BH 2-25-92 JSO

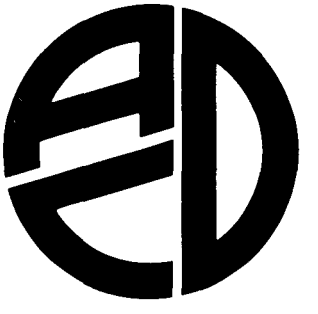
ornl

ORNL-6701

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

Analytical Chemistry Division Annual Progress Report for Period Ending December 31, 1991



This document is
PUBLICLY RELEASABLE

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL--6701

Distribution

DE92 007804

ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1991

W. D. SHULTS
Director

Date Published - January 1992

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U. S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

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 with 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 divisions 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. An Operations section was created this 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, 1991. Chapter 5 summarizes the education programs, which have grown in both magnitude and importance. Supplementary professional activities, publications, and presentations are given in Chapters 6 and 7.

During 1991, the division continued to publish and present its work: 21 reports, 39 proceedings and/or book chapters, 65 journal articles, and 156 oral presentations. Some 322,339 analytical determinations were performed.

HIGHLIGHTS

The following paragraphs highlight some of the technical activities carried out during 1991. They illustrate the diversity of programs and technical work performed within the Analytical Chemistry Division.

After a four-year shutdown, the High Flux Isotope Reactor (HFIR) was restarted late in 1990. Our neutron activation analysis (NAA) laboratory at HFIR was placed into operation during 1991. It attracted national attention in 1991 when two samples of hair and two samples of fingernail from the remains of former President Zachary Taylor were brought to ORNL by Dr. George Nichols, State Medical Examiner of Kentucky, on June 20, 1991. The samples, which ranged form 2.7 mg for the smaller hair sample to 12.3 mg for the larger nail sample, were irradiated that evening for one minute in a thermal neutron flux of 4.61×10^{13} n cm^{-2} s^{-1}. Gamma spectra were acquired for a number of periods of several hours over a three-day interval following irradiation. The specimens were not cleaned for these initial analyses. Following these initial analyses, sections of the hair specimen (~ 5 mm) containing the hair roots were removed, re-irradiated, cleaned to remove much of the ^{24}Na and ^{42}K, and reanalyzed. One root specimen weighing 0.75 mg was irradiated five minutes and found to contain 0.8 μg/g of arsenic. The other specimen was irradiated 10 minutes and found to contain 0.3 μg/g. Both of these observed concentrations are within normal levels observed in hair within the past 30 years. As a result of these analyses by neutron activation and results from other analytical methods, the Kentucky State Medical Examiner concluded that the former president was not poisoned with arsenic.

We have combined inductively coupled plasma mass spectrometry (ICP/MS) with a preparation procedure developed at the Argonne National Laboratory to measure ultra-trace levels of U, Pu, Np, and Am in body fluids, primarily urine. The sensitivity of the ICP/MS for the specific nuclides of interest has been demonstrated, on both

synthetic solutions and spiked urine specimens, at the 10 parts-per-trillion (ppt) concentration level for ^{234}U. Detection limits for ^{237}Np, ^{239}Pu, and ^{241}Am are near the 25 ppt concentration level. The significance of this development is that ^{239}Pu, ^{237}Np, and ^{241}Am can be specifically measured without need for chemical isolation, as is required for alpha counting. The actual ICP/MS analysis time for U is less than 20 minutes, and Pu, Np, and Am can be measured in less than 30 minutes. Preliminary studies indicate that this same methodology is applicable to air filters, smear wipes, and soil leachate analyses.

Much progress has been made over the last year in the interfacing of an rf-powered glow discharge source to the VG-9000 double-focusing mass spectrometer. A significant element in this progress lies in a novel rf probe/discharge cell design and a new electrical coupling system that allows the elemental analysis of both conducting and insulating solid materials. Absolute sensitivities are in the low ppb range for conductors and are expected to be similar for nonconductors. In parallel experiments using Fourier transform mass spectrometry (FTMS) coupled with an rf glow discharge source, copper ions from a piece of copper stock were detected with a mass resolution of 37,000 (FWHM). These experiments demonstrate the potential for obtaining relatively high mass resolution spectra in the broadband mode and hence for simultaneously determining several elements. This can be particularly important for thin-film profiling and isotope ratio measurements.

Preliminary experiments using electrospray ionization combined with ion trap mass spectrometry show much promise for the analysis of metals in solution. Particular emphasis has been placed on using complexing agents, such as crown ethers, that allow selective extraction and concentration of species of interest. An additional advantage of using complexing agents is that the ion current is typically concentrated into one ionic m/z rather than several different ones with various degrees of solvation. The use of MS/MS to confirm the identity of the metal ion has also been demonstrated in these experiments.

A secondary ion microprobe has been constructed that permits determination of the distribution of organic compounds less than a monolayer thick on samples as large as 1 cm diameter. The instrument has made it possible, for the first time, to generate images of surfactants and nonsurfactants on liquid surfaces. The instrument's tandem

mass analysis (MS/MS) capability makes it ideally suited for study of biological samples.

FTMS has been demonstrated to be a highly effective tool for the detailed characterization of biopolymers, especially normal and modified oligonucleotides. Matrix-assisted laser desorption is particularly useful for the generation of intact singly charged ions from these polar compounds. Gas phase processes such as ion/molecule reactions, collision-induced dissociation, and photodissociation are then used to probe the structure of modified oligonucleotides and determine the identity of the adduct, the site of adduct substitution on a nucleoside, and even the position of the modified base in a short oligomer.

Exciting results have also been obtained in the area of biomolecule structure determination via MS/MS and MS^n in a quadrupole ion trap. Two distinct areas have been addressed: collision-induced dissociation (CID) and ion/molecule reactions. In the area of CID, very promising results have been obtained with oligonucleotides that allow sequence information to be determined. Ion/molecule reactions have been used to determine product ion identities of multiply charged peptides and proteins and to gather fundamental information on sites of protonation of these species.

Much has been accomplished in understanding the fundamentals of quadrupole ion trap mass spectrometry (ITMS). The most dramatic and significant advance has been in the area of high resolution capabilities of the trap. Resolution in excess of 100,000 has been demonstrated at m/z 502. A theory based on a damped harmonic oscillator has been developed to explain the results. Work has also progressed in understanding the trapping effects during ionization and the parameters that affect ion temperatures in the ion trap.

Work with ITMS instrumentation has led to the development of rapid methods for the detection of trace organics in environmental and physiological samples. All 34 EPA target compound list (TCL) volatiles can be detected at low ppb levels using direct purge into an ITMS. A method for rapidly (3 minutes) screening environmental samples for the presence of volatiles in water is nearing completion, with current effort being placed on the establishment of calibration and internal standards and quality assurance protocols. Additionally, a real-time monitor based on an ion trap mass spectrometer has been developed and very successfully field tested on water and soil samples, as well as

soil gas and air samples. Thermal desorption into the spectrometer has been used to analyze a wide variety of semivolatile organics in environmental samples. This same approach has been successfully used to detect ppb levels of drugs and toxic material in urine, saliva, meat, milk, and food.

A new type of time-of-flight mass spectrometer was designed for use with our positron ionization experiments. The spectrometer has a parabolic (quadratic) potential energy variation along the flight path making the ion transit time independent of axial position. This feature allows the use of a large volume ion source without loss of mass resolution. The large volume ion source enhances sensitivity and thus has applications beyond positron-molecule interactions.

A new approach for the chemical characterization of single microparticles (diam. < 100 μm) is being developed. The concept is to use the same quadrupole electrodynamic trap for particle levitation and ion trap mass spectrometry. Optical techniques such as absorption, fluorescence and Raman spectroscopy can be performed on the levitated particle. After nondestructive measurements have been performed, the trap is switched from particle levitation mode to ion trapping with the simultaneous application of an intense laser pulse. The desorbed ions are trapped and subsequently mass analyzed. Single particle desorption experiments have been demonstrated at the 100 fM level with a signal-to-background ration of more than 100.

The Laboratory Director's R&D program has supported a joint project between Analytical Chemistry, Metals and Ceramics, and Fusion Energy divisions with a goal of understanding growth processes of chemical vapor deposition materials at the molecular level. The Optical Spectroscopy group within ACD is leading the chemical diagnostics efforts of this project and has designed an apparatus that permits a more comprehensive investigation of the growth process. Whereas previous investigators have concentrated on bulk gas measurements, our approach concentrates on the boundary layer gases immediately above the growth surface and the monomolecular layer of species on the surface. The growth of thin diamond films is currently being studied.

A joint project has been initiated between the Dow Chemical Corporation, the University of Tennessee, the Oak Ridge National Laboratory to develop in-line chemical sensors for control of magnesium production processes. Successful completion

and implementation of this project can result in a 5 to 10% savings in energy use for magnesium production. A Cooperative Research and Development Agreement (CRADA) was signed in 1991 to provide joint funding between the DOW Chemical Corporation and DOE Office of Industrial Programs for the development of these sensors.

Fundamental research on chromatography at high concentrations and on gas-solid adsorption has continued. During 1991, we demonstrated the validity of the theory of non-linear chromatography and defined the range of applicability of the equilibrium-dispersive and the kinetic models of chromatography. We also developed a theory of optimization of the experimental conditions for maximum production rate in preparative chromatography. A new method of characterization of nonhomogeneous surfaces of powders using gas chromatography has been developed and validated.

The preparation of a monograph on the chemistry of environmental tobacco smoke (ETS) was completed this year. Special attention was given to respirable particulate matter, nicotine, carbon monoxide, volatile organic chemicals, trace organics (primarily polycyclic aromatic hydrocarbons and N-nitrosamines), oxides of nitrogen, and formaldehyde. The objective was to provide a comprehensive tabulation and review of data generated in studies of ETS exposure, and to provide background information on smoke chemistry, sampling and analysis methods, and non-ETS sources of indoor air contaminants as an aid for future research.

1. ANALYTICAL SPECTROSCOPY

J. A. Carter

The Analytical Spectroscopy section is composed of four groups: Optical Spectroscopy, Inorganic Mass Spectrometry, Organic Mass Spectrometry, and Secondary Ion Mass Spectrometry. The driving force in R&D is toward enhancing capabilities through new discoveries and toward developing a clearer understanding of fundamental physical processes that can be exploited in new instruments or analytical approaches for solving energy-related problems. Noteworthy accomplishments in optical spectroscopy for this past year are: (a) the first demonstration of the ability to count all target molecules in a given volume (micro-drop) with unit efficiency, (b) the first demonstration of single particle analysis by laser ablation using ion trap mass spectrometry, and (c) the first demonstration of boundary layer molecular diagnostics. In mass spectrometric R&D, advances in ion trap mass spectrometry have led to the development of a theory for understanding high resolution, and the demonstration of resolution with electrospray techniques in excess of 50,000. Electrospray techniques continue to be used for inorganic analysis and liquid chromatography experiments. The atmospheric sampling glow discharge ionization/ion trap mass spectrometry technique has a demonstrated sensitivity of 15 parts-per-trillion for explosives and CFC-type compounds. The CAMECA-4f instrument acquired last year is finding a useful niche in DNA sequencing and in geological R&D studies. The organic ion microprobe experiments have a demonstrated overall efficiency of 25%. The VG-9000 dc glow discharge mass spectrometer R&D effort has resulted in a novel radio-frequency powered source for elemental analysis of nonconductor materials.

About 40% of the section's research and development support is provided by the Division of Chemical Sciences of the Office of Energy Research, U. S. Department of Energy. This effort, broad in nature, provides the technical base from which current and future spectroscopic needs are addressed. Another 30% of the section's R&D funding is about equally distributed among the

DOE Offices of Safeguards and Security, Arms Control, and Industrial Processes. The balance of our effort is funded by Laboratory divisions and programs, the Y-12 and K-25 plants, various interagency agreements (FAA, NASA, ISPO/State, and IAEA) and from other work-for-others efforts.

OPTICAL SPECTROSCOPY

J. Michael Ramsey

This group continues to be involved in a broad spectrum of activities with chemical measurements based upon laser spectroscopy as a general theme. New techniques and instrumentation are being developed that address measurement problems in microparticle physics, materials science, and biotechnology. The more noteworthy successes of the past year include the first demonstration of the ability to count all the target (fluorescent) molecules in a given volume of solution with near unit efficiency, the first demonstration of single particle analysis by laser ablation in an ion trap mass spectrometer, and the first demonstration of boundary layer molecular diagnostics in a chemical vapor deposition reactor. Research also continues in resonance ionization mass spectrometry using solid-state diode lasers and positron spectroscopy. In addition, we are making further developments in chemical sensors for process control and document tagging concepts for advanced counterfeit deterrence. The signing of a Cooperative Research and Development Agreement (CREDA) with the Dow Chemical Corporation in support of our chemical sensor program is especially noteworthy.

Digital Molecular Detection

By using levitated microdroplets for samples together with laser excited fluorescence detection, we have recently shown that we can count the number of analyte molecules in a very dilute solution. That is, the signal-to-noise ratio is high enough that we can say with certainty (greater than 3σ) whether or not there is an analyte molecule present within a microdroplet. The ability to count the molecules in a solution not only makes possible a radically new way to determine very small concentrations but also changes

the way we determine the accuracy of the measurement. Now, the probability of declaring a false positive or of missing a molecule that was actually present becomes the important consideration. The detection threshold can be chosen so that one or the other probability has the heavier weight, depending on the application of the measurement. For example, when analyzing for a very toxic substance, missed molecules would be highly undesirable errors while false positives would be less serious. The selected detection threshold would be lower in this case than that which makes either error equally likely.

Our first experiments on digital molecular detection were made with the highly fluorescing molecule, β-phycoerythrin, a biological pigment. The analyte was dissolved in a glycerol-water solution so that when most of the water evaporated from the levitated droplets, the average phycoerythrin concentration in the droplets was 1.75 pM. The levitated droplets averaged 9.5 μm in diameter, or 0.45 pl in volume, so the probability that a given droplet had no analyte molecule present was 0.62. A series of 24 measurements was made on samples of this concentration. One droplet was found to contain three molecules, one contained two, and seven contained a single molecule of analyte. The remaining 15 droplets were blank. These occurrences are in good agreement with the probabilities calculated from Poisson statistics. Similar experiments have also been carried out with rhodamine-6G as the analyte molecule. Eight droplets with an experimental average concentration of 3.5 pM and diameters from 6 to 10 μm yielded six blanks, one droplet with three rhodamine molecules, and one with one. Again, Poisson statistics were roughly obeyed.

The minimum concentration that we can detect by fluorescence in levitated microdroplets is limited in part by the photostability of the dye molecules chosen for the experiment since the maximum useful integration time is the photochemical lifetime of the analyte molecules. We have begun to look at dye molecules that absorb and fluoresce at wavelengths much longer than those of rhodamine-6G and β-phycoerythrin, the analyte molecules that have received the greatest attention. The expectation is that there will be fewer impurity molecules that absorb in the same spectral region as the dye molecules and that because the excited state energy is lower, the molecules might be less photoreactive. A further advantage of these molecules is that they can be excited with inexpensive CW diode lasers.

The first new molecule to be studied was HITC iodide, a laser dye with an absorption maximum at 750 nm. With 670-nm excitation, where the molecule still has appreciable absorption, there is little overlap between analyte fluorescence and solvent Raman emission so that interference filters can be used to isolate the fluorescence. Photomultiplier sensitivity is adequate over the wavelength range of the detected emission, centered at 774 nm.

We modified our levitated droplet fluorescence apparatus so that a 670-nm diode laser could be used as the excitation source. Droplets of a glycerine water mixture to which HITC iodide had been added were levitated in the electrodynamic trap and excited with a laser intensity of 150 mW/cm^2. The fluorescence was isolated by an interference filter with a 45-nm bandwidth at 774 nm and a CS 2-64 Corning filter to partially block the elastically scattered light. The photostability of HITC was lower than expected. Under the excitation conditions described above, the fluorescence decayed with an average time constant of 350 s, while rhodamine-6G had a time constant of 3 s for 300 W/cm^2 intensity. Since the oscillator strengths and quantum efficiencies of the two molecules are comparable, HITC must be about five times less stable than rhodamine under our conditions.

Our investigations of microdroplet fluorescence have so far been restricted to droplets levitated in an electrodynamic trap. With relatively modest excitation, light collection, and detection efficiencies, we have been able to achieve a sensitivity sufficient to count single molecules in liquid microdroplets. While these studies are important in extending the limits of detectibility, most practical applications of ultrasensitive detection are associated with separations technology and require frequent sampling of an effluent, often from a column. We are therefore exploring methods for producing microdroplets from the output of a microbore column used for chromatography or electrophoresis and measuring the fluorescence at a rate commensurate with the flow.

The droplet generator that was used for the trapped droplet experiments uses an acoustic wave produced by piezoelectric strips to force a droplet from a glass tip with an orifice of 30 to 50 μm. The glass tip is about 1 mm inside diameter before the exit constriction. We have been able to insert a glass capillary 75 μm id and 190 μm od from the rear of the droplet generator so that it approaches the exit orifice within the glass

tip. With this setup, it is possible to introduce analyte from the inserted capillary into the droplets formed by the generator. Several modes of operation have been demonstrated. If the flow through the capillary is much less than the volume per second of generated droplets and diffusion of analyte back into the tip is not a problem, drops of the analyte diluted by the liquid within the tip are generated in the normal fashion. If dilution is not desirable, if diffusion in the tip must be avoided, or if the flow rate through the capillary approaches the maximum that the generator can handle, the fluid in the tip can be replaced by a lighter, immiscible liquid such as xylene or oil. The effluent from the capillary is thus displaced downward towards the orifice. The dead volume within the tip can be reduced to a negligible quantity if desired by making the exit flow rate slightly larger than the capillary flow rate. It should be possible to use the same idea with an additional electrically conducting capillary for buffer solution to interface the droplet generator with a capillary gel or open tube electrophoresis apparatus.

W. B. Whitten, J. M. Ramsey,
K. C. Ng, S. Arnold***

*ORAU Faculty Research Participant,
California State University at Fresno

**Polytechnic University of New York

Advanced Techniques for the Chemical Characterization of Microparticles

The development of a three-dimensional quadrupole electrodynamic ion-trap mass spectrometer for characterizing levitated microparticles by laser desorption mass spectroscopy was continued. This trap has already achieved widespread use in the mass spectrometry community in the form of the ion trap mass spectrometer. Charged microparticles can also be levitated within the electrode structure of the trap in a manner analogous to the trapping of molecular ions. Our concept is to use the same quadrupole trap for microparticle levitation, laser desorption of ions from the particle, ion trapping, and mass analysis.

For electrodynamic trapping, the applied voltage and frequency requirements for the trap are quite different for ions and microparticles. We chose, therefore, to first evaluate the laser desorption, ion trapping, and mass analysis process on microparticles

as they fall through the ion trap. This eliminated the immediate need for evaluating the requirements for switching from particle levitation to an ion trapping mode.

With our current experimental setup we can drop a microparticle into the ion trap under vacuum, hit it with a focused 532 nm Nd:YAG laser beam, and then trap and mass analyze the desorbed ions. We have performed this experiment with 50-μm iron and niobium microparticles and 125-μm silicon carbide particles covered with adsorbed quantities of quaternary alkylammonium and alkylphosphonium halides. Representative spectra are obtained for the quaternary salts and the metal particles.

The above results represent the first demonstration of laser desorption mass spectroscopic analysis of a microparticle in a quadrupole ion trap.

We are performing a series of experiments to determine the sensitivity of the method. At the time of this report our lowest loading of a silicon carbide microparticle has been with approximately 100 femtomoles of tetraphenylphosphonium bromide. This is estimated to be about 0.1 monolayer. The large signal-to-noise ratio obtained and the low laser power presently required indicates that the lower limit of detection has not been reached. We plan to continue the sensitivity experiments to determine the detection limit.

During this period the experimental equipment was disassembled for modification. The electrical connections to the ion trap and the channeltron detector were replaced with small shielded cables to eliminate rf pickup. This had been creating an unacceptable background in the detector output and was appearing as anomalous peaks in the mass spectra. A new rf shield was also installed for the connection from the rf coil to the ion trap. Two new transducers were installed in the vacuum system for pressure monitoring of the helium buffer gas.

An electron gun assembly was designed for calibrating and tuning the ion trap. The electron gun assembly is installed in the top cap of the ion trap and is easily interchangeable with the microparticle dispenser. The electron gun, controlled by the ITD electronics, produces energetic electrons for ionizing a standard compound for trap calibration and tuning.

We had previously demonstrated that we can electrodynamically levitate a 25-μm polystyrene microparticle in the quadrupole

ion trap in a vacuum. The particle was first trapped at atmospheric pressure to take advantage of the damping effect of the air molecules on the particle. This was followed by evacuation of the trap chamber while holding the trapping voltage below the electrical breakdown potential. This prevents a glow discharge which will expel the particle from the trap.

We have yet to demonstrate the laser ablation and mass analysis of a levitated microparticle. It may be easier to switch from a particle levitation mode to an ion trapping mode if the microparticle is levitated quasi-electrostatically as opposed to electrodynamic levitation. We plan to demonstrate microparticle levitation under quasi-electrostatic conditions in an evacuated ion trap.

J. M. Dale, W. B. Whitten, J. M. Ramsey

Fundamental Studies of Chemical Vapor Deposition Materials Growth Processes

Chemical vapor deposition (CVD) methods have become increasingly important for the manufacture of technologically significant thin films. The growth of polycrystalline diamond thin films from light hydrocarbons has recently generated great interest, and several U. S. and foreign manufacturers have already begun to market products.

There is generally little understanding of the detailed chemical mechanisms that occur in these CVD growth processes. A more thorough understanding of the chemistry - both gas phase and surface - could, however, lead to higher quality films or films grown at process conditions (e.g., substrate temperatures) that are less severe. Along with staff from the Metals and Ceramics Division and Fusion Energy Division, we are developing spectroscopic and materials characterization techniques to foster a more fundamental understanding of thin film deposition methods. We have now completed the second year of a three-year Director's R&D Fund project.

The diamond film growth results reported here were obtained using our hot filament reactor in which a reactant gas (1% methane in hydrogen) is activated at a 2000°C tungsten filament situated approximately 5 mm above a substrate (single crystal silicon). We have recently demonstrated orifice sampling through the

substrate into high vacuum for time-of-flight mass spectroscopy for examination of the boundary layer gases immediately above the growing film. Acetylene and methyl radical have been detected. The apparatus constructed for these experiments was described last year. The only change has been that the fragile quartz capillary nozzle was replaced with a removable ceramic nozzle with a 340 micron orifice diameter.

The reactor was filled with the reactant gas mixture at 2660 Pa for orifice sampling experiments under diamond growth conditions. The resulting gas composition in the boundary layer above the substrate was followed using time-of-flight mass spectrometry. Electron impact (EI) ionization was used to ascertain the full mass spectrum. With the reactor filament at room temperature, mass peaks due to methane and its EI fragments were seen. No mass signal was seen at m/z 26. When the reactor filament temperature was raised to 1970°C, the strength of the mass peaks due to methane and its fragments decreased greatly and a new signal, corresponding to acetylene, appeared at m/z 26. Acetylene is often cited as important carbon transport and growth species in diamond growth. This result clearly shows that acetylene is present in the boundary layer gases above the hot substrate.

Using laser diagnostic, resonantly enhanced multiphoton ionization (REMPI) spectroscopy, we have detected the presence of methyl radical in the sampled boundary layer gases with the reactor at normal diamond growth conditions. As in the case of acetylene, methyl radical is suspected to play an important role in diamond film growth. A known 2 + 1 REMPI process at 333.5 nm was used to ionize the neutral radical in the extraction region of the mass spectrometer. A 10 ns Nd:YAG-pumped dye laser doubled to near 333.5 nm with 12 mJ/pulse was used for optical excitation. It was focused with a 200-mm lens yielding approximately 7 GW/cm^2. Detuning the laser wavelength by 0.2 nm to either higher or lower values extinguished the m/z 15 signal from methane. This detection method is thus highly selective, due to both the optical and mass discrimination.

Additional diagnostic techniques need to be pursued and applied to diamond growth reactors before the chemistry of the growth process can be fully understood. Chemical species maps throughout the entire reactor as a function of operating parameters would be invaluable. Surface nonlinear optical methods - frequency doubling and sum

frequency generation - are under development for surface spectroscopy of growing films. Due to their nonintrusive nature, laser spectroscopic methods will play an important role as reactor diagnostics.

R. W. Shaw, W. B. Whitten, J. M. Ramsey

Resonance Ionization Mass Spectrometry

Tunable diode lasers offer many attributes that can be applied to the analysis of materials. These lasers are relatively inexpensive, simple to operate, possess very narrow bandwidth (< 50 MHz), and can be tuned over their operating range (10-15 nm) by variation of temperature and current. We have expanded our study of diode laser-assisted resonance ionization mass spectrometry (RIMS) to a study of dysprosium. This element is being investigated for several reasons. It will demonstrate the general applicability of the technique with a different atom. Dysprosium has both even and odd isotopes (amu of 160, 161, 162, 163, 164) so we can undertake a variety of spectral studies. There are several potential optical routes that involve two or more consecutive transitions in the diode laser tuning ranges that have been seen in emission. With the use of a diode laser, we have been able to promote the transition from the ground state to 13496 cm^{-1}; ionization was achieved using a 1+1 process from that level using either a Nd:YAG laser-dye laser system tuned to 434.8 nm or the copper vapor laser (CVL)-dye laser system tuned to 580.6 nm. It is of note that the RIMS process is much easier to accomplish with the CVL-dye system; we believe this is because of the higher repetition rate of the latter system, 6000 vs 10 pps, and the lower single color background ion count generated using the latter system. Isotopic selectivity of the diode laser-assisted RIMS has been qualitatively observed. By varying the wavelength of the diode laser, one can easily enhance the ion signal of Dy-160, 162, or 164; it is apparent that some ion signal from Dy-161 and 163 is also obtained indicating that the hyperfine structure of these isotopes with nuclear spin extends to near the energy positions of the zero nuclear spin even isotopes. It is assumed that the current observed effect is affected by the relatively high power of the diode laser, ~ 1.5 mW, and the large bandwidth of the CVL-dye laser, 30 nm. In lanthanum, our best isotopic selectivity was observed with diode laser powers of $\leq$ 100 μW and CVL-dye laser bandwidth of approximately 3 nm.

Over the tuning range of rhodamine 6G (R6G) in the CVL-dye laser system we have observed a number of wavelengths where one or two color routes to ionization occur. It appears that amplified spontaneous emission (ASE) may play a role in many laser excited routes to ionization. In the study of dysprosium, for example, we have found a number of single laser ionization routes (with only the CVL-dye laser tuned in the R6G range). A few have been demonstrated to be also single color. The other dysprosium ionization routes, however, appear to be 1+1 single color processes from excited levels at 17607 or 17707 cm^{-1} which lie in the center of the broad ASE emission and are populated by that emission. This is not surprising when it is realized that such bound-bound transitions do not require much power, $< 50\ \mu W$ in the case of earlier studies with lanthanum. We had, in fact, suspected ASE involvement in earlier single color studies of lanthanum, uranium, and other elements; the dysprosium case is one where we have the most concrete evidence for the effect.

