisted laser desorption ionization
MB	-	Methylene blue
MCA	-	Multichannel analyzer
MDL	-	Method detection limits
MECC	-	Micellar electrokinetic capillary chromatography
MS/MS	-	Tandem mass spectrometry
MTA	-	Multi-Threat Analyzer
NAA	-	Neutron activation analysis
NAAF	-	Neutron Activation Analysis facility
NAAL	-	Neutron Activation Analysis Laboratory
NASA	-	National Aeronautics and Space Administration

NCI	-	National Cancer Institute
NDP	-	Neutron depth profiling
NPDES	-	National Pollutant Discharge Elimination System
NRC	-	Nuclear Regulatory Commission
NSF	-	National Science Foundation
OM	-	Optical microscopy
OMVPE	-	Organometallic vapor phase epitaxy
ORAU	-	Oak Ridge Associated Universities
ORNL	-	Oak Ridge National Laboratory
OSR	-	Operation safety requirements
PAH	-	Polycyclic aromatic hydrocarbon
PBT	-	Performance-based training
PD	-	Plasma desorption
PET	-	Proficiency environmental testing
PGA	-	Prompt gamma analysis
PGDP	-	Paducah Gaseous Diffusion Plant
PHS	-	Public Health Service
PMC	-	Performance Management Council
PMT	-	Photomultiplier tube
PSA	-	Primary secondary amine
RCRA	-	Resource Conservation and Recovery Act
REDC	-	Radiochemical Engineering Development Center
REE	-	Rare earth elements
REMPI	-	Resonance enhanced multiphoton ionization
RFI	-	Remedial feasibility investigation
RIMS	-	Resonance ionization mass spectrometry
RMA	-	Radioactive materials analysis
RMAL	-	Radioactive Materials Analytical Laboratory
RMW	-	Radioactive mixed waste
RSF	-	Relative sensitivity factors
SAM	-	Standard analytical method
SBIR	-	Small Business Innovative Research
SDD	-	System design description
SEM	-	Scanning electron microscope
SFG	-	Sum-frequency generation
SIMS/MS	-	Secondary ion tandem mass spectrometer
SOP	-	Standard operating procedure
SPE	-	Solid phase extraction

TAAG	-	Transuranium and Activation Analysis Group
TAL	-	Transuranium Analysis Laboratory
TCLP	-	Toxicity Characterization Leaching Procedure
TEM	-	Transmission electron microscopy
TIC	-	Tentatively identified compound
TIMS	-	Thermal ionization mass spectrometry
TOF/MS	-	Time of flight mass spectrometer
TRU-Spec	-	Transuranic-specific
TSCA	-	Toxic Substances Control Act
UHV	-	Ultra high vacuum
UT	-	The University of Tennessee
VOC	-	Volatile organic compound
WAG	-	Waste Area Group
XRD	-	X-ray diffraction

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