We have not yet been able to demonstrate a two-diode laser assisted RIMS route to ionization. Such a process would involve, for example, two consecutive transitions pumped by two CW diode lasers followed by ionization with another laser. In this experiment, a forerunner to more complex processes, we are essentially sampling the population of a second intermediate level we have populated by the diode lasers. Work on this demonstration continues.

We have completed the study of diode-assisted RIMS of lanthanum. The study of the isotopic selectivity of this process has been refined. Although the selectivity factors did not change much from that reported in the last annual report, it has been demonstrated that we are limited by the statistics of the low count of the unwanted isotope. An ion counting system of greater dynamic range would be required to measure the true isotopic selectivity in this special case where both isotopes exhibit hyperfine structure and the corresponding hyperfine spectra overlap. It had been postulated that a pedestal effect, a relatively broad emission of the diode laser under the very narrow lasing emission, was limiting our isotopic selectivity; no evidence for such a pedestal effect was found in studies this year.

R. W. Shaw, J. P. Young

Document Tagging for Authentication Purposes

Over the past several years we have been developing a technique for the authentication of documents. The technique has application to any situation where a paper (or plastic) document requires authentication. Examples include currency, passports, and other important items where authenticity is an important issue. The basic concept is to use some characteristic random variable contained in the document as a signature for identification. This signature is read after document preparation and is either archived or encrypted and included with the document in some fashion. When authentication is required the signature is again read and compared with the encrypted or stored information. We are implementing this approach using special tags (dichroic fibers) that are included in the paper at production. The random distribution of these fibers in paper and their special properties give a unique signature that is virtually impossible to duplicate. Initial studies have been performed to confirm detection of the tags in paper. Our present work involves further feasibility studies to determine the viability of this approach.

Work over the past year has been theoretical in nature. We have developed computer codes to synthetically generate images of fibers that closely imitate those observed in papers containing the fluorescent fibers. The computer generated images facilitate the development of algorithms for confirming authentication and extracting fiber images from background signals.

The image generation consists of three stages. First, binary images (two intensities) are generated that contain a specified number of fibers placed on a uniform background. The fiber characteristics are determined using a random number generator. Two types of fibers can be generated: straight or curved fibers. A random number generator determines the angular orientation and length of the fiber. The fibers are actually determined as line segments, and the random number generator controls line orientation, length, and placement of the fiber in a plane. Curved fibers are produced using the random number generator to specify the radius and arc length.

By changing the seed for the random generator an arbitrary number of images containing a specified number of fibers that differ in placement, orientation, and length

(within a specified range) can be generated.

The second task is to turn the binary image into a gray level image where fibers have different intensities and possibly thicknesses. The fiber intensity can be made to vary due to different phenomena. Random variation can be added to mimic manufacturing imperfections or deterministic variations can be added to account for the dichroic nature of the fibers and the nature of the image collection optics.

The third task in generation of synthetic images is to produce a background signal similar to that experimentally observed. The background observed with laser excitation is largely due to speckle type spatial variations in intensity, i.e. random interference patterns from the various sources of scattered laser light reaching the document being illuminated. Such a textured background is generated using long-crested wave models. In these models, the choice of amplitude, frequency, phase, and number of waves allows generation of texture background with varying coarseness and intensity distribution. The changes in coarseness are useful for simulation of images acquired with various resolutions.

The codes to generate these synthetic images have been developed and tested. Images can be generated that simulate experiment to a high degree by appropriate adjustment of input parameters. The synthetic image generation capability will be used for testing fiber image extraction algorithms and authentication codes. Synthetic image generation allows these codes to be tested with deterministic data, thus facilitating diagnosis of code failure. In addition, extremely large image data bases can be produced inexpensively using this capability.

J. M. Ramsey, D. Brzakovic[*]

[*] University of Tennessee, College of Engineering

In-Line Sensors for Electrolytic Magnesium Cells

The purpose of this project, jointly funded by DOE Office of Industrial Processes and Dow Chemical Company, is to develop magnesium ion and fluoride ion sensors to be used for continuously monitoring the concentration of these ions in magnesium electrolytic production facilities. The sensors will be evaluated in Dow-type molten salt mixtures ($NaCl$-KCl-$CaCl_2$-$MgCl_2$, 35-35-15-15 mole %) at 700 to 800°C, but the final sensors should also work in other

magnesium process melts. The continuous monitoring, and control, of the concentration of the above ions is expected to decrease the energy consumption of the electrolytic reduction process by more than five percent.

A description of the sealed IR reflectance cell mentioned in the last annual report has been published. We have found this cell to be very useful in identifying hydroxide concentration in various salt-component purification processes we are studying. The analytical technique is applied to solids, and the samples are loaded in an inert atmosphere box. By the use of a ZnSe window in the cell, we have also found the cell useful for identifying oxide contamination in melt components. Oxide exhibits an absorption peak near 780 cm^{-1} that can be utilized in this analysis. The cell has proven very useful; another group at the University of Tennessee is using the cell to study the carbonyl group in organics on catalysis beads; these samples are hydroscopic.

Further Raman spectral studies of magnesium species, $MgCl_4^{2-}$, in molten NaCl-KCl-$CaCl_2$-$MgCl_2$ have been carried out. Data for the change in Raman intensity as a function of Mg concentration from 2 to 20 mole percent, in two different salt mixtures at approximately 720°C, were obtained. Adequate sensitivity was available to determine a change in concentration from 5 to 20 mole percent Mg in these melts. The Raman signal from $MgCl_4^{2-}$ essentially doubles as the concentration of the species varies from 9 to 15 mole percent. Further compatibility studies of transparent materials to the Dow-type melts have been carried out. Although diamond, Al_2O_3, and SiO_2 appear reasonably compatible to the melt at 750°C for short periods of time (perhaps days), addition of CaF_2 (1 wt %) or products of H_2O cause the melt to become very corrosive to SiO_2. It appears that any optical probe device to be designed for lag-term compatibility in the electrolytic melt will need to be protected by a diamond window. For shorter term studies in melts devoid of fluoride ion, silica containers and silica fiberoptic probes can be used.

Development of a probe for Raman spectral measurements of $MgCl_4^{-2}$ is under way. Various designs of a probe made from three silica fibers of 600 μm dia. have been tested. The spectra of $MgCl_4^{-2}$ are easily seen on top of a small background Raman signal generated within the fibers. As stated above, we plan to use a diamond window in the final probe assembly for chemical compatibility and the silica Raman signal is more pronounced when configuring the

fiberoptic probes with a diamond window interface.

The diamond window exhibits a Raman signal at 1330 cm^{-1}, far removed from the $MgCl_4^{2-}$ peak, so the diamond peak can serve two other purposes. It can be used as an internal standard for quantitative measurements. We demonstrated that both diamond and $MgCl_4^{-2}$ spectra can be obtained simultaneously. It was also found that the ratio of the Stokes/anti-Stokes Raman signal of diamond can serve as a temperature measuring device over the temperature range of 100°C to at least 1000°C, and probably higher in the proper environment. Such a temperature sensing device should have applications here and in other areas. Two patent disclosures have been submitted regarding fiberoptic probe design, and a paper has been written describing the diamond temperature sensor.

It is expected that the fluoride ion monitor will be of an electrochemical type. Electrochemical studies have been initiated on the NaCl-KCl-$CaCl_2$ portion of the anhydrous simulated Dow melts with and without $MgCl_2$ added. A cell has been designed and fabricated to perform these studies. Cyclic voltammograms (CV) have been obtained on both the above background solvent and the magnesium-containing molten salt solution. The CV for magnesium reduction has been obtained at tungsten, platinum, or glassy carbon electrodes. The most useful CV's are seen at a tungsten electrode. As expected, there is no evidence for alloy formation at tungsten. Addition of $MgCl_2$ to the melt caused an increase in the peak height for the reduction waves on both platinum and tungsten. Addition of $MgCl_2(H_2O)_2$ also produced an increase in the reduction wave at platinum plus a second small cathodic wave at -0.95 V versus a platinum quasi-reference electrode.

J. P. Young, Gleb Mamantov,*
*T. R. Mueller, Sheng Dai**,*
*J. E. Coffield***

*Department of Chemistry, University of Tennessee, Knoxville

**UT/ORNL Science Alliance Program

Modifications of the Quadratic Potential Time-of-Flight Mass Spectrometer for Positron Stimulated Desorption Studies

A new type of time-of-flight spectrometer has been constructed and put to use in studies of ionization process of large molecules by slow positrons. The

operating principle and application results were reported in the 1990 annual report. The quadratic accelerating potential causes the flights of the ions to the detector to assume the same equations of motion as those for harmonic oscillators. Ions further away from the detector are subjected to a higher acceleration potential than those that are closer, such that the flight times are approximately independent of the distances of the ions from the detector. This enables the spectrometer to use sources of ions that are extended in length. For the positron ionization studies a Penning trap source, 10 cm in length, was used. Remoderated positrons, having energies ranging from thermal to as high as 10 eV, could be captured and retained in the Penning trap for periods in excess of 0.1 s. The collision path lengths of the positrons with molecules present in the trap were extremely long. After allowing ionization to occur in the Penning trap the ions were pulsed out for TOF measurements by raising the potential distribution in the trap to the quadratic configuration.

The quadratic potential TOF mass spectrometer has been restructured in preparation to perform positron stimulated desorption spectroscopy. The Penning trap has been modified to allow the insertion of a grid in the field-free region between the input and output grids. Positrons will be remoderated and captured in the Penning trap where they will make repeated passes through the grid in the field-free region. Ions that are produced by collisions of the positrons with the grid will then be pulsed out for TOF measurements of their masses. In the Penning trap the positrons will have energies ranging from 1-10 eV. After times of three microseconds or less they will have made at least 20 trips through the 90% grid and will be almost totally consumed. During this time the desorbed ions will have traveled less than 0.5 cm from the grid, and should still be residing in the trap when the TOF pulse is applied. We calculate that this technique should make full use of the available positrons and be highly efficient for collecting and metering the ions produced.

*L. D. Hulett, Jr., Jun Xu**

*ORAU Postgraduate Research Program

The Design of a High Intensity ^{79}Kr Slow Positron Facility

Present sources of monoenergetic (slow) positrons, based on electron linear accelerators, can produce as much as 1 E+8 slow positrons per second. This amounts to a current of the order of 0.01 nanoampere. We use the nanoampere unit for convenient comparison to currents from electron microscopes and other electron spectroscopy devices. Electron microscopes use electron currents in the range of 10-100 nanoamperes. Positron microscopy is becoming a very important application of slow positron beams, and it is highly desirable that currents comparable to those of conventional electron microscopes be made available in order to achieve the same degree of resolution. Another very important application, entirely unique to positrons, is ACAR (angular correlation of annihilation radiation) spectroscopy. The ACAR method and positron microscopy will be discussed further in the following sections. Recently, an offer was made by a Bell Laboratories-University of Texas team to finance, build and install a high resolution ACAR spectrometer at ORNL. This offer required that ORNL first construct a ^{79}Kr source at the High Flux Isotope Reactor (HFIR) that would supply a slow positron current in excess of 1 nanoampere.

The suggestion for using a nuclear reactor to supply ^{79}Kr as a source of slow positrons was first made by A. P. Mills of AT&T Bell Laboratories to the Committee for the Advanced Neutron Source (ANS). Mills pointed out how such a facility could enable the ANS to supply both the highest available slow positron current (>100 nanoamperes) and the highest neutron flux. In response to this suggestion, calculations and preliminary planning have been started at ORNL to consider building a proof-of-principle facility which would make use of the HFIR, which is presently operating. Until the ANS is built, the HFIR facility will serve as the most intense slow positron source in the world (1-10 nanoamperes) as well as a proof-of-principle experiment.

The HFIR/ANS slow positron facility will employ a loop containing isotopically pure ^{78}Kr. The krypton will be cryogenically pumped into an irradiation bulb in the beryllium shield of the reactor, where it will be activated to the ^{79}Kr isotope. The primary mode of decay of this nuclide is electron capture, but about 7% of the events result in positron emission. Half life is 35 h. After the krypton has been activated to near-saturation it will be pumped out of the

reactor core and condensed in a cryogenically cooled cup. Slow positrons emitted from the cup will be accelerated and focused onto brightness-enhancement films. Calculations indicate that the resulting brightness-enhanced beam will be less than 1 cm in diameter and be greater than 1 nanoampere in intensity.

To allow the positrons to escape from the cryogenically cooled cup, the ^{79}Kr must be dispersed as a film, less than 200 μm thick, inside the cup. Total current of obtainable positrons is proportional to the area of the cup. Therefore, the linear dimensions of the cup, and the linear dimensions of the electron optical components required to focus and transfer the positrons coming from the cup, become proportional to the square root of the desired slow positron flux. About 0.1 mole of ^{78}Kr is required to obtain a slow positron current greater than 1 nanoampere. This will require that the cup have a diameter of 6 cm and a length of 12 cm. Solid krypton is an efficient positron moderator. Provisions will be made, however, to condense solid neon on top of the krypton film, if necessary, to achieve the required efficiency of moderation.

The initial beam coming from the cup will be 6 cm in diameter. This will be accelerated and focused with a specially designed lens which uses the "Soa" optics technique. To minimize spherical aberration, the diameter of the main Soa lens will have to be at least 12 cm, twice the diameter of the cup. The beam coming from the cup will be condensed to 1 cm in diameter onto a brightness enhancement film. Production of microbeams will be done by additional stages of brightness enhancement.

A symposium was held in October 1990, at the Materials Research Society meeting in Boston, on the uses of high intensity slow positron beams. A paper describing the above facility was submitted.

L. D. Hulett, Jr., D. L. Donohue

A Design for a Positron Specimen Imager

Positron beams will soon be used semi-routinely for microanalysis. This will require that the beam be focused exclusively on the micro specimen, otherwise, background signals will make the data uninterpretable. From experience gained with the scanning electron microscope, we know that the most effective way of insuring that the electron beam is focused on the specimen is to use

the beam to image the specimen while the analysis is taking place. For example, in the use of electron-induced X-ray fluorescence to analyze a small particle, the microscopist will simultaneously project a secondary electron image of the particle on a cathode ray tube as the X-ray spectrum is collected. In this manner the microscopist is able to visually monitor the area that the electron beam is striking and confirm that the beam is not straying to background objects.

Positrons striking solid material induce secondary electron currents of the same order of magnitude as those produced by electron beams. Therefore, a technique similar to that of the scanning electron microscope can be used to image small specimens with a positron beam. Given a positron current of the same magnitude as that available from electron guns, the achievable magnification will be as high as that from the scanning electron microscope. The positron current that will be available from the HFIR slow positron source is expected to be 1-10 nanoamperes, however, which is somewhat lower than that used in electron microscopes. The secondary electron current will be proportionately smaller, causing the achievable magnification to be probably no higher than 100-500X. For this reason we will refer to the device as a 'positron imager', rather than a 'scanning positron microscope'. The 100-500X magnification will be adequate, however, for a large number of applications. Eventually, the Advanced Neutron Source will be built and equipped with a positron source that will output positron currents in excess of 100 nanoamperes. The routinely achievable magnification for this facility will be as high as that from conventional scanning electron microscopes.

A second paper, describing the above design, was also submitted to the proceedings of the positron symposium of the 1990 Materials Research Society Meeting.

L. D. Hulett, Jr., D. L. Donohue

Plans for a High Resolution ACAR Spectrometer

Considerable consultation and planning have taken place between ORNL and workers at AT&T Bell Laboratories and the University of Texas, Arlington, on the possibility of attaching a high resolution spectrometer, that will measure the electron momentum distributions of solids, to the

HFIR positron source. Recently the University of Texas group published some spectacular results for the electron momentum distributions in the 123 YBCO superconductors. Evidence for the existence of a Fermi level has been obtained. This type of information is extremely important for determining the mechanism of the superconducting phenomenon.

Electron momentum distributions of solids and other materials can be measured by the ACAR technique. The spectrometry principle involves the law of conservation of momentum. When a thermalized positron annihilates with an electron, the momentum of the electron is transferred to the two 511 keV gamma photons that are produced, causing them to depart from each other at an angle less than 180°. If the electron has no appreciable momentum, the two gamma rays depart at 180° from each other.

An ACAR spectrum is collected by placing the specimen of interest between two position sensitive detectors. The detectors are spaced large distances (5-20 meters) on either side of the specimen. As the positrons annihilate with the electrons, the emitted gamma photons are registered in coincidence by the two detectors. For each coincidence event the detectors measure the angle between the directions of departure between the two photons. The angles of departure are directly proportional to the electron momentum components that are normal to the axis of the two detectors. In this manner the momentum spectrum of the electrons moving in the crystallographic plane that is perpendicular to the axis of the two detectors is measured. To acquire momentum spectra for the other planes the crystal is rotated with respect to the detectors.

L. D. Hulett, Jr., A. P. Mills, Jr.,*
*R. N. West***

*AT&T Bell Laboratories
**University of Texas, Arlington

SECONDARY ION MASS SPECTROMETRY

W. H. Christie

This group conducts research in both organic and inorganic secondary ion mass spectrometry (SIMS) and provides specialized analyses that require the unique capabilities of the SIMS technique. The CAMECA IMS-4f ion microscope/microprobe, installed during the last reporting period, has been used to address some interesting problems, several of which are discussed in the following paragraphs.

Inorganic SIMS

The Human Genome Initiative has stimulated considerable research activity at ORNL. Workers in the Biology Division have developed methods for labeling unique DNA fragments with a variety of chemical elements. By utilizing mass spectrometry, many elements and each of their isotopes are candidates for such labeling. Current methods for DNA sequencing are limited by the radioisotopes that are available as labels, and only ^{32}P and ^{35}S are utilized effectively. In a typical separation scheme the labeled DNA fragments undergo gel electrophoresis and the various fragments appear as distinct separated bands on the gel. Since the bands can be quite narrow (~ 50 μm) and show small separation, microbeam SIMS offers the possibility of detecting the label from a specific band because of the high lateral resolution offered by the microbeam. In collaboration with workers in the Biology Division, we have studied a series of Eu standards in Agarose to ascertain the utility of SIMS as a detector of labeled DNA fragments. The standards were prepared in the Agarose medium (1%) to simulate the presence of a biological matrix. In one of the SIMS studies, 125 μl of 10^{-7} Eu in Agarose were spread over a 2 cm diameter spot on a glass plate. This gave a total of 1.25×10^{-11} moles of Eu spread onto the spot. A 250 μm raster would contain 0.0002 of the total sample or 2.5×10^{-15} moles of natural Eu. In this study a 10 nA O_2^+ primary beam gave a $^{153}Eu^+$ signal of 300 c/s for about 4000 seconds from the 250 μm rastered area. A mass resolution of about 1500 was used to separate the Eu^+ signal from organic fragments of the same nominal mass number. Both isotopes of Eu were detected and the nominal ratio for natural Eu was observed, serving as a check that the

correct peaks were being monitored. The signal-to-noise ratio was better than 10:1. About 8 x 10^8 atoms of ^{153}Eu were present in the rastered area, and a total of 1.2 x 10^6 ions were detected for an overall efficiency of about 0.15%. Similar studies of Sn standards in Agarose were less successful because of the lower ionization efficiency of Sn compared to Eu. In an attempt to improve the efficiency, we tried low temperature ashing (atomic oxygen) as a means of eliminating the organic matrix and possibly improving the signal-to-noise ratio. Our first attempt met with mixed results. We were able to eliminate the organic material, but the sample was significantly contaminated with inorganic material. This probably occurred because an old asher that was dirty was used. Future experiments will center on solving this asher contamination problem. The prospects for using SIMS as a rapid easy means for detecting labeled DNA fragments looks promising.

W. H. Christie, T. M. Rosseel

Chemical Characterization of Microparticles

In collaboration with workers in the Optical Spectroscopy Group, we have used SIMS to provide a benchmark for the chemical characterization of microparticles using laser ablation mass spectrometry (LAMS). In this work four sets of silicon carbide particles (nominal size 100 - 300 μm) coated with 5 - 20 monolayers of either a quaternary ammonium or phosphonium salt were examined using the CAMECA IMS-4f microprobe. Samples were prepared by embedding particles in an indium planchet. Each set of particles was analyzed with a 12.5 kV O_2^+ beam for positive ions and a 10 kV Cs^+ beam for negative ions. The oxygen beam was limited to 100 pA in a 250 x 250 μm raster spot to minimize charging and to conserve sample due to the low film thickness. The parent cations of the three quaternary ammonium salts (trimethylphenylammonium chloride, triethylphenylammonium iodide and tetrabutylammonium iodide) were readily observed because they exist as "preformed ions" on the SiC surface. In fact, a depth profile of tetrabutyl cation (m/e = 242) produced a detectable signal for over 800 s using a 15 pA O_2^+ beam. Because the

tetraphenylphosphonium cation mass exceeds the mass range of the spectrometer, it was not observed. In addition to the parent cation, fragment ions of the quaternary salts were also observed. For example, we observed the loss of CH_4 and benzene from the trimethylphenylammonium cation as well as the methyl and phenyl ions. Similarly, we observed the loss of C_4H_{10} from the tetrabutylammonium cation. The triethylphenylammonium, however, produced both ethyl and propyl loss fragment ions, with the propyl loss having the greatest intensity. In contrast, the tetraphenylphosphonium cation produced intense fragment ions for only the loss of two and three phenyl groups.

Because of the ease of detection of these quaternary salts by SIMS, these data will provide a benchmark for the chemical characterization of microparticles using laser ablation mass spectrometry.

T. M. Rosseel, W. H. Christie

In-situ Micromeasurement of Isotopic Ratios

Microprobe ion beam techniques (e.g., the CAMECA IMS-4f) offer the possibility of in-situ measurement of isotopic ratios of minerals with the spatial reduction of several microns. The SIMS technique offers many advantages, if adequate precision and accuracy can be obtained. Conventional mass spectrometry requires the tedious selection and separation of several milligrams (1-10) of material, which results in a loss of any potential textural and spatial information. In contrast to conventional techniques, the ability to analyze small spots (2-10 μm spatial resolution) using SIMS techniques would represent a reduction of 10-11 orders of magnitude in sample size, with no need to prepare mineral separates.

Our first studies have been done on the mineral magnetite (Fe_3O_4). We have used a slightly defocused Cs^+ microbeam of 10-20 μm diameter to analyze oxygen from a number of points in several grains of the same magnetite standard. The nominal $^{16}O/^{18}O$ ratio is ~ 485, which dictates that the minor isotope (^{18}O) be measured for longer times as compared to the major isotope in order to optimize counting statistics. We accumulate at least 10^6 counts of ^{18}O to

provide a statistical precision of ~ 0.1% or 1 per mil on the ratio (as compared to ~ 0.2 per mil using a gas source mass spectrometer). This requires a total data acquisition time of ~ 45 minutes per analysis. Successive ratios taken from different points on the standard showed an external precision that was approximately equal to the internal precision (1 per mil) over a ten-hour period on several different days. This was somewhat surprising, as it demonstrates that we are operating at the statistical limit and that better data will only come via accumulation of more counts and extension of the statistical limit, which we are continuing to investigate. Our data compare favorably with that of Drs. John Valley (University of Wisconsin) and Colin Graham (University of Edinburgh) who are the only other workers to demonstrate the ability to obtain high precision (~ 1 per mil) oxygen isotope measurements in minerals using the ion probe. Dr. Valley visited our lab and we look forward to a continued fruitful collaboration with him in this area.

The goal of this work is to use the ion microprobe to study small-scale isotopic variations in minerals from natural samples. Isotopic variations yield important information regarding the temperature and mechanisms of mass transfer in fluid-solid interactions, as well as the type of reactions that occur at the mineral-fluid boundary. Species can be transported over great distances in geologic systems, but the actual chemical exchange processes occur at solid-fluid interfaces over micron scale distances. The ability to discern chemical and isotopic changes over small scales is particularly important in studies of low temperature systems (e.g., petroleum-containing sedimentary basins, groundwater interaction), as equilibrium between the bulk solid and fluid species is probably never attained. The record of the fluid-solid interactions are only preserved at or near the mineral surface. These studies will provide important new insights into the mobilization and transport of toxic, radioactive, and organic contaminants in soils and groundwater - issues that are central to waste management and environmental restoration programs. Small-scale isotopic zonation in minerals will also give information about the development of porosity and permeability and types of fluid flow in sedimentary basins, which has important implications in the exploration and exploitation of petrochemical resources.

L. R. Riciputi, W. H. Christie*

*UT Postgraduate Research Program

Digital Imaging for Particle Characterization

A digital imaging interface and software upgrade, obtained from Charles Evans and Associates, is being evaluated as a tool to improve our ability to characterize particles. The upgrade provides the capability to acquire scanning ion images for subsequent image processing and pseudo-color display. Our initial evaluation of the digital imaging software for particle analysis mimicked our previous "analog" procedures, i.e., images of individual elements or isotopes are produced using a fixed raster size and variable collection times. Unlike analog image collection, digital imaging allows us not only to enhance the analog output with an intensity coded color image, but also to process the image data (pixel coordinate versus intensity). For example, line scans of individual particles have been obtained and could be used with relative sensitivity factors to obtain semiquantitative analysis of the particles. Images of selected isotopes and/or elements can also be convoluted to provide images of only those particles having a selected suite of isotopes or elements of interest. Subsequently those particles can be analyzed with a complete mass spectrum or depth profile of the selected isotopes. The software can also be used to measure up to 14 elements or isotopes as the sample stage moves in a two-dimensional pattern. These maps of signal intensities of isotopes measured at each stage's position provide visualization of particle variability across a large sample area.

Our initial results indicate that in addition to the enhanced ability to communicate results with pseudocolor images, digital imaging greatly reduces the time needed to collect data by combining some of the data processing with image collection time. Because photographs often must be re-shot to obtain the optimum intensity and contrast, digital imaging has the added advantage of reducing beam damage to the sample. Future work will emphasize the two-dimensional scanning features which should reduce the time needed to select particles or regions for detailed analysis.

Although secondary ion mass spectrometry (SIMS) is an extremely sensitive probe of surface elemental distributions, it is well known that complex sputtering and ionization processes dictate the use of empirical relative sensitivity factors (RSF) rather than theoretical models for quantitative SIMS analysis. In addition, because the secondary ion signal intensity exhibits a strong matrix dependence, sets of

standards are usually prepared and analyzed to bracket the expected concentration range. A typical quantitative surface analysis of industrially created particulate matter, for example, may require a body of RSF values for steel alloys. For these reasons, three stainless steel standards of varying amounts of Cr, Fe and Ni were analyzed with the CAMECA IMS-4f ion microscope/ microprobe. The three standards were embedded in an epoxy matrix, polished and pre-sputtered to remove surface impurities. Each standard was analyzed with a 3 nA, 12.5 kV O_2^+ beam rastered over a 250 x 250 μm area. To avoid edge effects, data were collected only from a 60 x 60 μm area. Data were also collected from several spots and compared for each sample. Variations within a standard ranged from 20% to nearly 50%. Of the major elements, Cr exhibited the largest variation. The goal of this effort is to ultimately produce digital images that contain quantitative to semi-quantitative concentration information.

W. H. Christie, T. M. Rosseel

Organic SIMS

Among the capabilities of secondary ion mass spectrometry is imaging ability. That is, compositional maps can be generated from the intensity of analyte-characteristic secondary ions as a function of position on the sample. Imaging SIMS has been employed for over twenty years in materials sciences. SIMS microprobes are very much like secondary electron microprobes except that for SIMS the ionizing and the analyzed particles are ions rather than electrons.

The main method of characterizing secondary ions is by mass-to-charge ratio. This works well for inorganic samples, but simple mass dispersion does not provide the specificity necessary to identify organic secondary ions. Many organic compounds yield secondary ions that have identical mass-to-charge ratios. With biological samples, which are complex mixtures, an additional stage of analysis must be performed, namely tandem mass spectrometry, or MS/MS. Tandem mass spectrometry involves first selecting ions on the basis of their mass-to-charge ratio, then inducing fragmentation and mass analyzing the daughter ions. The problem with MS/MS is that, in general, it is an inefficient process so that perhaps up to 99.99% of all ions generated are lost before

detection. Naturally, such inefficiency reduces sensitivity of the technique. Our efforts have been directed at making the combination of SIMS and MS/MS efficient, particularly when used for a microprobe.

We have, in fact, been largely successful, and have designed, constructed, and tested an organic ion microprobe that shows an overall efficiency of 25%. This efficiency was accomplished by maintaining careful control and focus of the secondary ion beam from formation to entrance into the first quadrupole of the triple quadrupole mass spectrometer. We found, first and foremost, that under computer control, and after computer optimization of our primary/secondary ion sources, we could obtain a collection efficiency for our ion source of nearly 100%. Furthermore, by keeping the image size of the secondary ion beam small (<200 μm) at the entrance to the first quadrupole of our triple quadrupole mass spectrometer, transmission through one quadrupole could be made to be as high as 50% with unit mass resolution - the theoretical limit.

It is well known that the majority of ion losses in triple quadrupole mass spectrometers occur at the interfaces between the quadrupoles, particularly between the second and third quadrupoles. In the characterization of the triple quadrupole mass spectrometer he invented, D. C. McGilvery deduced that the losses were caused because the beam spread as it exited one quadrupole to enter the next, either from ion optical causes or due to fragmentation. He proposed using successively larger quadrupoles. We found that by restricting the ion beam at the entrance to a quadrupole to about 200 μm, the beam exiting the quadrupole would be of the same size, and circular in shape, rather than cloverleaf. The consequence of this finding is that the beam entering successive quadrupoles is kept small and the transmission is kept high - about 50%. Furthermore, the finding is consistent with McGilvery's; instead of using larger diameter quadrupoles, we simply use a much smaller diameter ion beam.

Having improved the transmission of the organic ion microprobe by about four orders of magnitude, our present efforts are directed to enhancing the secondary ion emission of organic compounds from biological tissue samples. These samples pose special problems because they tend to be insulators, and the compounds in them are not necessarily in the oxidation state most likely to lead to secondary ion emission. Chemical modification of these samples will

thus be necessary, and this work is ongoing. For comparison purposes, we use glycerol and its solutions. Glycerol is well known as a "good" reference for SIMS because, as a sample, it emits a consistent spectrum of secondary ions.

A spin-off of the work done in interfacing the organic microprobe to AT-type computers has been development of methods and programs that can be applied to other systems. During this year, we have, in collaboration with others, interfaced AT's to different mass spectrometer systems to control automated sample introduction, purge and trap techniques, as well as file handling and alteration. Development of these application programs has resulted in a significant improvement in productivity for the instruments modified, typically of the order of 300%.

Peter J. Todd, R. Tim Short

ORGANIC MASS SPECTROMETRY

Gary L. Glish

The Organic Mass Spectrometry group has as a goal the advancement of the state-of-the-art in mass spectrometry. This involves development of instrumentation and analysis techniques, studies of fundamentals of gas-phase ion chemistry and physics, and demonstration of mass spectrometry techniques for chemical analysis. Much of the work is synergistic and overlaps into several categories. The major general areas of interest are: fundamentals of quadrupole ion trap mass spectrometry, MS/MS, direct ambient air analysis, and ionization processes.

Quadrupole Ion Trap Fundamentals

Over the last several years one of the hottest topics in mass spectrometry has been quadrupole ion traps. We have been involved from early on in this area with emphasis on both instrument development and application to chemical problems. This continues to be a major focus of the group.

Some of the attributes of the quadrupole ion trap include high MS/MS efficiency, the capability for multiple stages of mass

spectrometry (MS^n), high sensitivity, the capability for ion/molecule reactions, and relatively low cost. However, the Finnigan MAT ion trap mass spectrometer (ITMS) has unit mass resolution and a nominal upper mass/charge limit of only 650 when operated in the standard mass-selective instability mode for acquiring mass spectra. The performance of the ion trap can be enhanced by the application of a supplementary ac signal to the endcap electrodes. When the frequency of this signal is resonant with the secular frequency for a particular m/z, such ions can become kinetically excited and ejected from the trap via a process known as resonance ejection. By using the technique in combination with the mass-selective instability scan mode, a mass resolution up to ≈ 2000 can be achieved. The nominal mass range of the ion trap can also be extended above 30,000 by ejecting ions at a q_z value other than that corresponding to the mass-selective instability boundary.

We recently demonstrated the capability to generate mass spectra of electrospray-generated ions by scanning the frequency of the resonance ejection signal applied to the end-cap electrodes. We have now used the swept-frequency resonance ejection method to further enhance the mass resolution of the ion trap by slowing the frequency scan rate and reducing the amplitude of the resonance ejection signal. A mass resolution in excess of 50,000 has been demonstrated for the m/z 502 ion generated via EI of perfluorotributylamine (PFTBA). The technique has also been used to acquire high resolution data from ions generated via electrospray ionization and subsequently injected into the ion trap. Such experiments with bradykinin produced a mass resolution of 32,000 for the doubly charged molecular ion at m/z 531 ($C_{50}N_{15}O_{11}H_{75}$), thus enabling the isotopic peaks corresponding to the ^{13}C- and $^{13}C_2$- containing species to be resolved.

To understand the high resolution experiment in the quadrupole ion trap a theory has been developed using the pseudopotential well approximation of the Mathieu equation, with terms included to account for the effects of ion-neutral collisions and scan rate variations, to analyze the lineshape. Solution of the resultant time-dependent differential equation of motion for the center of trapped ion charge enabled us to calculate line shapes as a function of scan rate and collisional damping. We have also been able to analyze the resolution in terms of fundamental ion trap operating parameters including rf drive frequency Ω and q_z by derivation of the relationship between mass and frequency linewidths. The effects

of the experimental variables mass/charge, neutral pressure, and scan rates on mass resolution were also evaluated in terms of the model. The model predicts that the mass resolution for a given mass at fixed scan rate and damping can be improved by independently increasing q_z or Ω. Results also indicate an increase in ultimate mass resolution with higher mass/charge and lower neutral pressure but this requires lower scan rates to attain. For relatively high scan rates the mass resolution will be inversely related to mass/charge and scan rate and proportional to pressure. The large disparity in mass resolution between the linear quadrupole operated in the mass-selective stability mode and the three-dimensional ion trap employing resonance ejection can be rationalized in light of these results. Although ion motion in both devices is governed by the Mathieu equation, the factors which influence resolution are different. Resolution in the former depends on the range of mass/charge values having a_u and q_u values which produce stable ion trajectories during their passage through the quadrupolar field. Because such motion is related to the number of rf cycles during transit, the resolution is limited by the practical length of the quadrupole rods. Resonance absorption is the mechanism for mass/charge discrimination in the latter device. As a consequence, the resolution is a function of the scan rate and degree of damping. At relatively high scan rates the apparent linewidth is proportional to the product of scan rate and relaxation time, so that increasing the degree of damping or reducing the scan rate results in narrower linewidths. However, for sufficiently low scan rates the inherent linewidth of a harmonic oscillator becomes smaller as the damping decreases. Because the damping can be reduced to an arbitrary level by decreasing the pressure, this suggests that the resolution will be limited by ion residence times, space charge, and signal/noise considerations.

Other theoretical work concerning the quadrupole ion trap has involved the investigation of the effect of rf and dc voltages on the volume in which ions have stable trajectories and the implications of this on ionization strategies. To do this modeling the ion trap simulation provided with the SIMION ion trajectory software has been modified to more accurately model the Finnigan Ion Trap Mass Spectrometer. First, the potential array was generated using "cylindrical symmetry" rather than "planar symmetrical" symmetry so that the potential array represents a ring electrode and two

endcap electrodes. The simulation provided with SIMION actually models an ion trapped within a quadrupole (four rods) assembly. The simulation was also changed so that the endcaps are held at ground potential as is the case in the quadrupole ion trap. The equation which calculates the rf and dc voltages applied to the ring electrode for a given m/z, "a" parameter and "q" parameter was modified accordingly. Four user adjustable variables were added to the ion trap program to simulate the auxiliary rf tickle voltage that is used for collision-induced dissociation on the quadrupole ion trap. These variables set the tickle delay time (i.e., the elapsed time before the tickle voltage is applied to the endcap electrodes), the tickle voltage (i.e., the maximum voltage applied), the tickle time (i.e., the duration of the tickle), and the tickle frequency (specific for a particular q value and thus a particular m/z). The SIMION program itself requires modification so that tickle times in the tens of milliseconds can be investigated. An iteration counter within the SIMION program is exceeded after about 0.5 to 1 millisecond and the program terminates. Axial and radial path lengths for ionization are being calculated using the new ion trap simulation. These path lengths represent the distance (centered at the center of the ion trap) where ions can be formed from neutral molecules (with thermal energy) and still be effectively stored in the trap. For example, ions formed in the vicinity of an endcap at the wrong rf phase will be lost from the trap. Experimentally we have measured relative ionization efficiencies with respect to ion trap parameters using both electron and photo ionization. Initially differences were noted between the two types of ionization as a function of the dc voltage. While it was thought that this might be due to the electric fields having an effect on electrons, it was found instead that it is due to the orientation of the ionizing beam, i.e., radially or axially through the ion trap. A decrease in relative intensity was also noted in the experiments when the rf was increased and no dc was used. This correlated well with calculations that showed that the effective pathlength of the electrons decreased thus decreasing the ionization volume.

Another area of fundamental study involving the ion trap is the ion internal temperatures under typical operating conditions in the quadrupole ion trap (i.e., when operated with bath gas pressures of up to ten pascals). We have approached this question by measuring the kinetics for desolvation of protonated water clusters and protonated methanol clusters. These clusters

are readily formed by electrospray ionization and can be studied in our electrospray/ion trap apparatus. Ion temperatures were found to range from 400-800 K depending upon conditions. In particular, we found an inverse relationship between ion internal temperature and bath gas pressure that has heretofore not been observed. The reason why this relationship was apparent in our studies is that the kinetics for cluster ion decomposition are highly sensitive to minor changes in temperature, unlike the "thermometer" reactions other workers have used to determine ion temperatures.

Another parameter that affects the "ion temperature" is the number of ions stored in the ion trap. A substantial effect on the rate constant of the reaction of $C_6H_5^+$ with methane has been observed when the number of ions in the trap during the reaction was varied. This effect is attributed to an ion experiencing an additional potential due to other ions in the trap. This leads to a higher maximum potential energy for the ions confined in the potential well of the trap. Since the trap is dynamic, the maximum (and average) kinetic energy of the ions also increases. The efficiency of the ion/molecule reaction increases because more collision partners collide with sufficient energy for the reaction to occur. The effect of the buffer gas on the rate constant of ion/molecule reactions in the trap is explained along similar lines. Since ions are cooled less at lower buffer gas pressures (i.e., there are fewer collisions), the maximum potential energy of ions confined in the potential well of the trap is increased. The "effective temperature" of these ions will then be higher and affect the rate of the temperature-dependent ion/molecule reaction.

D. E. Goeringer, K. J. Hart, S. A. McLuckey, K. G. Asano, G. L. Glish

MS/MS

The technique of mass spectrometry/mass spectrometry (MS/MS) and MS^n has long been an area of active research in the Organic Mass Spectrometry Group. We have continued our work in this with a variety of endeavors involving developing MS/MS based techniques for structure determination as well as the use of MS/MS for studies of gas phase chemistry.

We have continued the work in the area of MS/MS of multiply charged ions. One of the areas of interest is the determination of the charge of a product ion in the MS/MS

spectra of multiply charged ions which can be difficult when products from a single cleavage are not both present in the spectrum. This is often the case with peptides and proteins. We have demonstrated the ability to determine product ion charge states in the quadrupole ion trap by subjecting the ions to either proton transfer reactions or clustering reactions. Such experiments are difficult, at best, with beam instruments since they are MS^3 experiments and they require long reaction times. We have systematically studied several multiply charged peptides and proteins in reactions with 1.6-diaminohexane. These results have provided the first positive identification of multiply charged product ions and allowed us to make some deductions about the sites of protonation of these multiply protonated peptides. Similar studies of anions reacting with gas phase acids have been initiated.

We are interested in the possibility of obtaining structural information regarding the sequence of the oligonucleotide via MS/MS. Multiply charged anions are typically formed from oligonucleotides via electrospray. Surprisingly, no papers have yet appeared on the MS/MS behavior of these types of ions. We have studied several oligonucleotides of n = 4-8 and have found that the multiply charged anions derived from these compounds have several interesting characteristics under quadrupole ion trap MS/MS conditions. For example, we find that they fragment with very high efficiency to give structurally useful information and that both products from a cleavage generally appear in the spectra. The latter situation, which stands in contrast with that for multiply protonated peptides and proteins, simplifies product ion charge state determination. The application of MS^n experiments in the quadrupole ion trap appears to be very promising for these types of ions.

While MS/MS is routinely done in the quadrupole ion trap, there is still a poor understanding of the physical processes occurring during this experiment. We have therefore undertaken a study to gain a better understanding of MS/MS in the ion trap. There are several parameters that affect the MS/MS experiment. These include the q value, the amplitude and frequency of the resonant rf, the bath gas composition and pressure, and the number of ions in the ion trap. Perhaps just as important as these parameters are the physico-chemical properties of the ion undergoing resonant excitation. These properties vary for each ion structure and can have substantial effects

on the results of the MS/MS experiment. These results suggest that one can view the ion trap MS/MS experiment as a heating experiment with the products that are observed being dependant not only upon thermodynamic considerations but also kinetic stabilities.

Related to this latter point, we have studied the dissociation of some unsaturated oxygen containing cations in the ion trap and the QEB instruments. Such ions can have two potential isomeric structures, keto or enol. As neutrals the keto form is more stable but as ions the enol is generally more stable. Thus, after ionization, if there is sufficient internal energy and time, the keto ion can isomerize to an enol ion. This is what appears to happen with some C_4 and C_5 ketones in the ion trap. However, in the QEB, which has a time scale about three orders of magnitude faster than the ion trap, MS/MS experiments indicate that the keto form of the ions predominates.

In another related study of MS/MS in the ion trap, we have made comparisons of MS/MS results from the ion trap with those from the TSQ 700. One of the goals of this study was to determine if spectra obtained from other tandem mass spectrometers will be compatible with substructure identification rules generated using TSQ data. The results of this study indicate that the same CID product ions of phenothiazine compounds are formed in the quadrupole ion trap as in the TSQ when the TSQ is operated under single collision conditions. With only one exception, all of the major spectral features found in the rule to identify the phenothiazine substructure were observed in the quadrupole ion trap spectra of nine compounds containing the phenothiazine substructure.

Conversely, a key exception was found when multiple collision TSQ spectra were compared to quadrupole ion trap MS^n spectra. One of the major product ions of the m/z 198 parent ion of phenothiazine compounds is m/z 45 (HCS+). This product ion was not observed in any of the MS^n spectra of the m/z 198 parent ion on the quadrupole ion trap. One problem encountered in acquiring the MS^n spectra of this ion was the q value required to observe the m/z 45 product ion (approximately 0.20). This q value is rather low to efficiently obtain CID spectra (a value around 0.3 to 0.4 is preferable). To circumvent this problem, a photodissociation experiment was attempted using a Nd/YAG laser to excite the m/z 198 parent. The q value used for this experiment is much less critical. This experiment proved to be inconclusive

because photoionization of the neutral phenothiazine compound exceeded, by far, any photodissociation of the m/z 198 parent ions. The conclusion that can be drawn from these experiments is that the energy deposited and the timing of collisions in the ion trap differ sufficiently from those encountered in the TSQ to preclude some CID products ions from forming in the ion trap. Thus, substructure identification rules based on multiple collision TSQ spectra may not be as effective in predicting the presence of a substructure when using quadrupole ion trap MS^n spectra. The deciding factor will be whether the rule contains spectral features (e.g., CID product ions) that require conditions similar to those found on the TSQ in order to be observed.

In a study of gas phase ion chemistry, the utility of using ion/molecule reactions with neutral iodobenzene, followed by MS/MS on the products for ion structure determination, is being investigated. While formation of an even-electron ion and neutral radical is common for the ion/molecule reactions of radical cations, ion/molecule reactions involving even-electron reactant ions generally give even-electron product ions. One exception to this for even-electron reactant ions is when iodobenzene is the neutral reactant. With this compound the thermochemistry can often be favorable for the formation of the substituted benzene radical cation and I as products. For example, $C_2H_5^+$ reacts with iodobenzene to give ethylbenzene radical cation as the major product.

These experiments are being done with a quadrupole ion trap. The MS^n capabilities of the ion trap have been used to obtain kinetic data on these reactions. More importantly, the MS^n capabilities have been used to obtain structural information on the product ions. For example, $C_3H_7^+$ generated from isobutane forms propylbenzene radical cation when it reacts with iodobenzene. Subsequent MS/MS of the propylbenzene ion reveals that it is predominantly isopropyl, as expected, but that there is a small amount of n-propylbenzene also formed. With aromatic reactants such as phenyl and naphthyl cations, PAHs appear to be formed.

S. A. McLuckey, K. J. Hart,
M. J. Charles, M. R. Troutman,*
G. J. Van Berkel, G. L. Glish

*Summer Faculty Research Program,
University of North Carolina

Ionization

We have continued our work in the area of development and understanding of ionization processes. In addition to electrospray which is covered separately, we continue to study the glow discharge ionization of organics, and ionization processes in the quadrupole ion trap.

A new atmospheric-sampling glow discharge ionization (ASGDI) source that will permit fundamental studies of the discharge formation mechanisms and ion sampling process of organic species has been designed. An increased fundamental understanding of glow discharge ion formation amidst the free-jet expansion in the ASGDI is expected to lead to innovative design improvements that can enhance instrumental performance. Specifically, we would like to approach the sampling of the ASGDI source in an entirely different manner. Presently, the glow discharge is formed on the sampling cathode (front aperture) and becomes integrated into a free-jet expansion. The anode, which also serves as a skimmer (back aperture), is grounded typically and does not participate actively in the discharge formation or the ion-sampling process. In addition, skimming of analyte ions occurs far downstream where these species have undergone numerous collisions with background gases. The design objectives for this new source are threefold. First, skimming will be able to be performed at numerous axial positions before analyte ions have had time to interact with the background gas (i.e., skimming can be performed in front of the Mach disk). Second, the potential on the source vacuum-chamber walls will be able to be varied. As a result, the active anode will be the skimmer. Finally, both the source and mass spectrometer will be configured so that true ion-beam composition can be evaluated. To achieve this final objective the mass-spectrometer ion lens and detection system will be re-configured.

Overall, we are looking to exploit the role of the anode in both ion formation and extraction. Preliminary experiments on the current ASGDI indicate the extent over which the anode can influence ion sampling. For example, a nonconductive coating over the surface of the skimmer is believed to hinder negative ions from passing through the skimming orifice; faster moving electrons from the glow discharge will strike the nonconducting surface at a greater frequency than ions. As a result, the surface will charge negative and the plasma near the skimmer (ion sheath) will become positive.

Because sampling into the second stage is performed behind the Mach disk, ion velocities will not be greatly directed so as to pass efficiently through the skimming orifice. Consequently, negative ions will be repelled by the back aperture to some extent and attracted toward the positive region of the glow discharge.

We have undertaken several studies involving ionization in the quadrupole ion trap. Ion/molecule reactions of phenyl cations with neutral methane under normal methane chemical ionization (CI) conditions have been observed in the quadrupole ion trap. These reactions lead to unexpected ions in the spectra which may lead to erroneous interpretation of the data. These reaction products have been observed in MS and MS/MS spectra. Methods for identifying and possibly eliminating these products from spectra acquired on the quadrupole ion trap have been examined. The sources of reactive ions in a CI experiment on the quadrupole ion trap are residual EI ions created during the electron pulse to obtain the CI reagent ions, reactive CI fragment ions, and if CID is performed on CI-generated ions there is the possibility that reactive CID product ions will be formed. The reaction we have focused on is the reaction of phenyl cation, $C_6H_5^+$ with methane to yield $C_7H_7^+$. Elimination of EI-generated ions from a CI experiment on the quadrupole ion trap can be accomplished by lowering the low mass cutoff during the ionization pulse to an rf voltage that will not trap the higher mass EI-generated ions. Alternatively the EI ion can be eliminated by utilizing selected reagent ion chemical ionization (SRICI). A "clean" CI spectrum can then be obtained. It is important to note that a significant portion of reaction time for the EI-generated ions occurs during the analytical ramp where ions are ejected from the trap to be detected. For example, the quadrupole ion trap scan rate is 180 μs. Thus a scan from 20 μ to 77 μ allows 10.26 ms for reactive ions to interact with the neutral CI gas. This fact can be used to identify the presence of ion/molecule reaction products in CI spectra by changing the starting point for the analytical ramp, and thus the reaction time. While there are methods to eliminate reactive EI-generated ions, there is little that can be done to remove CI-generated reactive ions. These ions can at least be identified, however, by changing the starting point of the analytical ramp. A problem unique to the ion trap is reaction of CID-generated ions with a CI reagent gas. This problem occurs in the ion trap because the region in which CID takes place is the same as the region where CI is

accomplished. An MS/MS spectrum of the [M+H]+ ion of p-dichlorobenzene acquired on a TSQ, a beam instrument, was markedly different than the MS/MS spectrum of the same ion taken on the quadrupole ion trap. The only peaks observed in the TSQ spectrum were m/z 111 and a very low abundance peak at m/z 75. In contrast, ion/molecule reaction products were observed in the quadrupole ion trap spectrum at m/z 91 and m/z 125. If an additional reaction time was allowed, other ion/molecule reaction products were observed at m/z 79, m/z 105 and m/z 107. Once again, the presence of ion/molecule reaction products can be conveniently detected by varying the starting position of the analytical ramp (and thus the reaction time).

Another aspect of CI in the ion trap which we are investigating is the relative sensitivity of it versus electron ionization (EI). A theoretical analysis of EI and CI sensitivities for benzophenone showed that EI should have lower detection limits and better sensitivity than CI in an ion trap. These results prompted us to experimentally obtain EI and CI mass spectra on an ion trap as well as a beam-type instrument. These results are to be compared with the theoretical results.

For the beam instrument, data were taken on the Finnigan TSQ 700 equipped with a GC. Concentrations ranging from 1 picogram to 100 nanograms of benzophenone, methyl stearate, and N,N-dimethylaniline were injected onto the GC. EI mass spectra were taken with an electron energy of 70 eV and CI spectra were taken with methane as the reagent gas. The major ions in the EI mass spectra and the protonated molecule from the CI mass spectra were plotted versus the amount injected. The linearity of these plots was fairly good for EI spectra between 10 pg and 100 ng. CI seemed to be a little more sensitive toward molecular ion species than EI but did not show good linearity. CI showed better sensitivity as expected on a beam-type instrument.

The ITS 40 was used to compare the sensitivity for EI and CI in an ion trap. During this report period, the only ionization mode available was EI since the CI upgrade kit for the system had not yet been received. The EI mass spectra, however, of benzophenone and methyl stearate have been collected. Injections of the same concentration range as on the TSQ 700 onto the ITS 40 were made for the two compounds. Mass spectra were collected at various ionization times for each

concentration and a linear response of the signal as a function of ionization time was obtained for each of the major ions at each concentration. The plots showed different slopes (or sensitivities) for each ion, reflecting their relative intensity. At longer ionization times for the higher concentrations, nonlinearity, probably due to space charge effects, became evident. The automatic gain control (AGC) utility of the ITS 40 should allow greater dynamic range but at the expense of sensitivity. CI experiments will be performed upon implementation of the CI utility on the ITS 40.

In a new development, we have been the first to demonstrate matrix-assisted laser desorption (LD) in a quadrupole ion trap. The matrix-assisted laser desorption technique is fast becoming a well-reputed approach to form molecular species from compounds that are either thermally labile or are contained in matrices that hinder other ionization methods. Because laser desorption mainly produces singly charged species, it is useful for providing molecular-weight information of large, nonvolatile molecules. The quadrupole ion trap is attractive for this ionization method because it serves as a rugged, compact alternative to other mass spectrometers in the field. In addition to these attributes it provides high sensitivity, MS^n capabilities, mass-range extension to 75,000 m/z, and high-mass resolution.

Studies thus far have been limited to leucine enkephalin and bradykinin as a means to refine sample preparation. At this time development of both the sample preparation and mass-range extension techniques is near completion. Currently, we are able to sustain ion signal up to 100 laser shots with sub picomole amounts of material loaded on the probe. This capacity to maintain ion signal readily permits MS/MS to be performed.

D. M. Chambers, K. J. Hart, D. E. Goeringer, K. G. Asano, S. A. McLuckey, G. L. Glish

Electrospray Ionization

Our work on electrospray ionization has evolved into two separate paths. The first of these comprises studies of fundamental processes involved in electrospray. The second is the demonstration of the utility of the electrospray/quadrupole ion trap combination for chemical analysis.

Electrospray ionization has already been proven to be useful in the study of the gas-

phase chemistry of multiply solvated or coordinated metal ions by other researchers. This utility derives in part from the facility with which the metal ions are solvated by or from complexes with the ES solvent or other reagents added to the solvent. We are investigating a number of different metals and solvent compositions in studies of this type. Solvation and complexation can be a hindrance, however, in the application of ES to the analysis of trace metals in solution, particularly water, if "pure" ES is used. We have found that these problems can be overcome by extracting the metal ions out of the aqueous phase and into an organic phase using crown ethers or similar complexing agents such as cyclic amines. In addition to transferring the metals to a solvent more amenable to the spraying process (e.g., methylene chloride), concentrating the metals by reduction in solvent volume (thereby lowering detection limits), and providing the possibility of preferential metal extraction, the use of crown ethers results in a single 1:1 metal-ligand complex of the same charge as the metal. Thus, preformed ions of the various metal-crown ether complexes exist in solution which enhances the ES process. Based on the m/z value of the complex, the metal ion and its charge state can be determined.

While the detailed mechanism for ion evaporation or ion desorption is currently at issue, it has become clear that best ES-MS results, both in terms of sensitivity and detection limits, are achieved for compounds that are ions in solution. Species that are ionic in solution and have been analyzed by ES-MS include, for example, metal salts and organic salts. Compounds with functionalities that can be ionized via solution phase acid/base chemistry, such as carboxylic acids and amines, are also amenable to ES-MS. 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 (e.g., Na^+ or CH_3COO^-) that are present in the analyte solution.

Current and potential methods for preforming ions in solution for ES-MS can be divided into three broad categories, viz., chemical, electrochemical and photochemical methods. To date only the acid/base solution chemistry of an analyte has been exploited to preform ions. As a result, the applicability of ES ionization is currently limited to

compounds that are ionic in solution or that can be ionized in solution (or in the desolvating droplets) by acid/base chemistry or by adduct formation. Several important classes of compounds, such as the polycyclic aromatic hydrocarbons (PAH's), cannot, at present, be analyzed using this technique. Additionally, the ions formed in solution via acid/base chemistry or adduct formation are limited in positive ion mode to cationized species and in negative ion mode to the deprotonated molecule or an adduct ion. Radical cations, $M^{+\cdot}$, and radical anions, $M^{-\cdot}$, which directly provide the molecular weight and might be of use in other mass spectrometric analyses, such as MS/MS, are typically not formed by ES ionization. We have demonstrated that charge-transfer (CT) complexation and electrochemical reactions are viable means by which to form radical cations or anions in solution, both for compounds that display acid/base behavior and also for compounds that are otherwise not amenable to analysis by ES-MS.

CT complexes are formed by electron transfer between an electron donor (D) and electron acceptor (A) as shown in the equation

$$D + A \text{ ---> } (D^{+\cdot}A^{-\cdot}) \text{ ---> } (D^{+\cdot})_{solvate} + (A^{-\cdot})_{solvate}$$

Thus, this method can be used to form both radical cations and anions from species that undergo these reactions. Electron donors and acceptors are usually compounds of low ionization energy (IE) and compounds of high electron affinity (EA), relative to one another, respectively. Typical electron donors include PAH's and other aromatic species that contain electron-donating groups such as -OH, $-OCH_3$, $-N(CH_3)_2$, and $-CH_3$. Common electron acceptors usually contain several electron withdrawing groups, such as $-NO_2$, -CN, or halides. For example, the quinones chloranil (tetrachloro-p-benzoquinone) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are good acceptors. For example, without the addition of the acceptor DDQ, the positive ion ES mass spectrum obtained from a solution containing the donor N,N,N'N'-tetramethyl-1,4-phenylenediamine (TMPD) shows the protonated molecule as the major ion. When DDQ is added, the radical cation is the ion observed. In negative ion mode, the molecular anionic species observed corresponds in mass to $(DDQ+1)^-$. This observation suggests that the original molecular anion formed from DDQ by CT with TMPD undergoes reactions in solution. CT complexation with DDQ was also used to form the radical cation of

2,3-benzanthracene, a neutral PAH which normally gives no signal in ES-MS.

Electrochemistry can also be used to form ions in solution for ES. The setup used in these experiments consisted of an electrochemical LC detector in which both electrodes of the cell were floated at the high voltage necessary to promote ES. The cell was operated via a battery and variable resistor connected to the cell electrodes and also floated up to the ES voltage. With this setup, no high voltage ES needle is required since the solution is charged in the cell. The setup was tested using the PAH perylene. When the voltage difference between the two electrodes in the cell is zero (cell off) no signal is observed. However, when the two electrodes are offset by 1.5 V (cell on), the radical cation of perylene, formed by the electrochemical oxidation of the analyte within the cell, is observed.

One of the more important factors in observing the ions produced in solution via electrochemical processes under normal ES spray conditions is the nature of the solvent system employed. Typical solvent systems are comprised, to as large a degree as feasible, of methanol and acetonitrile with as little water as possible. Such solvent systems are chosen because of the solubility of the more common analytes analyzed (e.g., peptides and proteins), because they produce a stable spray, and also because they allow for solution phase ionization of the compounds (typically ionization via salt dissolution and acid-base chemistry). Observation of radical cations (as well as radical anions) must involve a more careful selection of the solvents used. Radical cations, depending on the structure of the molecule, can be extremely susceptible to nucleophilic attack by the solvents or by contaminants in the solvents. The products of such nucleophilic reactions can be charged, but are more typically neutral, and therefore are to be avoided in this context. We found that the formation of porphyrin radical cations is enhanced in a solvent system comprised of methylene chloride/methanol/trifluoracetic (TFA) (50/50/0.1% v/v/v). A search of the literature found that methylene chloride and methylene chloride/TFA were solvent systems of choice in electrochemical oxidation of porphyrins and polycyclic aromatic hydrocarbons. The TFA in these solvent systems is said to stabilize the radical cation formed, although the mechanism of this stabilization is not clear. When we used the same solvent system as that used for the porphyrins, we were largely unsuccessful in generating radical cations from other compounds that

would have been thought to be easily oxidized electrochemically (i.e., PAH's and aromatic amines). However, spraying from a solvent system comprised of methylene chloride (dried over alumina)/0.1%TFA resulted in the observation of radical cations from a host of PAH's including perylene, tetracene, rubrene, pyrene, and anthracene, and the compounds tetramethylphenylenediamine and phenothiazine. More care in the choice of solvent system for these compounds is required because they are much more susceptible to nucleophilic attack than are the porphyrins. Because methanol and water are both excellent nucleophiles, they must be removed from the solvent system.

While solvent systems and spray conditions necessary for observation of radical cations produced in a normal ES system have been arrived at, it is yet to be determined where the electrochemical reaction is taking place, although the metal ES needle is almost certainly involved. Experiments to gain more insight into the role of the needle are under way. Based on the apparent electrochemical oxidation of species in electrospray, we incorporated an electrochemical flow cell, normally used as an HPLC electrochemical detector, into the ES source to deliberately produce ions by electrochemistry. In this setup, both electrodes of the electrochemical cell, and a variable potential battery wired across the electrodes, were floated to the high voltage necessary to promote a spray. With this setup no high voltage needle is required since the solution is charged in the cell. Using the PAH's as model compounds, we found that no ions from the analytes were observed when the two electrodes were maintained at the same high voltage (cell off). However, when the two electrodes were offset by 1-2 V (cell on), the radical cation of the species of interest was observed. (Note that since no reference electrode is used in this setup, the actual potentials within the cell are not known, but will increase as the voltage gradient induced by the battery is increased.) Control of the electrochemical process, of course, is the major advantage of this setup. For example, a mixture of the three PAH's, pyrene, perylene, benzo[ghi]perylene, was analyzed with the cell electrodes offset by different voltages. By offsetting the electrodes by 1.5 V, perylene could be ionized exclusively. With the electrodes offset by 2 V, the radical cations corresponding to the three components in the mixture were observed.

Electrospray, because it is a solution phase ionization method operating at

atmospheric pressure, presents a convenient means to directly couple liquid separation methods such as HPLC and CZE directly with mass spectrometry. Coupling of a separation method with ES-MS has been shown by several research groups, including our own, to be an analytically useful combination. Last year, for example, in collaboration with Jack Henion of Cornell, we demonstrated the successful coupling of on-line microbore HPLC with the ion trap via a pneumatically assisted ES ionization (sometimes called ion spray) source. Since that time we have constructed a new ion trap instrument dedicated to electrospray and have been working toward interfacing separation methods with this system, including a newly acquired microbore HPLC system, with a long-range goal of advancing the capabilities of the ES/quadrupole ion trap combination in biomolecule analysis.

We have interfaced a microbore HPLC (ABI Model 140B) to an atmospheric sampling ion trap using a sheath flow ES system by means of a split flow interface that delivers only a portion of the total chromatographic eluant to the spray. The sheath flow setup and flow splitter were assembled in-house from low cost chromatographic fittings and syringe needles. A sheath flow system is used to enable solvents containing a high percentage of water to be sprayed. The splitter arrangement, employing two low dead-volume tees, was designed to obtain about a 50:1 eluant split delivering approximately 1 μl/m to the electrospray. When spraying at the typical 50 μl/m employed in microbore HPLC, as was done in our work with the Cornell group, an auxiliary means of nebulizing the effluent must be implemented such as the coaxial flow of gas over the ES needle used in ion spray. While such an interface works well, it is found that signal levels in ES are enhanced at lower flow rates. Two possible explanations are given for the observation. First, the number of ions produced from charged droplets in ES might be related to the concentration of ions in the droplets and not the absolute amount of analyte. Second, at the lower flow rate the ionization efficiency may be enhanced. As the split ratio increases, although less material goes to the spray, more ions are produced. Thus, the split flow arrangement we are now using is expected to give us better sensitivity than ion spray with the added benefits of recovering over 90% of the analyte for subsequent analyses and allowing for the use of parallel detectors.

The operation of the splitter and sheath flow interface were evaluated in positive ion

mode by flow injection analysis using tetrabutylammonium iodide as a model compound. Using methanol as the sheath, a stable spray and stable ion signals were obtained using aqueous methanol mixtures containing as much as 30% water. Operation of the system with an HPLC column has also been tested, and found to be satisfactory, using porphyrins and methanol/water mobile phases. Evaluation of the system for the analysis of model peptides and proteins using solvent systems comprised largely of water and acetonitrile is ongoing.

In addition to the coupling of chromatographic techniques with electrospray, complementary work in the development of chromatographic techniques and procedures has become part of the effort of this group. Tryptic digests of nanomolar quantities of cytochrome C, apomyoglobin, myoglobin, and melittin have been prepared for coupled HPLC/MS analysis. These digests have been analyzed on two different C_8 reversed phase microbore HPLC columns, containing large pore 0.03 μm or smaller pore 0.01 μm packing materials. Maximum resolution for the fragments was obtained using water/acetonitrile (ACN) solvents containing 0.1% trifluoroacetic acid in a shallow gradient up to 70% ACN. The analysis times on the column containing the smaller pore packing were slightly longer but the resolution of early eluting small peptide fragments was greater. These differences may be exploited to obtain the maximum amount of structural information. The tryptic digest of apomyoglobin has also been analyzed by capillary electrophoresis (CE) using a citrate buffer. High column separation efficiencies were obtained with reasonable analysis time (less than 25 minutes). These advantages combined with the low solvent flow rate make CE attractive for future coupling experiments with ES-MS.

Additional work in CE involves the development of new gels (in collaboration with the Chemical Technology Division) for separation of oligonucleotides. Polyacrylamide gel-filled columns may be used to obtain separations based on size or molecular weight in capillary electrophoresis (CE). These gel-filled columns are especially important for the separation of oligonucleotides since long strands have similar charge densities and electrophoretic mobilities in free solution. Baseline separations of fragments differing in size by one base unit are obtained only for short segments (up to 10 bases) in zone electrophoresis (i.e., free solution) but may be extended to over 400 bases using gel

columns. The low diffusion of the solutes in the gel results in extremely high column efficiencies. This factor, coupled with significant reductions in separations time as compared to conventional slab gel techniques, indicates that capillary gel electrophoresis may be useful in nucleotide sequencing. Polyacrylamide, however, has limited stability at high applied potentials. Furthermore, the methods for preparing these gel-filled columns are not straightforward and have been reported to yield irreproducible results.

Hydrous aluminum oxides prepared by internal gelation methods are being examined initially. Compositions have been formulated which gel slowly at room temperature to enable loading of the liquid broth and gelation within the capillaries. The columns that have been prepared are free of any voids indicating that there is little shrinkage as the material gels (a problem encountered with polyacrylamide). As voltage is applied across the columns, however, the gels have been found to migrate. This "creeping" may be due to surface charge on the capillary walls and efforts to eliminate this problem either by silanizing or using bonded coated capillaries are being investigated. Compositions which provide a rigid gel but with low ionic strength to maintain reasonable currents at typical operating voltages are also being formulated.

G. J. Van Berkel, R. S. Ramsey,
S. A. McLuckey, G. L. Glish

Direct Atmospheric Analysis

We have several ongoing projects involving detection of trace organics in ambient air. These are based around the atmospheric sampling glow discharge ionization (ASGDI) source. There are two major classes of compounds which we have focused on: explosives and halocarbons.

Work during this year in the area of halocarbon detection has concentrated on characterizing the second-generation ASGDI/ITMS combination for its detection and identification. Previous studies performed with the tandem quadrupole/time-of-flight (QT) instrument equipped with the ASGDI source produced substantially better results for halocarbons in negative ion mode. Therefore, experiments with the ASGDI/ITMS also concentrated on negative ion detection and characterization. The ITMS mass and MS/MS spectra contained the same ions as seen with the QT instrument. However, the ITMS mass

spectra exhibited considerably less fragmentation in general when a relatively low rf amplitude was used during injection. The degree of fragmentation could be enhanced considerably by raising the amplitude of the rf voltage. Therefore, such a technique allowed MS/MS type spectra to be obtained without knowledge of the requisite frequency as needed with resonance excitation MS/MS. In addition, the ITMS has improved mass resolution for daughter ions over the time-of-flight mass analyzer used in the QT instrument.

ASGDI detection limit data for the C_7F_{14} were also obtained using the exponential dilution technique to vary the concentration. Such data were then used to construct calibration curves from which the detection limit was determined. The ASGDI/ITMS real-time detection limit (15 parts-per-trillion) using a 50 ms injection time was about a factor of four better than obtained with the QT instrument. The MS/MS detection limit, using either the resonance excitation or elevated rf injection amplitude technique, was about 400 ppt. Because the MS/MS efficiency of the ITMS is normally quite high, it would seem that the MS/MS detection limits should be somewhat closer to those seen in normal MS mode. The relatively poor results seen for the halocarbon anions apparently results from the high efficiency of electron detachment compared with fragmentation.

To obtain real samples, air and water samples from Paducah were obtained for the purpose of analyzing for 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114). Portable hand-held air samplers were used to obtain air samples in Tedlar bags. Water samples were collected by direct connection to water cooling lines. The samples were brought back to Oak Ridge and analyzed on a quadrupole ion injection trap. On the first trip samples were taken within the plant perimeter as well as inside one of the Cascade buildings. The second trip concentrated on collecting water samples from one of the cooling lines inside the Cascade buildings and sampling outside the plant perimeter.

Results from the first trip showed fairly high levels (300 ppb) in the sample collected in the Cascade building. A site centrally located between the Cascade buildings had a freon level of approximately 20 ppb. On the second trip all outdoor air samples, including those taken up to two miles upwind from the facility, had levels around 60 ppb.

Preliminary experiments were also performed to evaluate ion mobility spectrometry (IMS), or plasma

chromatography, for halocarbon detection. The halocarbon sample vapor was introduced into a corona discharge by passing a nitrogen stream over the halocarbon liquid. The anions produced in this manner were then pulsed into the IMS; after transit through the drift region, the ion signal was monitored with a Faraday cup detector. Results for the halocarbons investigated revealed only slight differences in ion mobilities (retention times).

In the area of explosives detection, we have initiated a project to build a prototype explosives detector based on MS/MS for the FAA. A Finnigan TSQ 700 was purchased to serve as the analyzer and an ASGDI source was designed and installed on the TSQ. Preliminary experiments show signal-to-noise levels for the detection of TNT vapor to be comparable between the TSQ and our custom-designed quadrupole/time-of-flight (QT) instrument. The TSQ has better resolution, though, giving it better specificity. The trade-off for this is the fact that the TSQ costs more than twice what a QT costs.

D. E. Goeringer, B. C. Grant,
K. G. Asano, G. J. Van Berkel,
S. A. McLuckey, G. L. Glish

INORGANIC MASS SPECTROMETRY

D. H. Smith

This group carries out both research and support activities. The major effort in research this year was in the area of glow discharge mass spectrometry, while support activities included spark source mass spectrometry, isotope ratio mass spectrometry, and gas mass spectrometry.

Last year at this time, we reported that two mass spectrometers had been moved from the Y-12 site to Building 5505 at ORNL. These instruments have been brought on line and are now operating routinely. Funds (FY 1991) have been approved for renovation of more space in 5505 to house our ORNL-designed mass spectrometers. One of these is the instrument that analyzes transuranium samples; its move to 5505 will be a boon to all involved as recent changes in transportation regulations have made it increasingly difficult and costly to ship radioactive samples between sites. Estimated completion date for the renovation project is March 1993.

A new gas mass spectrometer has been ordered and is in transit. It will replace our aged instrument, which has become a

maintenance nightmare and is essentially inoperable during the summer months.

Collaboration with Professor George Swihart of Memphis State University continued. We used our VG-354 mass spectrometer to make precise isotopic ratio measurements of boron.

In a joint effort sponsored by DOE and the Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan, the lutetium double spike method we developed some years ago for use in tank calibration was carried out and evaluated for potential use at PNC.

Development of a radio-frequency probe for use in glow discharge mass spectrometry continued. This work is a collaborative project with Professor R. K. Marcus of Clemson University.

RF Powered Glow Discharge Mass Spectrometry on the VG-9000

Noteworthy progress has been made over the last year in the interfacing of an rf-powered glow discharge to the VG-9000 double focusing glow discharge mass spectrometer. A significant element in our progress lies in a novel rf probe/discharge cell design and a new electrical coupling system that allows the elemental analysis of conducting and insulating bulk solid materials.

The new source design couples to the VG-9000 in a manner analogous to the dc cell. This source can also be cryo-cooled (to reduce interferences from residual gas ions) and houses the discharge. A direct insertion probe has been designed to introduce the sample into the discharge region, allowing higher sample throughput and maintaining vacuum integrity. Radio frequency power is coupled through the probe to the sample (cathode), thus sustaining a discharge. The potential for analysis of conducting and nonconducting materials has been demonstrated and the optimal operating conditions have been identified.

The improved electrical system accommodates the need for adequate shielding, high voltage accelerating potentials, and rf power. The isolation circuitry employed isolates the accelerating voltage from the rf electronics. This allows for adequate shielding of the rf noise from the associated electronics while still applying sufficient accelerating potentials to the extracted ions formed in the rf discharge. Hence, signal-to-noise has been increased by

~ 10000. Absolute sensitivities are in the low ppb range for conductors and are expected to be similar for nonconductors.

D. C. Duckworth, J. M. McMahon, D. H. Smith*

---

*Predoctoral Research Program, Clemson University

Isotope Ratio Mass Spectrometry

We continued our collaboration with Professor George Swihart of Memphis State University this past year. We can now reliably analyze boron samples, using the $Cs_2BO_2^+$ at mass positions 308 and 309. We have not been able to develop an automated procedure, our ultimate goal, but we can run samples manually. The procedure is extremely sensitive to proper temperature regulation. We analyzed a number of samples to the required levels of precision (100 ppm or better). The ratio of boron isotopes was used to estimate the temperature of the lake water from which the boron salts crystallized; this in turn yielded insight into the geothermal processes that affected the region in question.

In collaboration with C. K. Bayne of the Computing and Telecommunications Division, a new approach to the quality control of isotope dilution measurements is being investigated. Traditional control charts plot a critical parameter as measured from a reference sample (in this case concentration of the analyte element) versus time. Such an approach does not unambiguously identify the nature of the problem when results out of the acceptable range are obtained. We decided to investigate whether or not plotting two experimental parameters would yield more information. We chose to plot concentration versus the ratio of the spike isotope to one of the sample isotopes. We conclude that there are cogent reasons for adopting this approach where applicable. In one test case, suspect values were traced to use of incorrect values for the reference parameters rather than to failure in sample preparation, as was first suspected. In a second case, gross outliers were readily identified (as the traditional plot did, also); in addition, near-outliers, where one might suspect a problem, were also identified. These new plots were much easier to use.

*E. H. McBay, D. H. Smith, C. K. Bayne**

---

*Computing and Telecommunications Division

Safeguards-Related Projects

We completed analysis of lutetium samples for the IAEA as part of the UK-German CALDEX experiment. Despite encountering a few problems, our results and those of two UK laboratories agree very well (to within 0.3% in most cases). The success of this experiment has encouraged the parties involved to perform another experiment, this one on a true dissolver solution. We have reservations about proceeding to dissolver solutions at this time, as described in the next paragraph.

Because its importance to international safeguards, DOE's Office of Safeguards and Security funds projects to help reprocessing plants in Japan meet the necessary requirements. One such project is the assay of holding tanks containing solutions of spent reactor fuel for fissile content. The lutetium double-spike procedure we developed some years ago is ideal for determining the amount of solution in such a tank, and implementation at PNC is being funded by DOE. Two staff members of PNC visited ORNL for a week while we went through a tank calibration experiment for them using a solution of depleted uranium in a tank at the Integrated Engineering Test Facility. Results were not as good as hoped or as good as we had achieved in the past. Investigation revealed our problem was in sample preparation (enough of an organic extractant was loaded on the mass spectrometer filaments with the lutetium to cause unacceptably high background). There are, in addition, other challenging problems at PNC that must be solved; one of them is the addition of a large excess of gadolinium to serve as a neutron poison from which lutetium must be separated. Our conclusion was that, until sample preparation chemistry has been worked out so that a clean lutetium sample can reproducibly be provided to the mass spectrometer, it is not advisable to proceed elsewhere.

A second problem uncovered in this experiment is that PNC is having difficulty in quantitatively delivering the natural lutetium tracer to the tank. This must be solved before progress can be made; failure in quantitative delivery of the tracer invalidates the whole procedure.

We will be addressing these two problems in the coming year.

*D. A. Bostick, E. H. McBay, D. H. Smith, J. A. Carter, M. H. Ehinger**

*Robotics and Process Systems Division

2. INORGANIC AND RADIOCHEMISTRY

J. R. Stokely

The Inorganic and Radiochemistry section was formed as a new organizational unit this year combining groups from the Inorganic Chemistry and Radioactive Materials Analysis sections. The new section consists of five groups: Inorganic Analysis, Radioactive Materials Analysis, REDC Analytical Laboratory, Low-Level Radiochemical Analysis, and Special Projects. The section supports a large number of Laboratory and DOE programs in the areas of environmental monitoring, waste operations, environmental remediation, transuranium element production, and basic R&D. Because of the heavy demand for analytical services mainly to support Laboratory environmental and waste programs, the past year has been a period of growth and diversification for the section.

After a four-year shutdown, the High Flux Isotope Reactor (HFIR) was put back into operation in 1990. Startup of the reactor allowed the transuranium element production program to begin again, and the REDC Analytical Laboratory group supported one processing campaign during the past year. Other campaigns are scheduled in the near future as well as special processing campaigns to separate and purify transuranium isotopes (^{243}Am). Our neutron activation analysis laboratory at HFIR is back in operation. Besides offering special neutron activation analysis services for Laboratory programs, the laboratory has become involved in a large project to determine mercury and other toxic metals in soils and sediments from the East Fork Poplar Creek flood plain. This project is providing characterization data for future remediation activities of the flood plain.

The Radioactive Materials Analysis (RMA) group has continued to be involved in regulatory characterization of radioactive mixed waste. Because of our experience in this type work, we have assisted other DOE sites in characterization work. A new developmental activity was funded by DOE this year to devise new and adapt existing regulatory methodology to radioactive materials.

The RMA group has also been heavily involved in hot cell and laboratory decontamination work for installation of a new liquid waste system for the High Radiation Level Analytical Laboratory.

Analyses for low levels of radionuclides in environmental materials continues as a major involvement for the section. Because of new regulatory requirements, support for the Laboratory's air monitoring program has grown considerably. Support to groundwater monitoring programs has increased somewhat. Special studies are under way to utilize new radionuclide-specific chromatographic materials (EiChrom) for routine separations needed for environmental analyses.

Considerable growth is now taking place within the Inorganic Analysis group due to demands of environmental remediation activities at ORNL and the other Martin Marietta Energy Systems plants. Much of this work is driven by regulatory (State and EPA) requirements. We are in the process of improving the technical capability and capacity of the group by addition of staff, acquisition of new instrumentation, and consolidation of similar laboratory operations.

LOW-LEVEL RADIOCHEMICAL ANALYSIS

J. W. Wade

The Low-Level Radiochemical Analysis (LLRA) group has continued to provide analytical support and development for the major environmental monitoring programs at ORNL and other Energy Systems installations. This year the LLRA group analyzed almost 7000 samples and reported over 23,000 results.

The air monitoring program at ORNL was dramatically upgraded during the past year. We measure gross alpha and beta on air filters and gamma emitting radionuclides on activated charcoal cartridges for this program. The data that we generate are reported to State and Federal agencies for verification that the Laboratory's air emissions do not exceed Clean Air Act guidelines or other permit obligations. The number of samples submitted through the air monitoring program increased approximately 45% from 1990. The groundwater monitoring program continued at a steady pace of approximately two wells sampled each day.

We were asked to analyze a large

number of waste samples during the past year. Most of these samples were some kind of waste oil but other matrices such as floor sweepings, absorbants, and other organic contaminated waste products were received. We were asked to perform gamma spectrometry and determine gross alpha/beta, tritium and ^{14}C on these samples. The oil and oil-contaminated waste were ashed overnight to destroy organics and digested in acid. We were able to improve our sensitivity for gross alpha/beta by taking a larger aliquot and counting for a longer period of time.

We provided the Paducah Gaseous Diffusion Plant with analyses in support of the deer herd survey at the Paducah site. Tissue, bone, and thyroid samples were analyzed for various radionuclides. A few of the bone samples showed elevated levels of ^{90}Sr, and some elevated levels of ^{99}Tc were found in other samples matrices. We were asked to analyze the annual environmental monitoring samples that included vegetables, fruit, fish, and rabbits from the Paducah area. A wide variety of radionuclides were measured in these samples.

Our counting intrumentation was upgraded with the addition of a new Packard 2500 series liquid scintillation counting system. The system has an onboard computer and an external PC that is interfaced to the system for versatility. The new system has a much lower background (5 cpm vs 10 cpm) than the 460c system that it replaced. The software on the PC is very user friendly, and allows custom reports to be generated easily. The system has the unique ability to reprocess an entire batch of samples with a different set of operating parameters. This feature is an enormous time saver because having to recount a batch of samples could take an entire day.

We continued to learn about and use the EiChrom chromatographic material with great success this past year. One good example was the use of the Sr-Spec material for the analysis of ^{90}Sr in frogs. We had to dissolve the entire frog and pass a large aliquot of the dissolution through a column of the packed material. The major advantage of the Sr-Spec for such an application is that neither calcium nor the ^{90}Y daughter of ^{90}Sr is retained while 100% of the strontium is retained on the column. Residual calcium was removed with further washes with strong acid and the strontium was eluted with water. The classical separation for strontium using nitric acid is very difficult to follow when such large amounts of calcium are present.

Other materials available from EiChrome include tetravalent specific

materials which hold great promise for the separation of the actinides from uranium and other interfering metals. We have also used another material (TRU-Spec) for the separation of uranium and the actinides.

We have been heavily involved in a program to better characterize areas of possible radiological contamination at the Paducah Plant. This occurred when personnel at the Y-12 plant asked us to help them develop an analytical scheme for analysis of the proposed samples generated by the program. Initially, the radiation control department had planned on requesting that samples be analyzed for uranium, americium, plutonium, and neptunium. During the initial meeting with Y-12 and Paducah personnel, we were told that an area found to be contaminated with uranium would fall into one control category, and if contaminated with one or all of the TRU elements would fall into another category. Based on these criteria, we suggested an abbreviated analysis scheme for the analysis. We suggested running an aliquot for uranium and a separate aliquot for a gross TRU measurement using praseodymium as a carrier. The radiation control department accepted our proposal and we quickly developed a procedure and qualified it by running three batches of controls made up by the Y-12 Quality department. We routinely process 40 samples each week that include both air and smear samples. Each batch of samples includes blind controls that are supplied by Y-12. Our performance on the controls has been excellent.

L. S. Barringer, L. D. Bible, M. C. Doherty, G. M. Gibson*, P. S. Gouge, C. C. Granger, S. M. McClellan*, N. E. Owen, H. H. Ross, N. A. Teasley, C. L. Watson*

*Oak Ridge Research Institute

Analytical Chemistry Participation in the DOE-TWRA Deer Hunts

Since 1985, the Analytical Chemistry Division has operated the radiological survey laboratory during the DOE-TWRA-managed deer hunts. Until this year, we have used the same counting equipment and database computer. After suffering a breakdown with the multi-channel analyzer (MCA) during one of the hunts and a hard-disk crash of the database PC after the hunt, consideration was given to using a PC-based MCA system. Since the files are backed up at the end of each day's hunt, nothing had been lost. The

database has been installed on a "notebook" type computer and we now have a PC-based MCA system for use on the deer hunts. Both new systems were used during a recent hunt (November 9 and 10) with no problems. The new systems will allow us to interface the database PC and the MCA PC for electronic transfer of counting data into the database. TWRA personnel are checking with their database persons on the possibility of our getting an ASCII file of the hunter data from the state which will enable us to electronically enter the hunter information into the deer hunt database. This will greatly simplify the data entry process in the counting room at the checking station.

N. A. Teasley, C. C. Granger

REDC ANALYTICAL LABORATORY

J. M. Keller

The REDC Analytical Laboratory (REDCAL) has continued to provide analytical support to the Radiochemical Engineering Development Center (REDC) of the Chemical Technology Division (CTD) and to the monitoring of radioactive waste effluent for Waste Operations (WO) of the Office of Waste Management and Remedial Actions. In addition, the group has provided analytical support to the Remedial Action Program (RAP) and the Waste Tank Characterization Program within CTD. More than 16,700 samples were received by the REDCAL with approximately 49,000 analytical determinations completed during 1991. This sample load only increased slightly this year over 1990, but the total analytical measurements increased by 20%. The work for Waste Operations was comparable to last year but there was a significant increase in work from REDC. The analytical support work for REDC operations included a TRU processing campaign, characterization of the Mark-42 fuel assemblies from SRP, and support of routine REDC operations.

Special Projects

The REDCAL has provided analytical support for the Mark-42 Assembly Process flow sheet development during the past year. The development of a flow sheet to ultimately obtain pure ^{243}Am from the Mark-42 assemblies from SRL is a major project for REDC. The REDCAL will provide most of the analytical support for this project. Several other groups within ACD will also participate. Over the past year the REDCAL has been involved with an extensive characterization of the Mark-42 fuel assembly. This characterization has involved the dissolution of seven samples taken longitudinally along the target assembly and three samples taken from concentric cylinders that make up the assembly. The characterization involved radiochemical measurements for both fission products and actinides. In addition, samples were prepared on resin beads for isotopic measurements by mass spectrometry for plutonium, curium, and americium. The high activity level of the samples from this project will be similar to samples from a HFIR target campaign. Current plans indicate that REDC will alternate between the Mark-42 Assembly Process and the TRU Processing Program to increase the overall productivity of the operation.

The REDCAL provided analytical support to a joint research program between the U.S. and U.K. in which the higher actinides were incorporated into fuel pins for irradiation in the Dounreay Prototype Fast Reactor in Scotland. A major part of this effort is to determine the cross sections of a wide variety of actinides in this type of reactor. The fuel pins were dissolved in the hot cell at Building 2026, and a small portion of each sample was sent to REDCAL for actinide and other radiochemical measurements.

Another project involved the need for a rapid separation of berkelium and cerium. A separation by anion exchange, which is described by Moore[1], was chosen for evaluation. The separation is based upon the anionic nitrate complex formation with Bk(IV) and Ce(IV) in the presence of 8M HNO_3. Moore's procedure was studied on routine radioactive samples in which two methods were employed. The first method involved a lead dioxide-loaded anion exchange resin column in which a pre-oxidation step is not needed. Beta and gamma measurement demonstrated that the Bk-Ce separation was not achieved. The

second method using sodium bromate as a pre-oxidizer produced an efficient separation. Sodium bromate was added to the sample prior to loading on the anion exchange column. Results showed that Ce(IV) remained on the column and Bk(IV) was eluted. However, bromate salts present in the elution contribute to mass absorption problems when beta counting by a gas-flow proportional counter; the bromate may not be a problem by liquid scintillation counting. A scheme was proposed using a TRU-Spec column to remove the bromate from the berkelium.

A. M. Bray, C. D. Parks*, J. M. Keller*

*Oak Ridge Research Institute

[1]Moore, F. L., *Anal. Chem.* 39, 1874 (1967).

Methods Adaptation/Development for Mixed Waste

An ongoing project is being conducted which involves the study of RCRA metal (and other metals of interest to EPA) recoveries from a solvent extraction procedure. The extraction procedure uses tri-n-octylphosphine oxide (TOPO) to extract uranium and thorium from radioactive liquid wastes containing RCRA metals. The extraction eliminates severe spectral/matrix interferences caused by high levels of uranium and thorium present in samples being analyzed by inductively coupled plasma (ICP) and graphite furnace atomic absorption (GFAA). A draft of this procedure in SW-846 format was submitted at the beginning of the project for inclusion in the DOE/HQ Methods Compendium (Method PM100R). Previous studies at the High Radiation Level Analytical Laboratory (HRLAL) in 1988 and various literature references provide thorough information about the extractability of uranium and thorium by TOPO. This project focuses on obtaining information about RCRA metal recoveries in the TOPO extraction employing variation in acid concentration of the sample and sample replication for precision. Radioactive tracers of the RCRA metals required for this study were obtained from fission product waste, standard radioactive solutions, and neutron activation of metals and metal salts in the HFIR Neutron Activation Analysis Laboratory. The sample mixtures and standard solutions also contain non-RCRA metals. The recoveries of these other elements are being studied as well.

Also included in the study is scandium which is frequently used in ICP analysis as an internal standard.

Results from the radioactive tracer work show that the RCRA metals studied are not extracted by TOPO, whereas scandium is. After results are obtained on two remaining RCRA metals, thallium and nickel, the project will be complete. The evaluation of nickel and thallium will require beta detection due to the absence of useful gamma ray emitting radionuclides.

In addition to the results obtained from the TOPO extraction, metal recoveries from extraction chromatography are also being evaluated. The samples prepared for the TOPO extraction are applied to an EIChroM™ TRU-SPEC chromatographic column which retains actinide and lanthanide elements. Experimental results have shown the RCRA metals are not retained by the TRU-SPEC column. This method is another possibility for removing uranium and thorium from radioactive liquid wastes without the production of organic wastes. The TRU-SPEC column has the potential to provide complete removal of actinides prior to other analytical measurements. This reduction in alpha activity would both reduce the health hazards and simplify many of the analytical measurements required for radioactive waste materials.

A strontium specific column (SR-SPEC, available from EIChroM™) has been tested as a possible replacement for the EPA ^{90}Sr procedure to separate strontium from other waste constituents. Experiments conducted with the SR-SPEC column were designed to confirm the manufacturer's specifications as well as characterize the performance of the column using typical waste samples. Experiments included the generation of breakthrough curves for the column under different nitric acid concentrations, elution curve profiles for ^{90}Sr, strontium recovery, and temperature effects on the strontium elution. Overall, test results closely matched the manufacturer's claims for the column. Experiments were conducted with actual waste samples on the SR-SPEC column to evaluate effects of the complex matrix. Also, the accuracy of using the SR-SPEC columns was compared with the EPA procedure on real waste samples. A batch of liquid waste samples was analyzed using each method. Both the Radioactive Materials Analysis group and the REDCAL analyzed the waste samples using the EPA Sr procedure; the SR-SPEC column extractions were performed by the REDCAL. The results

from this experiment illustrated that, on average, the SR-SPEC column and EPA Sr procedure gave comparable results.

The transuranium specific column (TRU-SPEC) is also being tested for possible use by the REDCAL. Thus far, tests to confirm the manufacturer's specifications for the column have been performed. Experiments included the determination of the free column volume, generation of breakthrough and elution curves at different acid concentrations, and the percentage of product recovery using both standards and previously analyzed actinide production samples. Results from these tests have closely matched the manufacturer's claims for the columns, with actinide recoveries ranging between 92 and 95 percent. An experiment testing the percentage recovery of transuranics while using the column under a vacuum was also performed with positive results. Planned uses for the TRU-SPEC columns include sample cleanup to remove solids before plating, fission product removal in order to reduce background radiation, and the removal of actinides prior to metal analysis.

A. M. Bray, C. D. Parks*, B. K. Larkins,*
R. A. Jones, R. T. Pack, R. F. Peacher,
D. A. Caquelin, J. S. Delashmitt,
R. D. Johnson, J. A. Seiter, C. S. White*

*Oak Ridge Research Institute

RADIOACTIVE MATERIALS ANALYSIS

J. L. Botts

The Radioactive Materials Analysis (RMA) group located in the Building 2026 High Radiation Level Analytical Laboratory 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 3000 samples performing some 8000 determinations.

The characterization of mixed radioactive/hazardous waste continued to be the principal activity as during the previous 2-3 years. These characterizations included the analysis of the waste for radionuclide and chemical content, as well as the determination of some physical properties. The data generated from these determinations are essential to meet both regulatory and engineering treatability requirements for this waste. These measurements have been provided to determine and classify the waste as RCRA, TRU, or mixed, and to evaluate methods for treatment and disposal of the waste. As we have done in the past, we follow EPA-approved analytical procedures insofar as possible. In characterizing these waste samples, procedure modifications sometimes become necessary due to high radiation levels, high salt content, and problems with matrix interferences. These characterizations have been made using gross alpha and beta measurements, gamma ray spectrometry, ICP/AA and ion chromatography.

Due to the lack of processing hot cell capability at ORNL, the HRLAL facility has assumed responsibility for processing palladium isotopes that are used for cancer treatment. This treatment, mainly for prostate cancer, consists of placing a tiny implant (about the size of a grain of rice) of ^{103}Pd, encased in a titanium tube, in the tumor. With a radioactive half-life of 17 days, the palladium emits therapeutic radiation for a month. The palladium is irradiated in the HFIR and transferred to HRLAL for processing. Because of the short half-life of this nuclide, processing must be completed and delivery made within 24 hours after receipt from the reactor. This work consists of processing one ^{103}Pd capsule per month which yields enough product to treat about 50 patients.

A considerable amount of time and effort has been required in the Phase I hazard screening for the HRLAL. The hazard screening process utilized the facility's

existing level of activity and radionuclide inventory to determine the hazard classification of the facility. As presently operated the classification has been determined to be "generally accepted". However, due to the unique capability of the facility within the DOE complex to characterize high radiation level waste, this classification has been determined to be too restrictive. Based on this concern it has been determined that the facility be identified as a "moderate" hazard facility and the screening process be revised to incorporate the projected limits of a moderate hazard classification. The facility has a limit of operation that will restrict the activities and inventory limits to the levels that now exist. This restriction will be lifted when the hazard screening is revised for a moderate hazard level.

The HRLAL has been designated as the top priority for completion as part of the Bethel Valley Low Level Waste Project. This project is being performed by DOE to upgrade portions of the liquid low-level waste collection and transfer facilities at ORNL. The upgrade consist of replacing all existing underground transfer lines that handle radioactive solutions with double wall piping as a RCRA requirement. Associated with this upgrade is a new monitoring and control station (MCS) located just outside the northwest corner of Building 2026 and consisting of a below-grade, vaulted collection tank; monitoring instrumentation including indications of pH, temperature, pressure, and tank level; a caustic addition system; and an above-grade control room which contains a sampling system. Radioactive waste will be directed from the facility to the MCS where the tank content will be monitored, sampled and pH adjustments made, and periodically discharged downstream to the low level liquid waste (LLLW) system. Extensive internal piping modifications will be made in the hot cells and C-zone laboratories to connect to double-contained headers which provide containment for the building radioactive LLLW drain system. Facility personnel have the responsibility to decontaminate the hot cell and C-zone hoods to enable the contractor to proceed with the piping upgrade. All equipment and contaminated work pans have been removed from hot cells 1 through 4. We are now proceeding with the decontamination work using ultra-high-pressure water washing. An ultra-high-pressure pump system capable of generating up to 2.8×10^8 Pa water pressure is being

used to decontaminate the interior of these hot cells. Two cells, 5 and 6, will remain operational until cells 1 through 4 are upgraded and are back on line. The target completion date for the facility upgrade is mid 1993, with a total projected cost of about $10 million.

C. Cook, Jr., J. P. Jenkins, H. J. Hall, L. R. Hall, L. C. Tabor, M. E. Peters, R. T. Pack, M. T. Davis, J. Giaquinto**

---

*Oak Ridge Research Institute

Support to the Robotics and Process Systems Division

The satellite laboratory located in Building 7602 continues to provide analytical services for the 7600 Robotics facility. Presently the process and engineering R&D work which requires analytical services is associated with the AVLIS uranium enrichment program. Chemical analyses and physical measurements are performed as required to support this work.

M. G. McClung

Building 3019B Decontamination

Due to limited funding for 3019B decontamination in FY-91, this work was curtailed to a large degree. Lead shielding was installed on the cell windows which reduced the activity level to acceptable background in the operating area. In addition, a highly contaminated filter was removed from the exhaust in cell 7. Two of the three enclosed access ports were removed from the cell fronts. The projected plan for future decontamination work will depend on the availability of funding from DOE.

*C. Cook, Jr., J. P. Jenkins**

---

*Oak Ridge Research Institute

Determination of Hg and Other Trace Elements in Soil and Sediment from East Fork Poplar Creek by Neutron Activation Analysis

Neutron activation analysis (NAA) is being used to determine Hg, As, Cr, Sb, Se, ^{235}U, and ^{238}U in soil and sediment samples from East Fork Poplar Creek. A procedure

has been developed that is similar to that used in Contract Laboratory Protocol (CLP) methods for the analysis of metals by atomic absorption and inductively coupled plasma spectroscopy. This is a new application for neutron activation analysis at ORNL and elsewhere. To perform the soil analysis it was necessary to complete the development and preparation for NAA in approximately two months. This effort included making the delayed-neutron counting (DNC) system operational to measure ^{235}U, completing software to calculate NAA results from gamma spectral data, calibrating four Ge detectors for gamma spectra of the soil samples, procuring two additional computers for data processing and backup for the PC-based multichannel analyzer (MCA) system, drafting a procedure for the analysis, and developing automated methods to handle the 4000 to 6000 samples. A number of changes and/or modifications in both the mechanical and software features of the DNC system were required. An intense effort was carried out to complete the development of software to perform NAA calculations using gamma spectral data acquired with the PC-based multichannel analyzer system described in the 1990 annual report. This effort has resulted in a system that functions totally with magnetic media without the need for paper records of analyses. At the present time, approximately 2600 soil samples have been irradiated and counted resulting in over 15,000 elemental determinations.

L. Robinson, F. F. Dyer, J. E. Carlton, A. L. Ondracek***

*Oak Ridge Research Institute

**Great Lakes Colleges Association

Status of the HFIR Neutron Activation Analysis Laboratory

Activities of the HFIR Neutron Activation Analysis Laboratory have been highlighted this year by two major events: the measurement of arsenic in the remains of former President Zachary Taylor (see below) and the start of a program to determine mercury and other trace elements (Cr, As, Sb, Se, Zn, Cd, ^{238}U, and ^{235}U) in approximately 4000 soil samples from the East Fork Poplar Creek (see above). At the present time, approximately 2600 soil samples have been irradiated and counted resulting in over 15,000 elemental determinations.

Work with the remains of the former president resulted in a considerable amount of publicity both locally and nationally. The

local publicity served to inform the scientific community that neutron activation analysis is again being conducted at ORNL. Some amount of service NAA has resulted from this.

F. F. Dyer, L. Robinson

An NAA Method for Determining Sub-nanogram Amounts of ^{129}I on LWR Mixed Bed Ion Exchange Resins

A procedure was developed to measure microgram to sub-nanogram amounts of ^{129}I on the ion exchange resins of the primary coolant of light water reactors.

The procedure is based on the removal of iodine from the resin as iodate, reduction to iodide, precipitation as palladium iodide and evolution by heating as elemental iodine. The iodine is then absorbed on activated charcoal and irradiated to a neutron fluence of about 10^{18} n cm^{-2} and allowed to stand overnight to permit decay of the ^{128}I and other short-lived activities. The iodine is removed from the activated charcoal with a solution containing sodium thiosulfate, converted to elemental iodine and extracted into carbon tetrachloride. The carbon tetrachloride phase is washed extensively with distilled water to remove water soluble radionuclides and radioactive particulates. The iodine is extracted into a small volume of water containing sodium thiosulfate and counted for several hours to determine ^{130}I.

A novel aspect of the procedure is the removal of iodine from charcoal with solutions containing sodium thiosulfate. Another new feature is the method of determining the chemical yield of iodine. The original resin is analyzed for normal iodine by NAA and a known amount of carrier iodine is added to the resin before the analysis is begun. Following the measurement of ^{130}I the normal iodine in the final solution is measured and compared with the original quantity of iodine in the starting resin.

*F. F. Dyer and Julie Graudons**

---

*DOE Fellow

A Search for Arsenic in Hair and Nail Remains of Former President Zachary Taylor by Neutron Activation Analysis

Two samples of hair and two samples of fingernails from the remains of former President Zachary Taylor were analyzed for arsenic by instrumental neutron activation analysis (INAA). The samples were brought to ORNL by Dr. George Nichols, State Medical Examiner of Kentucky, on June 20, 1991. The samples, which ranged from 2.7 mg for the smaller hair sample to 12.3 mg for the larger nail sample, were irradiated that evening for one minute in a thermal neutron flux of 4.61×10^{13} n cm^{-2} s^{-1}. Gamma spectra were acquired for a number of periods of several hours over a three-day interval following irradiation. The specimens were not cleaned for these initial analyses.

Neutron irradiation of arsenic yields ^{76}As which decays with a 26 hour half-life and the emission of a 559 keV gamma ray with a yield of 42 percent. Spectra were acquired with a source-to-detector distance of 40 mm with two Ge(Li) detectors with resolutions of about 2.1 keV FWHM and counting efficiencies of 1.0 percent for the 559 keV photon. No photopeaks of ^{76}As were observed for any of the specimen. After much of the induced ^{24}Na had decayed, limits of detection for As were estimated to be about 2 μg/g.

Following these initial analyses, sections of the hair specimen (~ 5 mm) containing the hair roots were removed, re-irradiated, cleaned to remove much of the ^{24}Na and ^{42}K, and reanalyzed. One root specimen weighing 0.75 mg was irradiated five minutes and found to contain 0.8 μg/g of arsenic. The other specimen was irradiated 10 minutes and found to contain 0.3 μg/g. Both of these observed concentrations are within normal levels observed in hair within the past 30 years.

As a result of these analyses by neutron activation and results from other analytical methods, the Kentucky State Medical Examiner concluded that the former president was not poisoned with arsenic.

F. F. Dyer, L. Robinson

Status of Analytical Chemistry Facilities in the Advanced Neutron Source

One major revision has been made in the proposed analytical chemistry facilities in the ANS since last year's report. It was previously proposed, due to space limitations

in the main reactor building, that a free-standing building be constructed to house a number of the analytical chemistry facilities. This facility, NAAF-2, would complement smaller laboratory and office space, NAAF-1, in the main reactor building. In the interim, however, more space was created in the existing experiment support building which provided a convenient location for NAAF-2. Not only is the size of this space adequate, but the fact that the counting rooms are underground creates a favorable situation for low-level radiochemical analysis. The exact location of NAAF-1 in the containment dome is presently being determined.

No major revisions have been made in the cold neutron beam facilities.

L. Robinson, F. F. Dyer

INORGANIC ANALYSIS

N. M. Ferguson

The Inorganic Analysis group provides technical support to ORNL programs, to other Martin Marietta facilities (Y-12, K-25, Paducah) and to external organizations including Tennessee Valley Authority, Nuclear Regulatory Commission, the Strategic Petroleum Reserve, Science Applications International Corporation, and Westinghouse Electric Corporation. New methods and modifications of existing procedures were needed to meet the requirements for these programs. Significant efforts were also necessary to meet the stringent time limitations for completion of the analyses. Approximately 95,000 analytical results were reported during this period. The Office of Safety and Health Protection continued to generate the largest number of samples.

We provided technical support for new and continuing programs. Groundwater and effluent samples were received for the National Pollution and Discharge Elimination System (NPDES), Resource Conservation and Recovery Act (RCRA), and special programs of the Office of Safety and Health Protection. There was a tremendous

increase in the WAG (Waste Area Group) RCRA well samples. The Remedial Feasibility Investigation (RFI) of the Clinch River by the Environmental Sciences Division (ESD) produced fish for PCB, lipid, and metal determinations. Work for the Industrial Hygiene group was heavy; blood, urine, air filters, and waters were analyzed. Numerous wastes (solids, oils, and aqueous) were characterized for ORNL groups. Asbestos was measured in water, air, surface, and bulk samples for ORNL, K-25, and Y-12 groups. Metals (Cr, Zn, As, Se, Sb, Cd, Hg) were measured in soils and aqueous samples using Contract Laboratory Program (CLP) protocol for Science Applications International Corporation (SAIC) as part of the East Fork Poplar Creek Remediation program. The Smoky Mountain Parkway study produced aqueous samples for anion and metal determinations. The White Oak Creek Embayment (WOCE) project generated daily samples for turbidity and total suspended solids determinations during the preconstruction, construction, and postconstruction phases of WOCE CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) removal action activity.

The workload for the ICP/OES laboratory was heavy during this year. The increase in work was due in part to the large number of WAG RCRA well samples. These wastes were analyzed for total and dissolved metals using the CLP protocol. The CLP inorganic target list metals were reported. The lab experienced minimal instrument downtime with the JY polychromator. However, much time was lost due to instability of intensities. All NPDES deadlines were met in a timely manner. In October we obtained a new Jarrell Ash ICP/OES instrument. This should provide us a very stable, dependable instrument with new capabilities (lower detection limits, 43 channels, Ward-Scientific CLP data package).

Ion chromatography analyses increased this year. The Smoky Mountain Parkway Study, NPDES, and RCRA programs generated the largest number of samples. Two Dionex ion chromatography systems were used for anion determinations. Most programs required a complete anion scan (fluoride, chloride, bromide, nitrate, phosphate, sulfate). Considerable time was required for anion determinations for compliance samples since the holding time for phosphates and nitrates is 48 hours. Recently the Dionex 2110i ion chromatograph was set up to detect and quantitate the perchlorate anion. Separation

is achieved by an Ionpac NS1 separator column preceded by an Ionpac NG1 guard column. The eluent is tetrabutyl - ammonium hydroxide/sodium carbonate/acetonitrile. The Dionex anion micromembrane suppressor enables suppressed conductivity detection of perchlorate. This isocratic method elutes perchlorate in approximately eight minutes. All other species present in the matrix elute in the first three minutes and do not interfere with perchlorate determinations.

The Inorganic Analysis group performed polychlorinated biphenyl (PCB) determinations for several groups in the Environmental Sciences Division. We measured lipids and 1254 and 1260 PCB isomers in fish and clams from the Clinch River and a Kansas City site. Blanks, duplicates, spiked samples, and International Atomic Energy Agency (IAEA) samples of fish homogenates were extracted and analyzed with each batch of samples to determine analytical quality levels.

Work for the VG ICP/MS analyzer progressed very well this year. We had minimal downtime and the instrument continued to perform well. There is an increasing demand for ICP/MS analyses for new and continuing programs for ORNL.

The Industrial Hygiene group generated numerous samples for analysis. We have measured metals (Ag, As, Be, Cd, Cr, Ni, Pb, V) at the parts-per-billion concentration in several hundred air filters. Blood samples were analyzed for lead for the ORNL and K-25 Industrial Hygiene groups. Lead was also measured in urine samples from the ORNL Industrial Hygiene group.

The Inorganic Analysis group continued to provide support for the Remedial Feasibility Investigation (RFI) of the Clinch River Project. Fish tissues were analyzed for As, Tl, Be, and U for the ESD.

We continued to monitor Be in soils for a program of the Health and Safety Research Division for the Formerly Utilized Site Remedial Action Plan (FUSRAP).

For several years graphite furnace methods have been used to measure metals in RCRA wells for the Office of Safety and Health Protection. The graphite furnace was used to determine metals requiring reporting limits which could not be obtained by ICP/OES. Since ICP/MS is not yet an "EPA Approved Method" for some environmental programs, we requested EPA Region IV guidance for analysis of RCRA wells by ICP/MS. During this period we were given approval by EPA to measure metals in

RCRA wells using EPA ICP/MS Method 6020 and the CLP protocol. This increased our workload considerably. Hundreds of well samples have been analyzed for total and dissolved metals (As, Se, Pb, Ag, Sb, Tl) at the five parts-per-billion concentration. The auto sampler has been placed in operation for these samples since the CLP protocol is very time consuming.

We continued to evaluate the VG Micro Therm Electrothermal Vaporization System for the ICP/MS analyzer as a method to measure femtogram concentrations. Initially we encountered some intermittent problems with the software in the system which caused excessive heating of the graphite tubes. Using a 50 μl injection and single ion counting mode, we have been able to consistently obtain linear response for ^{234}U, ^{237}Np, ^{239}Pu, and ^{241}Am over a concentration range of 20-300 fg.

We have continued to provide technical and service support in the fields of transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), optical microscopy (OM), and electron-excited X-ray analysis (EDX). In particular, a sizable group of samples have been analyzed for asbestos for ORNL Industrial Hygiene, Y-12 Industrial Hygiene, K-25, and ORAU. Our TEM-asbestos services were requested by the Portsmouth facility, but unfortunately, the paperwork and "red tape" involved in transferring the samples and funds for analysis proved daunting to the prospective customer. Although we were inadequately staffed for three quarters of the year, we still met all routine and rush deadlines for these analyses. In practice, this means that rush samples are "turned around" within 24 hours and routine samples are analyzed within one week. In addition to the TEM-asbestos services, we provided emergency backup to Y-12 and ORNL Industrial Hygiene for polarized light microscopy (PLM) measurements for asbestos in bulk samples. The TEM techniques were also employed for examination of air and bulk materials for "man-made" fibers. A new individual is being trained for asbestos analysis and has already provided significant relief for the problem of understaffing.

We have begun to investigate methods and equipment by which we can upgrade our SEM imaging and measurement services. In particular, we are investigating a promising PC-based imaging system which can be interfaced with an analog SEM to provide digitization of the images. This would open

up many improvements in image processing and global and feature measurements.

All sample preparations for graphite furnace work, ICP/MS analyses for RCRA wells, total Kjeldahl nitrogen, and total phosphorus analyses were done in the "clean room facility" at Building 2026. The mercury laboratory provided results for a variety of samples (waters, soils, sediments, fish, urine, charcoal filters, TCLP extracts, etc.). For years we have used both EPA procedures (waters, sediment) and Feldman's $HNO_3/HClO_4$ preparation procedures (tissue, charcoal filters, etc.) for mercury determinations. During this year, the ORNL Safety Department stopped the use of $HClO_4$ in Building 2026. Therefore, we continued to prepare samples using EPA preparation procedures in the "clean room facility" but used a perchloric hood in Building 4500S after regular working hours for preparation of tissue and charcoal filter samples. This is a very inefficient operation.

During this period, we began to experience instrument instability and reduced sensitivity with the Feldman mercury analyzer. This led to a decision to upgrade the analyzer. The monochromator was cleaned, a different photomultiplier tube was installed, the photomultiplier power supply was replaced with a Fluke power supply and the output recorder was cleaned and repaired. The UV light source (tungsten lamp) was replaced with a fluorescent-type mercury lamp to permit instrument power to remain on at all times. The modified analyzer is very stable, has instant run capability, and an approximate tenfold increase in sensitivity. The instrument is now capable of measuring 0.2 nanograms of mercury, compared with the 2 nanograms previously obtained.

Even though graphite furnace work decreased this year, ORNL programs still required approximately one man-year support in this area. Most work was for NPDES and CLP programs. NPDES programs produced weekly, biweekly, and monthly effluent samples and all work required a seven day turnaround time. Two graphite furnaces (Perkin Elmer Zeeman 5000 and 5100) were used for this work.

Flow injection analyses decreased considerably this year. NPDES programs generated most flow injection work.

The increase in RCRA well samples caused a significant increase in total organic carbon determinations. Four samples were analyzed from each well for organic carbon. For quality assurance purposes it was

necessary to measure inorganic carbon, organic carbon, and total carbon in each sample.

A tremendous amount of time and effort was required to provide support for ORNL programs for the following analyses: oil and grease, total suspended solids, total dissolved solids, fecal coliform, chemical oxygen demand, phenols, ammonia, total cyanide, reactivity cyanide, sulfide, reactivity sulfide, turbidity, flash point, total organic halides, hardness, alkalinity, Leco carbon, Leco sulfur, vacuum fusion (oxygen, hydrogen, nitrogen) methylene blue active substances (MBAS), biochemical oxygen demand. Many of these have holding times of 48 hours or less.

S. J. Bobrowski, K. R. Crane, D. L. Denton, P. V. Ditavong, J. H. Hackney, S. Hayes*, W. W. Herring*, C. S. MacDougall, S. A. MacIntyre, M. L. Martin**, T. L. Mims, M. L. Moore, S. J. Morton, J. T. Oliver*, B. Philpot, J. C. Price, F. Rogers, J. Summers.*

---

*Oak Ridge Research Institute

**Temp Systems

SPECIAL PROJECTS

J. H. Stewart, Jr.

The Special Projects group performs analytical methods development, nonroutine specimen analyses, and coordinates divisional analytical services for requesters of unusual technology. The group has responsibility for preparing purchase specifications for major capital equipment, performing acceptance testing, and coordinating facility preparation and installation. During this period a Nd:YAG laser ablation system for the VG inductively coupled plasma/mass spectrometer (ICP/MS) was funded, purchased, and delivered to ORNL on September 30. Installation site preparation has been completed and arrangements for acceptance testing have been made.

The Jarrell Ash 61-E Polyscan ICP optical emission spectrometer (ICP/OES) was received and installed. The hardware and routine software performance has been excellent. A specialized software program to automatically develop the Contract Laboratory Program data forms is yet to be accepted.

Sealed-vessel high-temperature dissolution equipment has been evaluated versus microwave sealed-vessel and the

focused microwave open-vessel techniques for the preparation of petroleum crudes and of powdered iridium metal, prior to ICP or ICP/MS determination. Recommendations for purchase have been prepared.

The evaluation of methodology for measuring the perchlorate residue within laboratory hoods and ventillation systems was completed and three candidate methods were selected for field testing.

X-ray fluorescence spectrometry was evaluated as an alternate methodology for measuring mercury in East Fork Poplar Creek flood plain sediments. The XRF detection limit was 15 parts-per-million for mercury with laboratory equipment. A detection limit of 50 ppm using field portable XRF systems seems feasible.

A comparison of open vessel, microwave, and high-temperature sealed-vessel oil preparation methods, followed by both ICP/OES and ICP/MS analyses, demonstrated that xylene-dissolved oil could be successfully analyzed at the parts-per-billion elemental concentration range. The microwave and the high-temperature preparations provided a cleaner specimen for analysis, and volatile arsenic and selenium were retained in all tests. This completed the ORNL milestone for the Strategic Petroleum Reserve program, and a final report is being prepared.

A major new assignment for the group is to identify potential environmental concerns at DOE sites nationwide, and recommend portable or field transportable analytical technology to provide immediate support during survey and during field environmental remediation activities. This assignment includes radionuclides, inorganic, organic, and anion components in soil and water specimens. Volumes of documentation have been examined and a concise summary of concerns for DOE facilities has been completed. Laboratory evaluation of conventional and of innovative new technology is under way to identify candidate methodologies for field testing.

Communication and coordination are also important functions of the group. During this reporting period more than 400 requests were processed for information, analytical support, specification assistance, or referral for assistance at other facilities. A recurring interest has been the ACD design of the ICP/MS laboratory, with special visits from Portsmouth, Los Alamos, PNL, Sandia, and Savannah River staff members to view the installation.

T. R. Mueller

Ultra-Trace Measurement of Radionuclides in Bioassay Fluids

The inductively coupled plasma/mass spectrometer analyzer has been coupled with a preparation procedure developed at the Argonne National Laboratory to measure ultra-trace levels of U, Pu, Np, and Am in bioassay fluids. The sensitivity of the ICP/MS for the specific nuclides of interest has been demonstrated, on both synthetic solutions and spiked urine specimens, at the 10 parts-per-trillion (ppt) concentration level for ^{234}U. The initial detection limits for ^{237}Np, ^{239}Pu, and ^{241}Am are at the 25 ppt concentration levels. Minor modifications of the preparation procedure will permit measurements at the 10 ppt levels. The significance of this development effort is that the ^{239}Pu, ^{237}Np, and ^{241}Am can be specifically measured without need for chemical separation, as is required for alpha counting. The ICP/MS sensitivity permits preparation of 100 ml specimens in small laboratory equipment, compared with the liter-sized specimen required for counting. The actual ICP/MS analysis time for U is less than 20 minutes, and the Pu, Np, and Am can be measured in less than 30 minutes. Preliminary studies indicate that this same methodology is applicable to air filters, smear wipes, and soil leachate analyses. Further development of an optimum routine preparation and analysis procedure is under way to demonstrate the viability of ICP/MS as a rapid, cost effective, bioassay screening methodology.

J. H. Stewart, S. J. Morton, P. S. Gouge

Computer Programs for Mercury Analysis by Cold Vapor Atomic Absorption Chromatography

A commercial program sold by LABTRONICS, INC., was purchased for the cold vapor mercury atomic absorption (CVAA) determination. After several attempts to use this program we found that 1) it required hardware not compatible with the 3Com board needed for data transmission, and 2) it did not make a proper correction for background.

In our laboratory, two methods for CVAA are employed. Samples that have no appreciable matrix effects are analyzed without the addition of a spike. Many samples derived from animal tissues do display significant matrix effects. These must be spiked and the results corrected for recovery of the spike.

For these samples, the background can only be measured after the mercury has been sparged from the system.

Two programs were written to accommodate these variations of the CVAA method. One is HGMAN; the other, HGRTSPIK (for Hg Runtime Spike). HGMAN is so named because it is a manual method. Both programs are written in Microsoft's Quick BASIC, and the runtime versions are used in compiled form.

The HGMAN program requires that a calibration curve be generated before analysis. This program is used with CLP protocols, also. Sufficient supporting data are recorded for this purpose. After the calibration data have been acquired, a plot of the calibration curve may be displayed. Statistical data are displayed and recorded. The calibration data are stored in a file independent of the sample data. Calibration data may be printed in report form from this file at any time.

The program operates in a dialog mode with the operator prompted for data as needed. It accommodates dilutions, multiple blanks, and the incorporation of preparation data. Since data are entered manually, provisions are made for editing the data after analysis. Reports may be displayed on the screen for review or printed. The values reported are calculated on the basis of the samples as received. Thus, results may be sent directly to the division's data base after they have been approved. Since data from this mode of operation can be reported in several ways, a separate program, MANREP (Manual, Report) was written for report writing.

The program HGRTSPIK is also written in dialog mode. Here, the operator is prompted with the amount of spike to add so that a peak of about the same height as that obtained for the sample is obtained. After adding the spike, the actual amount of spike added is requested. A spike recovery is reported immediately, so that the operator can assess the validity of the result. The data may be edited also before reporting.

A printout is generated with both programs for easy reference. Access to the programs requires a password. The report form has identifying captions and a summary and signature block at the end. Samples are reported with sequence numbers, dates and times of analysis, calibration data used, blank corrections made, operator performing the analysis, and dilutions, along with results in ng, ng/g, or ng/ml, depending upon the types of samples and the requirements of

customers. Appropriate data for AnaLis are extracted and an AnaLis-compatible file is generated within the program.

Both programs were prepared and are used and maintained with QA provisions addressed. HGMAN has been in use since February and HGRTSPIK since about mid-year. Improvements in presentation have been made since the first versions were introduced. The version number of the program is always printed at the end of a report.

T. R. Mueller

Spot Test for Perchlorates

A rapid check method was required for the semiquantitative analysis of perchlorates. The samples were rinsates collected from fume cupboards and associated ductwork and fan housings. The test was to be used for quick screening, on site if possible, to detect large amounts of perchlorate.

Perchlorate salts are usually soluble in aqueous solution, and only a few are colored. Some ion-pairing with dyes has been reported. One such reaction with methylene blue (MB) forms the basis for a fire underwriter's test. This test is recommended in most laboratory safety manuals as a quick test for perchlorate. The original source of this test warns against interference by zinc. We found that by carefully controlling conditions, a purple, annular ring could be obtained for perchlorate mixed with a nearly saturated solution of zinc sulfate.

The test is performed as follows. One ml of 50/50 zinc sulfate/water solution is placed into a 5ml plastic cup. One ml of the sample is mixed with the zinc solution. When the solution is at rest, a 3 µl drop of 0.3% solutions of MB (aqueous) is placed carefully onto the center of the surface of the mixture. If the perchlorate concentration is above 500 ppm, a purple ring that is about half the diameter of the cup is formed on the surface. Below this concentration, a precipitate is formed, but the ring does not develop. The ring is actually a precipitate, believed to be an ion-pair between perchlorate and MB. If allowed to remain open to the air, the ring remains stable in form and color, even after the solution has reached dryness.

The main limitation to the MB method lies in the lability of the dye to oxidation. In strong $HClO_4$, the MB is oxidized, and the test is negative for perchlorate.

We have not made an in-depth study of interferences. Although there are other species that form colors with MB, the perchlorate color is distinctive.

A number of other tests for perchlorate have been described in the literature. Most of these are spectrophotometric and most utilize MB. While portable spectrometers exist, there are problems with using the MB methods in the field. The methods we tested required fairly long times for development of color. With most, temperature was important; with some, more than a single reaction appeared to be involved. The MB also tends to adsorb on the wall of cuvettes not only making absorption measurements invalid, but also requiring rather vigorous (acetone) cleaning for removal of the adsorbed dye from the cuvette walls.

We intend to compare this method with the use of a specific ion electrode for perchlorate. Both specificity and ease of application will be considered. At present, solutions are being analyzed, after the quick screening, by ion chromatography.

We are serving on a Laboratory-wide perchloric acid committee formed to assess the hazards attendant on servicing or replacing fume removal systems. Over 700 fume hoods receive routine maintenance; about 70 of these are known to have been used with fuming perchloric acid. The committee is charged with developing a plan to address the task of servicing or decommissioning them safely. We have made a number of suggestions which were incorporated in the plan.

T. R. Mueller

Strategic Petroleum Reserve Studies

The primary purpose of these studies was to find a way to subdivide samples of crude oils so that the aliquots would be representative of the original samples. This required that the aliquots be analyzed for all of the elements of interest. This is a concluding report of work that extended over a two-year period.

Original work by Cyrus Feldman involved the preparation of five sets of five crudes and a NIST standard, 1634b, each 200 ml in volume. The crudes were supplied in 1 liter containers. The 200 ml samples were prepared by homogenizing at 60°C.

Feldman conducted several studies on the dissolution of these samples in attempts to obtain quantitative results. For a suite of

eight samples of one of these, he was able to show, using open beakers for dissolution and inductively coupled plasma (ICP) spectrometry for determinations, a precision of 8% for nonvolatile metals.

Some of the volatile species, arsenic and selenium in particular, are of considerable interest from the standpoint of both storage and use of the oils. Other elements, such as lead, tin, beryllium, and mercury, pose different problems for selection of a chemical dissolution medium.

We investigated two closed systems for dissolution of the crudes: 1) microwave heating with concentrated nitric acid and 2) sealed tube, high pressure 'ashing', also with concentrated nitric acid. The work with microwave digestion was carried out in conjunction with the CEM corporation, a manufacturer of microwave equipment. The high pressure ashing was performed by Tom Oatts at K-25 using the Auton Parr system.

Each of these techniques is capable of total dissolution of the oils. Analytical results compare quite well for a number of elements. Arsenic and selenium are recovered at the 100% level with both techniques. Recoveries of tin were not quantitative using either technique. Materials used for the containment vessels also present contamination and elemental-loss opportunities. A considerable amount of silica is dissolved from the quartz vessels used with the high pressure asher. Penetration of some elements into the fluorocarbon polymer linings of the microwave digestion vessels presents a path for loss. Tests with both systems were justified in that the cost of the high pressure digester is about $50,000 and that of the microwave digester is only $15,000.

We also did one experiment where the crudes were 'dissolved' in p-xylene and aspirated directly into an ICP mass spectrometer. Good results were obtained for most of the elements measured, but the machine was fouled by the oils after about four hours.

Dissolution by microwave heating in closed vessels followed by determination using ICP/MS seems to be the best compromise to obtain results for the most elements when nitric acid is used for oxidative destruction of the oil. We have not investigated mixed reagents for dissolving the oils. Also, more than one dissolution step might be required to effect complete recovery of some elements.

We demonstrated that samples could be reliably subdivided, and that reproducible

results could be obtained on the various aliquots. We have further shown that ICP/MS has the sensitivity required to obtain reliable results on the dissolved, decomposed oils at concentrations of elements well below 1 ppm.

T. R. Mueller

3. ORGANIC CHEMISTRY

M. R. Guerin

This section is responsible for a diverse program of research, methods development and analytical services. Research is directed toward separations and spectroscopic techniques that can yield faster and more accurate methods for identifying and quantitating trace organics in complex media. Fourier transform mass spectrometry and ion trap mass spectrometry are being studied for this purpose both alone and in combination with separations techniques. High performance liquid chromatography and supercritical fluid chromatography are the principal analytical separations methods under development. Fundamental studies of preparative scale chromatography, novel approaches for the rapid isolation of trace organics from physiological media, and supercritical fluid extraction of pollutants from environmental samples are currently the primary preparative separations activities. Solid sorbent sampling and solid phase extraction are being evaluated in combination with the separations techniques. Research continues to emphasize environmental media. Field sampling and direct-sampling mass spectrometry methods are being developed for the rapid determination of organic pollutants in water, soil, wastes and air. Progress has also been made in applying our unique analytical capabilities to biological and materials sciences problems. Examples include the use of laser desorption Fourier transform mass spectrometry for the study of fullerenes and of nucleic acid components, and the use of reverse chromatography to characterize ceramic surface properties. New or expanded activities are under way in field analytical methods and radioactive mixed waste characterization. Our analytical services operation has continued to expand in size and capability. Environmental compliance and survey services are being routinely provided for both ORNL and other DOE installations. Specialty services involving various chromatographic and mass spectrometric techniques as well as infrared and nuclear magnetic resonance spectrometry are carried out in support of life sciences and physical sciences research at ORNL.

ORGANIC SPECTROSCOPY

M. V. Buchanan

The principal goal of this group is to develop spectroscopic techniques for the unambiguous identification and quantitation of trace organics. Specific areas being addressed include the detailed structural characterization of normal and modified biomolecules, rapid detection and quantitative analysis of trace organics in environmental and physiological matrices, and new techniques for materials characterization. Our research continues to focus primarily on trapped ion mass spectrometry, both Fourier transform mass spectrometry (FTMS) and ion trap mass spectrometry (ITMS). Other organic spectroscopic tools are also employed, including conventional quadrupole GC/MS, Fourier transform nuclear magnetic resonance spectroscopy (FTNMR) and Fourier transform infrared spectroscopy (FTIR), especially in special spectroscopic studies.

In addition to research activities, numerous special spectroscopic studies using FTMS, GC/MS, FTNMR and FTIR were conducted in support of programs in the Organic Chemistry section as well as other research groups within the Laboratory.

Structural Characterization of Normal and Modified DNA Adducts with Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry

Matrix-assisted laser desorption (MALD) combined with FTMS continues to be an active research area for the characterization of normal and modified oligonucleotides. Previous experiments have indicated that this technique is quite useful for peptides and oligonucleotides with molecular weights up to 3,000 amu. However, investigations of larger biomolecules revealed that the fundamental parameters of this technique need to be examined and optimized. Numerous studies have been initiated in an attempt to understand the factors which affect the desorption, ion trapping and ion detection in order to extend the MALD technique to larger biomolecules. For example, retarding field measurements have been used to examine the kinetic energy distributions of the laser desorbed ions. These retarding field studies suggested that ions with m/z < 1,000 have kinetic energies below 5 eV and can easily be trapped in the FTMS cell.

However, experiments with larger ions indicated that retarding fields up to 10 V did not significantly alter the trapping efficiency of the ions, suggesting that Debye shielding of the ion cloud may counteract the effect of the retarding fields. A device to slow the ions using electrostatic deceleration is currently being designed.

Accurate mass measurements, collision induced dissociation experiments, and ion/molecule reactions have been further developed for the structural characterization of modified nucleic acid constituents. For example, gas phase deuterium exchange reactions have provided information useful for resolving methylated nucleosides and may prove to be quite useful for large oligonucleotides as well. For these experiments, the rate and number of hydrogen-deuterium exchanges are quite informative for adduct position and provide complete isomeric differentiation in most cases.

Collaborations have been continued this year with a number of scientists in the biochemical community. We have worked with Jean Cadet (Grenoble, France) to characterize nucleoside photodimers generated in his laboratory; this prompted a visit by him to ORNL in August. We have also worked with Steve Hecht at the American Health Foundation to characterize a series of PAH-modified nucleosides. Work with Hiroko Yoshida and Jim Turner of the Health and Safety Research Division on the characterization of radiation-induced damage to nucleosides and nucleotides has resulted in the awarding of a SEED money grant for further studies of the effects of X-rays and alpha radiation on nucleic acid materials. This research includes development of matrix-assisted LD-FTMS and HPLC for experimental identification and quantitation of radiation-induced products. These results will provide the basis for Monte Carlo calculations to model the radiation damage process.

*R. L. Hettich, B. D. Nourse**

*ORAU Postgraduate Research Program

Isolation and Ionization Technologies for Characterization of Biochemicals by FTMS

A number of approaches for interfacing separation techniques with FTMS for the investigation of biological mixtures are being developed. An electroelution method has been developed for rapid quantitative extraction of biomolecules from

polyacrylamide (PAGE) gels. This technique is quite useful for the extraction of picomole quantities of normal and modified nucleotides as well as oligonucleotides from PAGE gels for subsequent investigation by MALD FTMS. An electrospray source is being developed for use with the FTMS. The source has been modified and attached to a quadrupole mass spectrometer for further characterization and optimization. We are working with Pete Todd and Tim Short of the Analytical Spectroscopy section to optimize the injection of ions from the source into the FTMS. A major thrust of this work is to investigate the chemistry and mechanisms of the electrospray ionization phenomenon in order to extend this ionization technique to a broader range of compounds, especially larger DNA oligomers, and to make it more useful as an analytical method.

M. Shahgholi, K. D. Cook**,*
*E. L. Kerley***, J. C. Dunphy****,*
R. L. Hettich, M. V. Buchanan

---

*UT Laboratory Graduate Participation Program

**Consultant, University of Tennessee

***ORAU Postgraduate Research Program

****ORAU Graduate Research Program

Characterization of Fullerenes by FTMS

The fundamental properties of fullerenes (e.g., C_{60}, "buckyball") and related materials are being studied in an integrated program with R. N. Compton of the Health and Safety Research Division. Initial work using laser desorption FTMS was directed at optimizing methods for the generation and separation of the various fullerene species. Some of these early investigations resulted in the first observation of doubly-charged negative fullerene ions (C_{60}^{-2} and C_{70}^{-2}) in the gas phase. Experimental and theoretical examinations of these ions indicated that they most likely were generated by surface ionization from the laser vaporization process. Additional effort was directed to the development of laser ablation and discharge arc sample preparation methods for the synthesis of modified fullerenes, including those containing heteroatoms or metal ions. Investigations into the fundamental parameters controlling the growth of fullerenes in a laser plasma have also been facilitated using the FTMS. Examination of the effect of buffer gas composition and pressure has indicated that fullerene growth is very dependent on the cooling of the laser plume. Collaboration with Jim Adcock (UT Chemistry Department) has focussed on the

synthesis and characterization of fluorinated fullerenes, including $C_{60}F_{46}$ and $C_{70}F_{54}$. Due to our success in characterizing fullerenes, several groups have approached us to assist them, including V. K. Sikka of the Metals and Ceramics Division, P. Buscek of the University of Arizona and Ben Freiser of Purdue University.

*R. L. Hettich, R. N. Compton**

*Health and Safety Research Division

External Ion Injection and Glow Discharge FTMS

A collaborative project with Alan Marshall of the Ohio State University was initiated to investigate new methods of injecting ions into the FTMS from an external ionization source. An injection device has been constructed and will soon be tested on our instrument. This ion guide will constrict the ions along a path to guide them into the FTMS cell without imparting additional energy. Initial studies using this ion guide will include injection ions from an rf glow discharge ionization source which is used for analyzing inorganics. In a closely related project, Ken Marcus (Clemson University) and Bob Weller (Savannah River) have worked with us to demonstrate the direct injection of inorganic ions from an rf glow discharge ionization source into the FTMS. This was done with no lenses between the source and the FTMS cell. Conventionally, lenses or quadrupole rods have been used both to guide the ions and to control their energies so as to enable the ions to be efficiently trapped in the ion cell. In these initial studies where no lensing was used, ion beam currents on the order of hundreds of nanoamps were measured on the far side of the dual ion cell. A spectrum from a sample of copper stock yielded both ^{63}Cu and ^{65}Cu signals, along with Ar^+ and ArH^+. Under medium resolution conditions (256 K data point transform collected at a 1 MHz bandwidth), mass resolution of 37 K was obtained for the ^{63}Cu isotope. It must be noted that in these very preliminary experiments neither the rf plasma parameters nor the FTMS conditions were optimized and that substantial improvements in mass resolution should be obtained in the near future. However, these experiments have demonstrated the tremendous potential of using FTMS for elemental analysis with the rf discharge source. It also demonstrated the

relative ease of injecting ions of well-defined kinetic energy into the FTMS cells. Especially noteworthy in the GD FTMS experiment is the ability to obtain relatively high mass resolution spectra in the broadband mode to simultaneously analyze a number of elements; this is particularly important for thin film profiling and isotope ratio measurements. Preliminary experiments using the GD source for metal chemical ionization were run, generating iron ions and reacting them with olefins. This demonstrated the utility of this approach for the study of ion/molecule reactions for structure elucidation.

M. V. Buchanan, D. C. Duckworth, P. Limbach***

*Predoctoral Research Program, Clemson University

**ORAU Professional Intern, Ohio State University

Direct Sampling Ion Trap Mass Spectrometry for Rapid Environmental Analysis

Significant progress has been made in the area of direct sampling ion trap mass spectrometry (DS ITMS) for the analysis of volatile organic compounds (VOC) in environmental samples. Improvements in instrumentation have included the design and construction of modular sampling units which couple to the open/split interface by means of a quick connect system. With this system, the ITMS can be rapidly (2 to 3 minutes) converted from one sampling mode to another (e.g., direct purge of water samples to direct air sampling) without having to vent the mass spectrometer.

Direct purge methods for the analysis of VOCs in water and soil slurries have been extended to the analysis of all 34 EPA target compound list (TCL) volatiles. Previously, it had been difficult to achieve detection limits better than 100 ppb for water soluble compounds, such as acetone, 2-butanone, 2-hexanone, vinyl acetate, and 4-methyl-2-pentanone, using electron ionization. Because of their poor purge efficiency, it was necessary to enhance the sensitivity of detection and this was accomplished by

employing water chemical ionization. In this approach, the water in the sample is used to protonate the target compounds to form $(M + H)^+$ ions. This approach improves the detection limits of these compounds by a factor of approximately 100, allowing detection at low ppb levels. The software for data acquisition was revised to include alternating electron impact and chemical ionization scan functions which are switched at approximately one second intervals. This allows both types of spectra to be obtained in a single analytical run. In addition to lowering detection limits, the additional information provided by the chemical ionization data improves the ability to identify compounds confidently.

The development of a rapid screening method for VOCs in water is nearing completion. This method is aimed at a quick (3 minute) screen of samples for the presence of target VOCs at levels of 5 ppb or higher. This has involved the establishment of quality assurance methods to develop a standard protocol for sample screening. Instrument performance standards have been developed and internal standard methods have been developed to provide optimum quantitative performance. A spectral library is being established which will include standard spectra, relative peak heights, and relative response ratios versus internal standards. This information will be used to develop a spectral subtraction routine to enable quantification of individual compounds in a complex sample.

Methods for direct air monitoring using ITMS instrumentation have been developed. A major factor in the success of this work has been the development of an active air monitoring interface. Detection limits are on the order of 10 ppb or lower using this device.

DS ITMS has also been used to monitor the biodegradation of trichloroethylene (TCE) in a collaborative Director's R&D project with the Environmental Sciences, Chemical Technology, and Health and Safety Research Divisions. Methods for monitoring TCE in bench and pilot scale bioreactors have been developed. It was found that if the samples contain many dead bacteria, surfactant-like compounds are released which cause foaming of the samples during the purge procedures. Using an anti-foaming compound (such as the medicine Gas-X) significantly reduced this problem.

Work has also progressed on the development of ITMS methods for the analysis of semivolatile compounds. These

compounds are analyzed by thermal desorption rather than by purging, which is used for VOC. By varying the split ratio in the thermal desorber interface to the ITMS, a significant increase in sensitivity was observed. Many of these compounds may now be detected in the low ppb range.

M. B. Wise, C. V. Thompson, G. B. Hurst, R. L. Hettich, M. V. Buchanan, M. R. Guerin

Development of a Real-Time Monitor for Environmental Measurements

A smaller version of the ITMS (which does not perform MS/MS experiments) has been tested for applicability to environmental monitoring. The GC interface was replaced with the same modular interface system used on the larger ITMS instruments. Laboratory experiments have shown low ppb detection limits for VOCs in water samples using this instrument. This instrument was also modified for testing as a prototype real-time monitor to allow it to be transported and used in a field situation. It was also outfitted with a larger pump and a ceramic multiplier to deal with high background levels of water and oxygen. It was field tested initially at ORNL using a portable 4 kW gasoline powered generator. It was then tested at the Savannah River Integrated Demonstration Site. These tests demonstrated the ability of this real-time monitor to detect target volatile organics in the field under different sampling situations. Samples of ground-water were analyzed by direct purge for TCE and tetrachloroethylene (PCE) and found to contain 50 to 150 ppb of these contaminants. Analysis time was approximately three minutes per sample, compared with several weeks required to get the results back from an analytical laboratory. Soil gas was measured directly by coupling the real-time monitor with probes implanted in the vadose zone, and equilibrium concentrations of soil gases were measured in the headspace of a continuously screened vadose zone well.

M. B. Wise, C. V. Thompson

Rapid Detection of Targeted Compounds in Physiological Samples

DS ITMS methods are also being developed for the rapid extraction and detection of compounds in physiological media, such as urine, saliva, milk, meat, and food. For example, in a project being conducted for the Food and Drug Administration, methods are being developed to detect two anthelmintic drugs, phenothiazine and piperazine, in meat and milk in order to assure that the foods are safe for human consumption. Ideally, one would like to test every animal prior to slaughter to assess whether illegal drugs are present or if the levels of legal drugs present are unsafe. Present testing methods take considerable time and are only run after the animal is slaughtered. Our goal is to reduce the total analysis time to a few minutes so more animals may be tested and to reduce the size of the sample required for analysis so that a simple needle puncture can be taken from a live animal. Dialysis and solid phase extraction methods for rapid sample cleanup and concentration are being developed by John Caton and Larry Waters of the Separations and Synthesis group. In both of these approaches, the targeted compound is trapped on a sorbant material. Thermal desorption methods are then used to introduce the material into the ITMS. To date, ppb levels of the two anthelmintic drugs have been detected. This approach has also been used to detect ppb levels of nicotine, cotinine, and both legal and illegal drugs in one microliter of raw urine or saliva. In a related project being conducted for the Army, chemical agent simulants have been detected using similar methods in alfalfa, meat, wheat and milk.

R. L. Hettich, J. Xu, M. V. Buchanan*

---

*GLCA Student, Denison University

Instrumentation Advances in Ion Trap Mass Spectrometry

A new type of ion trap mass spectrometer is being developed in our group. The overall goal of this work is to develop a more versatile and analytically useful ion trap which is easy to use and can be transported readily. A novel shaped-field ion trap cell has been designed and simulated using a computer program to model the cell's performance. The electrodes and insulators are constructed and are being assembled with the aid of the Instrumentation and Controls

Division. Testing of the new cell should begin before the end of the calendar year.

A test bench for the new cell has been constructed. This test bench uses commercial components of a Finnigan ITMS which are packaged into a single electronics rack along with the vacuum pumps and power distribution system. This test bench has a smaller vacuum chamber and will be used for testing the new shaped-field ion trap cell and for performing comparative studies of new instrument components with the conventional cell. New pumping systems are being investigated to minimize the size, weight and power requirements of the new instrument without significant loss of pumping speed. Molecular drag pumps coupled with diaphragm roughing pumps appear to be especially promising. This new instrument will also incorporate new electronics and scan modes which are being developed to enhance mass range and mass resolution and to reduce the rf power requirements of the system. Finally, new software is under development for the ion traps which will provide greater versatility in terms of real-time data processing for the measurement of target analytes. This software is being designed to be compatible with the FORTH operating system provided with the commercial ion traps and will make the instruments more user friendly and the data processing less labor intensive.

M. B. Wise, A. V. Blalock,*
*M. V. Buchanan, S. A. McLuckey***

*Instrumentation and Controls Division
**Analytical Spectroscopy section

Unambiguous Identification of a Potent Carcinogen in Complex Mixtures

Methods are being developed to positively identify dibenz(a,l)pyrene (DBALP) in tobacco smoke condensate and in environmental samples. This compound is reported to be as much as 200 times more potent than the well-known carcinogen benzo(a)pyrene. Fractions were isolated from several samples and introduced onto a GC column by thermal desorption. Detection was accomplished with negative ion chemical ionization mass spectrometry. The detection limit by this approach was estimated to be 10 pg for pure DBALP. Many isomers of DBALP (M.W. = 302) can exist, but it is important to be able to unambiguously identify the DBALP isomer in the presence of many other compounds. In a water sludge sample, at least four

components with molecular weight 302 were detected. Their gas chromatographic retention times matched with those obtained from standards of four different dibenzopyrene isomers. However, after confirmatory analysis by HPLC, only one of these compounds could be unambiguously identified as dibenzo(a,h)pyrene and the presence of DBALP could not be confirmed. Work is continuing on determining whether this compound exists in tobacco smoke condensate or other sources.

C. Y. Ma, J. E. Caton, M. R. Guerin

Special Spectroscopic Studies

Special spectroscopic studies were conducted in support of many projects within the Organic Chemistry section and for other ORNL Divisions. Especially noteworthy is the high degree of support provided to the Organic Analysis group to confirm the identity of compounds using chemical ionization techniques. In addition, numerous samples were analyzed by negative ion chemical ionization to verify the presence of PCBs in environmental samples. A new method was developed for classifying Arochlors in environmental samples using negative ion chemical ionization ion abundance measurements for the prominent ions in the chlorine clusters of eight PCB homologs (Cl_2 to Cl_8). A BASIC computer program is used to facilitate Arochlor classification and this methodology is currently being used on a routine basis for the analysis of PCB in environmental samples. In addition, in support of several studies, thermal desorption GC/MS was employed to identify compounds adsorbed on resin traps.

Laser desorption FTMS was also used in a number of special studies in the Chemistry and Health and Safety Research Divisions to confirm the identities of compounds and to verify molecular weights and elemental composition using the accurate mass measurement capabilities of the FTMS.

In addition to mass spectrometry, samples were also analyzed using FTIR and FTNMR. We also have trained people within the Analytical Chemistry Division and the Chemistry Division to use these instruments as needed for their own studies.

C. Y. Ma, R. L. Hettich

SEPARATIONS AND SYNTHESIS

W. H. Griest

The focus of this group is the development and applications of separations methods for qualitative and quantitative analysis and isolation/purification of organic compounds in complex sample matrices. Gas and high performance liquid chromatography, and supercritical fluid and solid phase extraction technologies are the principal methods developed or utilized in the group's studies. Regulatory agency separations methods for sample preparation and for analysis also are adapted for specialized applications.

Principal activities in this period include the development of technology for rapid isolation of chemical warfare agent simulants, drugs, and explosives from biological media for ion trap mass spectrometric analysis, rapid extraction of chemical agent simulants from environmental matrices, and the isolation of ultra-trace amounts of dibenzo(a,l)pyrene from tobacco smoke and environmental media. Chemical and toxicological characterization has been completed for explosives decontamination from soil by composting. Physical testing and response surface modelling of munitions field service lifetimes have been drawn to a close and are being redirected to time-to-failure experimentation. Development of chemistries for visual indicators of munitions deterioration has passed the demonstration phase and will be continued to the prototype stage. EPA SW-846 and Toxicity Characteristic Leaching Procedure protocols are being adapted and applied in a major initiative for the regulatory characterization of radioactive mixed wastes requiring containment/shielding for safe handling.

Extraction and Isolation Methodology

Extraction and isolation method development continues as an important focus of this group. The development of supercritical fluid extraction (SFE) for off-line recovery of chemical warfare agent simulants from soil has been completed, and the technology has been transferred to the sponsor, Rocky Mountain Arsenal. It has been found that a 5 minute SFE with 5% methanol in carbon dioxide at 3×10^6 Pa and 6°C produces high recoveries of simulants spiked into 1 g of soil at 2 ppm each: dimethylmethylphosphonate (DMMP, 79 ± 23 %), 2-chloroethyl-ethylsulfide (CES, 93 ± 14 %), diisopropylfluorophosphate (DIFP, 92

± 13%), and diisopropylmethylphosphonate (DIMP, 95 ± 17 %). SFE of 10 g soil samples produced similar recoveries. The polar modifier is necessary for efficient extraction of the phosphonates and phosphates. With straight carbon dioxide, only the CES was recovered well (93-95%) and the extraction recoveries of DMMP, DIFP and DIMP were 12, 17, and 43%, respectively. The SFE produced better recoveries than conventional ultrasonic extraction with methanol (DMMP = 8 ± 3.5 %, CES = 85 ± 15 %, DIFP = 63 ± 4.2 %, and DIMP = 87 ± 6.1 %). However, the precision of the SFE was poorer, possibly because of sample-to-sample flow variations in the supercritical fluid. Flow control technology for SFE is still rather poor.

Work was initiated this year on methods for isolating large-ring (≥ 5 rings) polycyclic aromatic hydrocarbons from complex matrices such as cigarette smoke condensate (CSC) for determination of trace concentrations of dibenzo(a,l)pyrene and other potent carcinogens. The higher molecular weight aromatic hydrocarbon components (five rings and higher) of cigarette smoke condensate have been isolated by a fractionation scheme involving partitioning between cyclohexane, aqueous methanol, dimethyl formamide, and aqueous dimethyl formamide followed by semipreparative liquid chromatography. A cleanup and enrichment procedure for higher molecular weight PAHs in cigarette smoke condensate (CSC) utilizes an extraction scheme modified from that devised by W. Schmidt[1] for hard-coal flue gas condensate. The CSC is first subjected to a mixture that is 35% (volume-percent) methanol, 15% water, and 50% cyclohexane in order to eliminate polar compounds in the aqueous methanol fraction. The cyclohexane fraction is then diluted to a mixture that is 45% dimethyl formamide (DMF), 5% water, and 50% cyclohexane which effects the elimination of aliphatic compounds in the cyclohexane fraction. After dilution with water to bring its composition to 70% water by volume, the DMF/water fraction is extracted with cyclohexane. This final cyclohexane fraction (which contains neutral polyaromatic compounds and compounds related to polyaromatics such as carbazoles, etc.) is then concentrated and solvent exchanged (to 80% methanol or acetonitrile and 20% water) by rotary evaporation.

The product from the above extraction scheme is further refined by pumping the entire fraction onto a semipreparative (10 mm o.d. x 250 mm long) C18 reversed phase column which can then be washed with

an 80:20 methanol:water solution to eliminate smaller aromatics (< 5 rings) and compounds such as heterocyclics that are even slightly acidic or basic. The larger PAHs (> 5 rings) are recovered from the reversed phase column by elution with methanol or acetonitrile. Subsequently, the entire fraction recovered from the semi-preparative column is focused onto an analytical reversed phase column from a solution that is 80% methanol (or acetonitrile) in water. The focused sample is then analyzed by gradient elution. The final HPLC analytical step is nondestructive, thereby allowing the sample to be recovered for further analysis by mass spectrometric techniques.

This isolation/enrichment/analysis scheme has been applied to a pilot sample of CSC that had been spiked at the 50 ppm level with dibenzo(a,h)pyrene (DBahP) and pyrene. More than 70% of the DBahP was recovered in the final analytical sample; pyrene was not detected. In the future this total scheme will be applied to a 50-gram sample of CSC and also to an environmental sample known to contain high molecular weight PAHs. The ultimate goal will be to focus the entire refined fraction into a single analytical run and recover the further refined sample for additional characterization.

Methods are being developed for the rapid preparation of samples from animal tissues that are suitable for analysis by ion trap mass spectrometry (ITMS). Tissue homogenates have been prepared by applying ultrasonic energy from a probe-type ultrasonic homogenizer to a mixture consisting of a known weight of finely divided tissue and several volumes of water. The resulting aqueous homogenate is a crude, somewhat intractable, mixture of cell debris, macromolecular constituents related to fats, protein, and nucleic acids, and smaller chemical constituents. In this form the sample is not amenable to direct analysis by ITMS because the cellular material and macromolecular constituents will char in the inlet and transfer lines. Several routes to further clean up the sample are being investigated.

Our first approach toward the further preparation of tissue homogenates has been to separate the small molecules, (M.W. < 5000), from the cell debris and macromolecules by filtration and dialysis. The dialysis step has evolved from a static equilibrium approach to a countercurrent procedure utilizing a hollow fiber system with two circulating pumps. The fluid circulating on one side of the dialysis barrier contains the sample and a suitable particulate filter.

On the other side of the dialysis barrier, a stream of water is pumped through a solid phase extractant which has been selected to remove target molecules from the circulating stream. Subsequently the sample is concentrated on the solid phase material from which it may be either analyzed directly by thermal desorption or collected for analysis by elution with a small volume of the appropriate solvent. The system has been tested on samples spiked with a marker dye, with two drugs (piperazine and phenothiazine) and with simulants of chemical agents. Preliminary results have indicated that the system will function effectively in preparing sufficiently clean samples from homogenates. However, the smallest hollow fiber dialysis device currently available to us has a membrane area of 100 sq cm which is excessive for the sample size required for analysis by ITMS. In addition, sample constituents present at very low concentrations might be lost upon exposure to such large surface areas. Present efforts are thus being devoted toward scaling down this approach. Ultimately our goal is to be able to process smaller samples at lower concentrations so that a significant portion or all of the final isolate can be directly introduced into the ITMS. Recent studies have indicated that both the tracer dye and drugs can be recovered from the filtered homogenate on approximately 50 milligrams of Tenax and on a much smaller amount of C18 modified silica contained in the tip of a disposable Pasteur pipet after which the entire contents of the disposable pipette may be thermally desorbed into the ITMS. Future studies will be directed toward combining this reduced amount of solid phase extractant with a disposable syringe. The ideal result of this effort would be to develop a method whereby a hand syringe could be used to force a tissue homogenate across a filter, through a single disposable hollow fiber, and onto a solid phase extractant which could be thermally desorbed in the measuring instrument.

J. E. Caton, C. -h. Ho, L. C. Waters,
R. S. Ramsey, W. M. Caldwell,*
W. H. Griest

---

*Analytical Spectroscopy section

[1]W. Schmidt, G. Grimmer, J. Jacob, G. Dettbarn, and K. W. Naujack, Z. Anal. Chem. 326, 401 (1987)

Characterization of Composting Efficiency for Decontaminating Explosives in Soils

In the continuation of a project for the U. S. Army, the chemical and toxicological characterization of the field composting experiment conducted at the Umatilla Army Depot Activity (Umatilla, Oregon) by Roy F. Weston, Inc., has been completed. Samples of lagoon soil contaminated with 2,4,6-trinitro-toluene (TNT), hexahydro-1,3,5-trinitro-triazine (RDX), and octahydro-1,3,5,7-tetranitro-tetrazocine (HMX) were composted at various volume percents in static and mechanically stirred piles. Samples were collected by Weston at intervals during composting for characterization at ORNL. EPA Synthetic Precipitation Leaching Procedure (SW-846 method 1312) leachates were generated for determination of leachable explosives and TNT metabolites in our laboratory and for measurement of toxicity to Ceriodaphnia dubia and Ames bacterial mutagenicity by collaborators in the Environmental Sciences and the Health and Safety Research Divisions, respectively.

The relative rates of explosives biotransformations were TNT>RDX>HMX. The extent of TNT biotransformation in static piles was 98% or better for up to 30 volume % of soil. For RDX, 72-82% was biotransformed at up to 10% soil, and for HMX, 42-67% for up to 20% soil. Sharp drop-off in detoxification was noted above 30% soil. This is probably because increasing the % soil decreased the % amendments which supported biotransformation. The mechanically stirred piles were generally more efficient than the static piles, probably from their better aeration and mixing. However, it also could be a result of the different amendment composition for the stirred composters.

The importance of amendment composition was evident in two static piles with 10% soil and two different amendments. Both composts achieved better than 99% reduction in TNT concentration, but one was 25% more efficient in RDX biotransformation and 22% more for HMX. Composting in windrows will now be investigated as an alternate to static pile or mechanically stirred composting for the Umatilla site decontamination.

The fate of the biotransformed explosives still is not known. The metabolites of TNT determined by HPLC accounted for less than 30% of the initial TNT, and the % accounted decreased with

composting time. This suggests that TNT was either mineralized, converted to non-extractable products bound to soil components, or a combination of both, as laboratory scale composting studies have suggested. The observed TNT and metabolites also do not account for the measured mutagenic activity, which shows that some biotransformation products which retain toxicity are not observable by HPLC. Study of a compost from soil inoculated with ^{14}C labelled TNT may help resolve this question.

W. H. Griest, C,-h. Ho, J. E. Caton,
R. L. Tyndall, K. S. Ironsides*, A. A. Vaas*,*
*A. J. Stewart**, W. M. Caldwell*

*Health and Safety Research Division
**Environmental Sciences Division

Predictive Surveillance of Munitions

As noted in the last ACD annual report, the U. S. Army is interested in mathematical models describing the tensile strength of an adhesive joint in the 120 mm M829 armor-piercing, fin-stabilized, discarding sabot, kinetic energy round fired by the M1A1 Abrams main battle tank. Some cases of joint disbonding and loss of the penetrator assembly have been observed in the field, leading to the need for a predictive tool to forecast useful service lifetimes under various field conditions and to identify limits for storage conditions.

For this study, M829 rounds were subjected in groups of four to accelerated environmental exposures in temperature and humidity controlled chambers at the Milan Army Ammunition Plant (Milan, Tennessee) according to a central composite statistical design with temperature, humidity, and time as variables. After the exposures, the tensile strength (and other properties) of the adhesive joint was measured. After 13 of the 18 originally scheduled exposures had been conducted, the experiment was halted for evaluation of the data and probability of modelling success. As noted last year, the more severe exposures considerably reduced the tensile strength of the adhesive joint. However, several exposures resulted in joint failure (tensile strength of zero), and round-to-round variation in the tensile strength was large (ca. 800 lbs), especially compared to the range of tensile strengths (0 to ca. 3,700 lbs) measured for the exposed rounds. Such behavior could complicate the accuracy and

precision of predictive models.

Several types of expressions were used to construct response surface models of the tensile strength data in terms of the severity (temperature and humidity) and length (time) of the exposure. Polynomial, Arrhenius, kinetic, and logistic models were evaluated. Only the logistic model fit the necessary boundary conditions of an initial limiting value at time zero and ambient exposure conditions and a decrease to positive near-zero value for exposure conditions resulting in disbonding (zero tensile strength). Some of the other models also behaved erratically when extrapolated to exposures outside of the experimental region of data. The best fit was achieved with the equation:

$$TS = 3570 / [\ 1 + \exp(\ -\ 42.08 + 2.439t + 0.267\ T - 1.818H + 0.029TH)]$$

Where TS = tensile strength (lbs), t = time (weeks), T = temperature (°C), and H = relative humidity (% RH). The adhesive joint strength as a function of time for a set of exposure conditions is predicted to follow a sigmoidal curve. The fit of this equation to the data is very good and the model accounts for 91% (out of a maximum value of 93%) of the total variation of measured tensile strengths from the average. The major problem, however, is that the predictions for joint disbonding are premature in view of field experiences. At 21°C/80% RH, the average tensile strength is predicted to fall to zero in 57 weeks whereas M829s have been fielded for more than five years without major numbers of failures. The upper 95% confidence interval around the prediction reaches an asymptotic limit of 1051 lbs at the time the average tensile strength is predicted to be zero. Therefore, the short time predicted for failure is the time beyond which the tensile strength could be in the interval of 0 to 1,051 lbs. This wide interval reflects the uncertainty created by the large variability in the measured round-to-round tensile strength. Project management has decided to terminate this modelling approach and switch to a time-to-failure experiment which has been successfully used for predicting lifetimes of other munitions components such as fuses and batteries. Arrangements are being made to solicit bids for a subcontractor to measure the times required for the adhesive joint to fail under different exposure conditions. The results will be modelled using standard time-to-failure approaches.

Laboratory experiments have been conducted with coupons cut from the M829 case wall around the adhesive joint. The effects of temperature and relative humidity in isolation from each other and from secondary effects of the propellant have been determined using the explosion proof temperature and humidity-controlled chamber installed last year. Exposures at constant temperature (21°C) and different humidities (5, 70 and 7% RH) were supplemented by tests at constant water vapor pressure (1.18×10^4 Pa) at different temperatures (50°, 70°, and 85°C). The data are now being modelled to evaluate temperature and humidity effects. In separate experiments the effects of sulfur dioxide and/or nitrogen dioxide are being determined.

The scoping study of chemistries for detection of nitroesters using an indicator strip has been completed and a report is being prepared. Because one of the main mechanisms of adhesive joint failure in the M829 is from glue solvation by nitroesters migrating from the propellant, a color change strip which shows nitroester migration into the M829 case wall could identify those rounds liable to failure. As noted in last year's annual report, the Griess reagent system was selected as the most compatible with the case wall material. However, in its adaptation to the required solid state reaction using dry reagents, the zinc dust reducing agent (a grey color) obscures color detection. This problem was overcome by using a two-layer solid state indicator system in which the zinc dust is covered with a second layer containing the color-generating reagents. The concept of this two-layer indicator is briefly illustrated as follows: Two adsorbent strips overlap each other. Zinc dust is placed between these two strips. The upper strip is treated with a modified Griess reagent system (sulfanilic acid and N-(1-naphthyl)ethylenediamine dihydrochloride salt) and the lower strip is untreated. This two-layer strip system is placed on the case well at the skive joint. If nitroesters are present in the case wall, these liquid compounds can diffuse into the lower strip and sequentially contact zinc and Griess reagent. A laboratory experiment using filter paper developed a positive color when 10 μg of diethyleneglycol dinitrate (a propellant nitroester) was placed on the lower layer. All negative controls (lacking one of the reagents) failed to develop color. This demonstration of solid state reagent color development suggests the feasibility of

developing an indicator strip. Funds have been approved for continuing this work, utilizing both case wall coupons and full-up M829 rounds.

W. H. Griest, C. K. Bayne,*
C.-h. Ho, J. E. Caton,
*W. M. Caldwell, R. H. Baldwin**,*
*H. E. McCoy**, S. R. Nance****

*Computing and Telecommunications Division

**Metals and Ceramics Division

***Martin Marietta Ordnance Systems, Inc.

Radioactive Mixed Waste Characterization

Progress has been made in the adaptation of conventional sample preparation/analysis methods and their application to radioactive mixed waste (RMW) in services to clients inside and outside of ORNL. The DOE ALARA principle and reasonable method performance are the main guides in method adaptation.

The Toxicity Characteristic Leaching Procedure (TCLP) zero headspace extractor (ZHE) for leaching volatile organic compounds has been adapted to RMW requiring radiochemical hood containment. The main adaptations are the addition of procedures for radioactive sample handling, slight modification of the tumbling apparatus for radiochemical hood use, and development of a glove box cleaning station for safe cleanup and decontamination of the ZHE. This method has been applied to radioactive wastes from the Paducah Gaseous Diffusion Plant (PGDP).

Lower cost and lighter alternatives to the conventional ZHE are being evaluated, including a commercial aluminum alloy ZHE, and ZHEs fabricated in-house from nylon and Teflon. All three pass leak tests, function properly, and do not contribute contaminants to the volatile organics analysis. They may be more practical where ZHE disposal is less costly than cleanup from wastes with high chemical or radioactive contamination. A scaled-down ZHE has been constructed from a 100 ml gas syringe and other commercial parts. This will be far more practical for glove box and especially hot cell operations than the conventional ZHE.

The TCLP regulations permit direct analysis of wastes for TCLP constituents.

This is a much more reasonable approach than conducting leaching in the confines of a glove box or hot cell. We have installed an ultrasonic bath in a glove box, and can now do the necessary extractions for wastes requiring this level of containment. The extractions have been applied to high level alpha-emitting wastes from Nuclear Fuel Services, Inc. Other analytical capabilities added this year included the setup of a volatile organics purging apparatus in a radiochemical hood and its interface with a trap and gas chromatograph with flame ionization detector (GC-FID) outside of the hood. Many radioactive oil, sludge, and soil samples from Bettis/Westinghouse, PGDP, and Bechtel have been analyzed for volatile organics. Semivolatile organics screening by GC-FID and herbicide analysis in TCLP leachates by high performance liquid chromatography also have been set up and applied. Extractant degradation products (i.e., dibutylphosphate and bis(ethylhexyl)phosphate) have been determined using a chemical derivatization and GC-FID method developed this fall.

Late this year, the first project specifically addressing RMW analytical methods was initiated for the DOE Office of Technology Development, Laboratory Management Branch (LMB). The objective of this project is to provide the LMB with protocols for the preanalytical preparation and analysis of beta/gamma-emitting RMW. The approach includes method adaptation where necessary, performance validation, and protocol preparation. The protocols will be reviewed, submitted through the LMB to the EPA for approval/acceptance, and will be included in the DOE Compendium of Analytical Methods. Three protocols based on our previous work with RMW have been submitted to the LMB, and work is now focusing on protocols for TCLP organics, reduction of actinide interferences in heavy metal analyses, and improvement in semi-volatile organics analysis sensitivity for small sample amounts.

R. L. Schenley, P. F. Wolfe, G. A. Sega, J. E. Caton, J. M. Keller**, W. H. Griest.*

*Oak Ridge Research Institute

**Inorganic and Radiochemistry section

SPECIAL PROJECTS

R. A. Jenkins

The principal goal of this group is to address issues which require specialty expertise developed as a result of earlier investigations. That expertise includes tobacco smoke chemistry, aerosol generation and characterization, air sampling and monitoring, and field analytical methods. A characteristic of this work is that it requires combining sampling, separations, spectroscopy, and instrumental capabilities of the section and the division to achieve its objectives. The integrated product is implemented independently or in collaboration with other section and division organizations, depending on the nature of the issue being addressed. Our principal initiatives are in the development of improved analytical methods for Army-related contaminants and the development and demonstration of field analytical technologies in support of Department of Energy environmental remediation and waste management activities.

Tobacco Smoke Studies

We have continued our work on the generation and characterization of test atmospheres of environmental tobacco smoke (ETS). The University of California - Davis is conducting a study of the effects of ETS on the lung development of rodent neonates. Last year, we installed an exposure system developed for the generation of a controlled atmosphere of simulated ETS, using as a surrogate highly diluted sidestream cigarette smoke (SS). The system functions by serially diluting SS through two chambers, the second of which is used for the animal exposures. The dilution scheme can be adjusted so as to provide a range of exposure conditions. Real-time monitoring systems employed for exposure documentation include nondispersive infrared and electrochemical monitors for carbon monoxide and small automated piezobalances for determination of respirable suspended particulates (RSP). This year, we have continued to provide experimental design guidance, as well as analytical chemical documentation of the exposure atmospheres. Nicotine is determined by collection on XAD-4 resin traps, and analysis using GC with nitrogen specific detection. The volatile

organic gas phase composition is determined by collection on multisorbent traps, which are returned to ORNL for thermal desorption GC and/or GC/MS analysis. Results from the documentation studies have indicated that the relative composition of surrogate ETS is similar to that determined for more dilute experimental atmospheres generated at ORNL.

We have recently completed a monograph entitled *Environmental Tobacco Smoke: Concentrations, Composition, and Measurement* for the Center for Indoor Air Research. The objective of the book is to provide a tabulation and integrated review of field studies of ETS and its relationship to indoor air pollution. A secondary objective is to provide background information on smoke chemistry, sampling and analytical methodology for the primary ETS constituents, and non-ETS sources of indoor air pollution. The book is comprised of chapters on field studies of RSP, nicotine, CO, volatile organics, trace organics, oxides of nitrogen, and formaldehyde, as well as chapters on the chemical composition of ETS, SS, and mainstream smoke. Based on our review of the literature, conclusions include:

While most human exposures are $\leq 150\ \mu g/m^3$, study comparisons between smoking and nonsmoking locations inevitably find higher levels of RSP in smoking areas. The differences can range from small to quite large, but, typically, smoking levels are a factor of 1.5 to 2 greater.

Most individuals in the most common public exposure settings (e.g., offices, restaurants, public buildings) encounter nicotine concentrations of 10 $\mu g/m^3$ or less. Higher exposure settings (e.g., bars, smoking sections of conveyances) yield nicotine concentrations 2-3 times greater.

Given the variation from, and multiplicity of, background sources, it is very difficult to discern the magnitude, if any, of excess exposure to CO, NO_x, or volatile organics from ETS.

It is expected that the book will be published before the end of CY 1991.

R. A. Jenkins, B. A. Tomkins,
J. H. Moneyhun, C. E. Higgins, M. R. Guerin

Aerosol Generation, Sampling, and Chemical Characterization

The primary focus of our studies involves atmospheres of significance to the Department of Defense. For example, as part of a joint study with the Separations and Synthesis group's Predictive Surveillance program, we have been developing and characterizing atmospheres to expose nitrocellulose shell casing coupons and depleted uranium penetrator rounds to high urban ambient concentrations of nitrogen dioxide and sulfur dioxide (300 ppb and 500 ppb, respectively). The purpose of these studies is to determine the effects, if any, of these common urban pollutants on the mechanical properties of the test media. The materials are exposed in a chamber fabricated of polycarbonate at thicknesses considered to be explosion proof. The test gases are mixed with dilution air and metered into the chamber at a fixed rate. Levels of the gases can be determined at many points within the chamber, using chemiluminescent monitoring for NO_2 and electrochemical monitoring for SO_2. Interestingly, gas concentrations within the exposure chamber are much lower (factor of 2-3) than those measured at the chamber inlet, probably due to reactions of the gases with the polycarbonate surfaces. Mechanical test studies following eight weeks of exposure have revealed no adverse effects on hardness or tensile strength of the coupons.

In a small project for the Engineering Division supported by the Air Force, we have developed and performed a preliminary characterization of test atmospheres from low-temperature combustion of plastic beads considered for use as a replacement for sand in high-pressure cleaning of paint from aircraft. To determine if the combustion process produces toxic species, two types of plastic beads were heated in an assembly through which air at 500° C was moved. The combustion atmosphere was expelled into a large exposure chamber, to simulate dilution with ambient air. Volatile organics, the target compound class, were collected on multi-sorbent traps. The traps were subjected to thermal desorption GC/MS analysis by the Organic Spectroscopy group. Decomposition products included several substituted aromatics, hydrocarbons and phthalates for one plastic, while the other produced a number of oxygenated species, including phenols, diols and esters.

In order to develop an initial database concerning the potential impact on residential structures of accidental or deliberate releases of chemical agents, we

have been determining the rate at which simulants of these agents [diisopropylmethyl phosphonate (DIMP), dimethylmethyl phosphonate (DMMP), and choroethylethyl sulfide (CEES)] permeate through porous building materials and evaporate into the sampled atmosphere. A permeation rate cell was developed for the purposes of this study. Cylindrical coupons of the test material were placed in the test cell, and three regions were isolated by seals. 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. Results from the scoping studies have been highly variable. Data suggest that this is most likely due to sample-to-sample variability in the individual coupons of porous media which were investigated. In some cases for duplicate experiments, the amounts of simulants permeating the coupons differed by more than factors of 10 - 100. In other experiments, there was evidence of simulant decomposition during transport through the media. Some of the important observations have been as follows: for gypsum board, permeation of the DIMP and DMMP through the material at normal ambient temperatures occurs within 10 hours. The rate increases with elevated temperatures. Lateral transport occurs much more slowly. For wood, the primary transport direction is laterally (with the grain). CEES penetrates wood much more rapidly, and in both directions. Not surprisingly, the transport of the simulants through large pore materials (concrete and brick) is much less reproducible.

We are planning a major upgrade of our aerosol testing and characterization capabilities with the installation of a room sized chamber at Building 5507. The system will feature temperature and humidity control over a range of conditions (10 - 30°C and 20% - 80%), and will be linked to several different aerosol and vapor generation systems. The system will be capable of control of air flow and exchange rates over a wide range, providing us with the capacity to generate large-scale test atmospheres over a concentration range of several orders of magnitude. While its purposes are potentially numerous, one of its primary missions will be the challenge of instrumentation being developed in this and other sections within the division under realistic conditions. For example, one challenge scenario may be to determine the

efficacy of portable explosives detection equipment in the presence of potentially confounding atmospheres of tobacco smoke or off-gassing components from furniture or carpet binders. Interfaced to the chamber will be a number of on-line analytical systems, including particulate sensors, non-dispersive infrared, chemiluminescent, and electrochemical monitors. These will provide independent documentation of chamber atmosphere compositions using more conventional parameters. We expect to finalize requisition of the chamber by the end of the calendar year, with installation by early spring.

J. H. Moneyhun, R. Merriweather,
*R. A. Jenkins, T. M. Gayle**

*Instrumentation and Controls Division

Field and Environmental Analytical Chemistry

An important aspect of our program has been the development of new analytical methods for contaminants related to previous operations at the Army's Rocky Mountain Arsenal (RMA). A major toxic byproduct of the manufacture of the chemical agent Sarin is diisopropylmethylphosphonate (DIMP). Because of the potential for DIMP present in groundwater to concentrate in growing plants irrigated with that water, we were requested to develop a method for DIMP in consumer vegetables. The target quantification limit was 50 ng/g. While a number of approaches were investigated, the one which proved most successful involved initial liquefying of the material in a blender, followed by cell disruption in a tissue homogenizer. For material with low moisture content, such as wheat, it was necessary to add water to facilitate DIMP extraction. The wet vegetable pulp is then extracted with methyl tertiary butyl ether (MTBE), which is further reduced in volume. An aliquot of the extract is subjected to GC analysis with a thermionic detector operated in the phosphorus specific mode. It appears possible to achieve good quantitation at levels as low as 10 ng/g without further analytical refinements.

Another important contaminant at RMA is the carcinogenic pesticide dieldrin. Since it was deemed likely that local regulatory pressure would push required quantification limits markedly below the current EPA standard of 50 ng/l, we were tasked with developing a method with detection limits near 1 part per trillion. To this end, we have

developed a rapid quantitative procedure for eight selected organochlorine pesticides (OCP) (aldrin, isodrin, gamma chlordane, alpha chlordane, DDE, dieldrin, endrin, and DDT) in natural groundwaters. The key feature in the method is the use of Teflon filter disks which have been impregnated with organo-modified (C_{18}) silica particles to extract the nonpolar OCP. The disks are conditioned with ethyl acetate, methanol, and water before passing 1 liter water samples through them under vacuum. The OCP are eluted with 10 ml ethyl acetate (later concentrated to a final volume of 1 ml), then separated and quantitated using a dedicated capillary column gas chromatograph with a high-sensitivity electron capture detector. In practice, the sample handling procedure is rapid and easily executed, while generating minimal volumes of hazardous waste. Recoveries for the eight pesticides ranged between 49% (aldrin) to 93% (dieldrin) at low ng/l levels. Limits of quantification were determined using the Army's Certified Reporting Limit (CRL) procedure and the EPA's Method Detection Limit (MDL) procedure. In both cases, the MDL and CRL values ranged between 2 and 8 ng/l for the eight target OCP, with a limit of ca. 4 ppt for dieldrin. Irreproducible results observed between 0.5 and 2 ng/l precluded detection limits at the target 1 ng/l level. The method has now been transferred to the Army, and a manuscript submitted for publication.

We have recently initiated a new project for the Laboratory Management Branch of the DOE's Office of Technology Development involving the validation of fieldable analytical methods. The ultimate goal of this project is reduction in laboratory-based analytical costs through the transfer of the technology to other DOE sites and inclusion in the DOE Analytical Methods Compendium. Important aspects are an emphasis on 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. In addition, staff from the group and the Inorganic and Radiochemistry section are involved in order to address the areas of radiochemical, organic and inorganic contamination. Since the project was initiated in mid-year, our efforts have been directed toward the assessment of DOE complex needs, decisions as to which

technologies each lab should stress, and development of strategies for the cost-effective field validation of candidate methods. The needs assessment has indicated that contamination by chlorinated organic solvents is the most common problem complex-wide, with radionuclides a near-second priority. Other contaminants which appear ubiquitous include selected metals, inorganics, and PCB's. As we move into the experimental phase of the project, our activities will shift to field validation using selected ruggedness testing and appropriate QA measures.

We have been investigating the use of carbonaceous multi-sorbent 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 advantages over earlier systems, including desorption at much higher temperatures, which enhances analytical efficiency and provides fewer chemical artifacts. One potential use is the stabilization of volatile organics purged from soil and water, so that actual environmental samples do not have to be returned to the laboratory for analysis, with all of the attendant holding-time difficulties. Tests performed this year with these small traps (75 mm long x 6 mm OD) showed that selected chlorinated organics, as well as benzene and toluene, could be purged from water, trapped, and determined with near 100% efficiency, and detection limits in the range of 100 pg. Their use in the field under high humidity conditions for soil gas sampling was demonstrated, in conjunction with the direct sampling ion trap mass spectrometer real-time monitor (RTM) being developed by the Organic Spectroscopy group, at the Savannah River Integrated Demonstration Project (SRIDP) site. Soil gases purged from an Army-deployed subsurface interface were collected on these traps and successfully analyzed upon return to ORNL, in order to provide qualitative and quantitative calibration for the RTM.

Another important use of these traps will be their deployment in a deep subsurface vadose zone sampler being developed by our group for use at the SRIDP. The device will house six traps, and be deployed at depths as much as 38 m. Because of the concentrating ability of the traps and the design of the sampler in which they are used, it will be possible to acquire time and/or spatially resolved soil gas samples which require so little sample that subsurface equilibria will not be disturbed. This capability is especially important in geologic strata of low

permeability. The sampler, sufficiently small to fit inside a 10 cm diameter well, has been fabricated and is undergoing final laboratory trials prior to field deployment this winter. As part of this project, the principal investigator has been acting as the head of the Monitoring Technical Support group for the Savannah River and Hanford Arid Sites IDP's. This group acts to review and evaluate chemical and geophysical monitoring technologies for support from and demonstration at the two projects, as well as coordinating monitoring-related field activities, and acts in an advisory capacity to the overall planning groups.

B. A. Tomkins, C. E. Higgins,
R. Merriweather, J. H. Moneyhun,
*R. A. Jenkins, T. M. Gayle**

*Instrumentation and Controls Division

ORGANIC ANALYSIS

M. P. Maskarinec

The Organic Analysis group performs quantitative analysis 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 work 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 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 20 full-time staff members, as well as supplemental staff from the Separations and Synthesis group.

The primary missions of the group are supported by four interdependent efforts: 1) sample receipt and tracking; 2) sample preparation; 3) gas chromatographic and gas chromatography/mass spectrometric analysis; and 4) reporting and quality control. The first three areas have designated task leaders;

the reporting and quality control function is the responsibility of the group leader. In each of these areas, both staff and equipment capabilities have been expanded and/or upgraded during the previous year. In addition, we have continued to maintain our drinking water certification for the analysis of volatile organic compounds by acceptable performance on EPA WS series quality control samples as required by the State of Tennessee. A significant effort has also been directed at adequate performance on the monthly performance evaluation samples provided by the Analytical Products Group.

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 24 months, 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 in a time when more and more of the data generated are being reviewed for use in litigation. In addition, many of the programs are now adopting a "contract analysis" system in which the terms of all work are spelled out in advance of initiation of the project. This is in some ways an advantage and in some ways a disadvantage. From the standpoint of the laboratory, there is a known and agreed-to flow of samples; from the standpoint of the customer, there is a known and agreed-to schedule for completion of the work. This puts additional pressure on the laboratory manager to assure that deadlines can be met, but allows that person to decide if work should be done elsewhere.

M. P. Maskarinec, L. F. Eberlein, S. E. Cox, R. L. Williams*

*Oak Ridge Research Institute

Sample Preparation

The major change in the sample preparation laboratory has been the appointment of a task leader whose function is to assure that current methodology and equipment are available and being used. The most visible and important effort by far has been the need to implement the Toxicity Characteristic Leaching Procedure (TCLP, method 1311). This procedure was developed in part at ORNL and has become a very important test in the classification of waste materials. At the time of promulgation, there were several issues which were not resolved to the point that reasonable audits could be made, or that reasonable training procedures could be implemented. The output of the test is an extract, which is an aqueous medium. The extract is analyzed for volatile organics, semivolatile organics, pesticides, herbicides, and the eight RCRA metals. Thus, in terms of the organic preparation, the test is run, and then the extract is prepared in the water preparation area. Furthermore, there are holding time limitations on all steps of the process.

The TCLP was implemented in this reporting period. After the successful development of the testing protocol, we turned our attention to the study of those variables which had an effect on the outcome of the test, and to those sample types for which results deviated from those observed using the previous method. A task group was convened consisting of staff members from each lab performing the TCLP within Energy Systems. The charter of this group was to assure that all Energy Systems facilities performed the test in such a manner that the data would be comparable. In the process, it was discovered that several relatively minor discrepancies in the conduct of the test had major regulatory implications. For example, the measurement of pH (normally considered a trivial determination) was shown to have a profound impact on the result of the TCLP test in a sludge contaminated with chromium. This sludge had always passed the formerly utilized EP-Tox test, and was therefore expected to pass the TCLP. However, the buffering capacity of this waste was right at the borderline for determining which extraction fluid must be used. Samples which required extraction fluid 1 (pH 4.9 acetate buffer) consistently passed the test with no chromium being leached. Those which required extraction fluid 2 (0.1N acetic acid) failed the test. The

subsequent work indicated that the entire process of measuring pH was fraught with sources of variability. The rate at which the waste is equilibrated with the titration fluid is critical: there was a significant difference between the use of a water bath and the use of a hot plate. The degree to which the waste was stirred also had a significant impact on test results (the method only states "slurry briefly"). The result of these studies has been the implementation of a Five Plant committee to standardize the methodology used in the test. Many other matrices have been tested during the year, including hood ducts, sorbents, and even fluorescent light bulbs.

Additional developments in sample preparation include beginning the implementation of the "Liquid Release Test", a test promulgated by EPA under RCRA and designed to prevent the land disposal of waste containing free liquids. This test has some of the same properties as the TCLP, and may require the same type of rewriting in order to assure that all labs get the same results. Basically, the test involves placing a waste sample in a closed cylinder with filter paper on both ends, compressing the waste using gas pressure, and then examining the filters for evidence of liquid release. As such, the test is completely manual and may be subject to significant variability.

We have also procured new equipment for Soxhlet extraction. This equipment will allow extraction of multiple samples in a reliable, reproducible manner.

M. P. Maskarinec, R. H. Ilgner,
G. M. Henderson, P. A. Marshall,
J. L. Slabaugh, C. M. Rogers*,*
C. A. Biggs, D. L. Trent,
B. L. Wilson, W. M. Caldwell,*
J. H. Moneyhun

*Oak Ridge Research Institute

Gas Chromatography

The gas chromatography laboratory is currently staffed by two chemists, one technician, and one hourly maintenance person. Available instrumentation includes ten gas chromatographs, including eight equipped with automatic sample injectors. Seven instruments are normally configured with electron capture detectors for pesticide/PCB analysis and three gas chromatographs have been configured with flame ionization detectors for screening, total

petroleum hydrocarbons, and TCLP phenols. In a separate laboratory, two automated purge-and-trap samplers are now coupled with gas chromatographs for the analysis of volatiles. All systems have capillary capability (either narrow bore or megabore); two remaining instruments use packed columns. Many of these chromatographs have considerable downtime due to the age of the instrument and also to the increased numbers of highly contaminated samples. The laboratory has added Nelson Analytical's Turbochrome PC-based data system, which is currently being utilized. In addition, two new Hewlett-Packard model 5890 instruments have been added along with the HP data system. This system is to be networked with the GC/MS data system for the automated generation of CLP forms.

An HP 5890 has recently been acquired from Metals and Ceramics Division (on loan). This instrument is equipped with dual packed column (megabore capillary) injectors, single flame ionization detector, single thermal conductivity detector, and robotic autosampler. It will be dedicated to the analysis of total petroleum hydrocarbons.

Methodology used in the gas chromatography laboratory includes SW-846 (RCRA) methods. Method 808 is usually used for samples requiring pesticide/PCB analyses, with the exception of those samples originating as a result of NPDES permit requirements, which are analyzed using method 608. The two gas chromatographs equipped with automatic purge-and-trap samplers are used to screen volatile samples before gas chromatography/mass spectrometry analysis; one instrument is devoted to screening TCLP extracts and the second instrument is used to screen waste dilutions and soil samples. BTEX (benzene, toluene, ethylbenzene, xylenes) determinations are also performed on the instruments in support of underground storage tank remedial actions.

Acrylamide in water samples was determined using a modification of SW-846 method 8032. This method as written involves bromination of the acrylamide double bond and extraction with ethyl acetate. Gas chromatographic analysis is performed according to SW-846 method 8000. The method is intended to detect acrylamide in groundwater at the part-per-trillion level. In practice, we were able to obtain reliable quantitation limits of 10 ppb after adaptation of the method. The primary modifications were the replacement of diethyl phthalate with tetrachloro-m-xylene as

the internal standard, and the use of two megabore capillary columns rather than the prescribed packed columns. In addition, we were able to obtain the pure calibration standard 2,3-dibromopropionamide from a Japanese manufacturer, which allowed the quantitation of the acrylamide without the bias associated with the derivatization procedure. Almost 400 samples were analyzed and/or reanalyzed using this method during 1990. An additional 100 samples were analyzed during 1991. In general, the performance has been good in terms of recovery, sensitivity, and reliability.

Ethylene glycol test kits (Chemetrics) are now used for water samples. The test requires approximately ten minutes and can detect 1 ppm ethylene glycol in water. Since relatively few samples are submitted, and those that are submitted usually require immediate turnaround, this has allowed us to provide better service while freeing up a gas chromatograph which was previously dedicated to this analysis. During 1991, the cooling system in the 4500S complex has been drained of ethylene glycol, and we have been asked to provide almost instantaneous support of this process. We were able to detect ethylene glycol at <.01% without great difficulty.

M. P. Maskarinec, R. M. Edwards,
S. M. Smith, S. C. James,
R. R. Smith, S. A. Harper,
C. A. Biggs

Gas Chromatography/Mass Spectrometry

The GC/MS laboratory performs routine analyses primarily on environmental samples. The effort has been divided during the previous year between the analysis of volatiles and the analysis of extractables. Currently, four staff members are assigned to the laboratory which is concerned with the analysis of volatiles, with an anticipated addition of one to two chemists in the near future. 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 volatile organic analysis (VOC) GC/MS systems have been purchased this year. One of the instruments has been dedicated to the determination of organics in drinking water (EPA method 524.2) and the other to increase our capacity for VOA TCLP analysis.

Both of the new volatile organic systems have been installed with wide bore capillary columns. Several wide bore columns, including a 75 m Restek column, were evaluated. A narrow bore DB-5 capillary column has proved to be the most reliable in terms of tuning and QA/QC acceptance criteria, and has allowed us to shorten our runtime by a factor of two compared to the packed column method. The importance of the reduction in runtime comes from the QC requirement for a GC/MS tune once every 12 hours. The shorter the analytical runtime, the more samples which can be analyzed within the 12-hour window.

A new purge and trap inlet 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 other early eluting analytes. 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.

M. P. Maskarinec, S. H. Harmon,
S. A. Harper, S. F. Glover,
J. C. Montgomery, J. T. Skeen

Reporting and Quality Control

Significant efforts during the past year were devoted to improving the quality of the work of the group. In the previous year, much of this effort was directed by the Tiger Team preparations, but other signs of improving quality can now be seen. For example, performance on external evaluation samples improved throughout the year, initiated with a perfect score on the third quarter FY-90 sample. As already mentioned, certification was obtained from the State of Tennessee for performing drinking water analyses and it has been maintained. This certification is a result of satisfactory performance on external samples for four consecutive periods, as well as an on-site laboratory evaluation. In addition, we have participated in the performance evaluation program administered

commercially by the Analytical Products Group. Our scores have been steadily improving, and have had no outlier results in the last four months. 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 taken to improve the situation. Where the group leader was previously reviewing all results prior to and after reporting to ANALIS, task leaders have been assigned the responsiblity 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 error. All data are still being reviewed at a minimum of at least two levels prior to release. All QC samples are now reported directly to the division QCO. Finally, an attempt is under way to allow all QA/QC data to be surveyed for usability by the group leader. Much work remains to be done (e.g., SOP's need updating, new methods must be implemented, and more data must be electronically reviewed) but significant progress has been made.

M. P. Maskarinec, R. L. Williams,
L. F. Eberlein, R. M. Edwards

ORNL/UT RESEARCH PROGRAM

G.A. Guiochon

Research on chromatography at high concentrations and on gas-solid adsorption has continued. During the past year, we have:

- demonstrated the validity of the theory of nonlinear chromatography and defined the range of applicability of the equilibrium-dispersive and the kinetic models of chromatography,

- developed a theory of optimization of the experimental conditions for maximum production rate in preparative chromatography,

- shown the relationships between equilibrium isotherms and band profiles, developed new methods of measurement of competitive isotherms and studied the modelling of these isotherms,

- developed, validated and applied a new method of characterization of nonhomogeneous surfaces of powders using gas chromatography.

Theory of Nonlinear Chromatography

The major aim of our research is to achieve a degree of understanding of non-linear chromatography such that the optimum values of the design and operating parameters of a preparative chromatograph could be calculated from a small number of laboratory scale experiments. To achieve this aim, we need an exact model of the behavior ofchromatographic columns under nonlinear conditions, and simple procedures to determine the competitive equilibrium isotherms of the feed components and the rates of the mass transfer phenomena involved.

Our work has led to serious progress in some of these areas and unexpected difficulties in others:

A. Based on a number of different comparisons between experimental and calculated individual band profiles for binary separations, we demonstrated the predictive value of the theory of nonlinear chromatography;

B. This theory can be used for the optimization of the experimental conditions in preparative chromatography;

C. Great difficulties are encountered in the experimental determination of competitive equilibrium isotherms, in their modeling, and in their prediction from single component data.

A few examples from our publications provide a summary of these results.

A. Validation of the Theory

One of the most important results of our recent work is the validation of the theoretical

model used to calculate the individual elution profiles of the components of a mixture.

The theory of chromatography is based on the integration of the system of mass balance equations which describe the system:

$$u\frac{\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + F\frac{\partial q_i}{\partial t} = D\frac{\partial^2 c_i}{\partial z^2} \quad (1)$$

This equation contains two functions, q_i and C_i, the mobile and stationary phases concentrations of each component i, two variables, the position (z) and the time (t), and three parameters, the mobile phase velocity (u), the phase ratio (F), and the axial dispersion coefficient (D). We need to relate q_i and C_i in Equation 1.

Three models are available, the ideal model (Box 1), the equilibrium-dispersive model (Box 2), and the kinetic models (Box 3).

- Equilibrium between phases is achieved at all times,
- The column efficiency is infinite, and D = 0 in Equation 1,

1 - The Ideal Model

- Equilibrium between phases is achieved at all times,
- The influence of mass transfer kinetics is accounted for by an apparent dispersion coefficient, and D = Hu/2 in

2 - Equilibrium-Dispersive Model

The ideal model gives an excellent description of the basic phenomena which control band profiles in nonlinear chromatography but cannot accurately account for actual profiles since it assumes a column of infinite eefficiency. Kinetic models require an equation relating the derivative $\partial q_i/\partial t$, the concentrations q_i and C_i and the isotherms. Most often their use is not required, the simpler equilibrium-dispersive model providing the same profiles, without the need of rate constants. We studied the properties of the solutions of the equilibrium-dispersive model, and compared the various procedures of numerical calculation and the errors made.

- Thomas model: Langmuir kinetics, no axial dispersion.
- Reaction-Dispersive: Thomas model with axial dispersion.
- Transport-Dispersive: Slow mass transfer kinetics with axial dispersion.
- General Rate Model: slow adsorption/-desorption, slow mass transfer kinetics,

3 - Kinetic Models

We investigated the band profiles of a number of binary mixtures. These include 2-phenyl-ethanol and 3-phenyl propanol, cis- and trans-androsterone, cholesterol and cholesteryl formate, N-benzoyl D- and L-alanine, N-benzoyl D- and L-phenyl alanine, D- and L-mandelic acid. In some cases, we measured the single component isotherms and used classical competitive isotherm models. In others (A,B), we determined the competitive isotherms.

The isotherm models used are the Langmuir (Eq. 2) and the bilangmuir (Eq. 3) equations for single component isotherms and the corresponding competitive isotherms (Eqs. 4 and 5). The Langmuir model assumes that the column saturation capacity is the same for both components (e.g., optical isomers). If these capacities are different (B), the Langmuir isotherm is not thermodynamically consistent, and the Levan-Vermeulen isotherm must be used instead.

$$q = \frac{a\,C}{1 + b\,C} \qquad (2)$$

$$q = \frac{a_1 C}{1 + b_1 C} + \frac{a_2 C}{1 + b_2 C} \qquad (3)$$

$$q_i = \frac{a_i C_i}{1 + b_1 C_1 + b_2 C_2} \qquad (4)$$

$$q_i = \frac{a_{i,1} C_i}{1 + b_{1,1} C_1 + b_{2,1} C_2} + \frac{a_{i,2} C_i}{1 + b_{2,1} C_1 + b_{2,2} C_2} \qquad (5)$$

We show in the following Figures the isotherms of N-benzoyl D- and L-alanine on immobilized bovine serum albumin (Fig. 1), the elution profiles of large amounts of the D-enantiomer (Fig. 2) and the interference profiles of the racemic mixture (Fig. 3). The isotherms are well accounted for by a bilangmuir equation (Eq. 3). The experimental band profiles determined by fraction

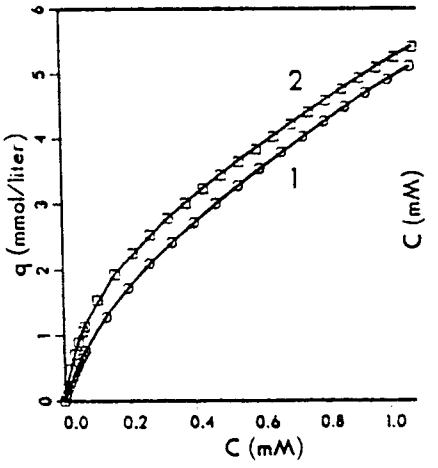


Figure 1. Isotherms of N-benzoyl-D, L-alanine on Immobilized BSA

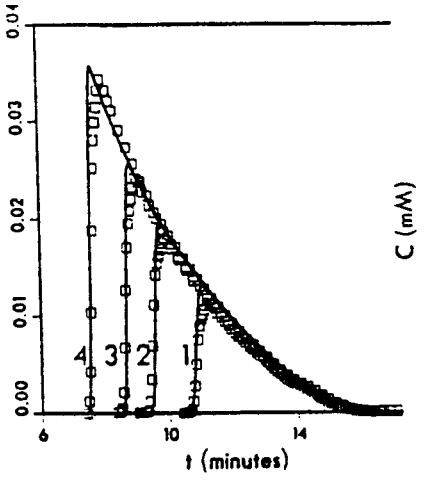


Figure 2. Elution Profiles of Large Samples of N-benzoyl-D-alanine on BSA

collection and analysis are in excellent agreement with those calculated from the competitive isotherms derived from single component isotherm measurements (Fig. 3).

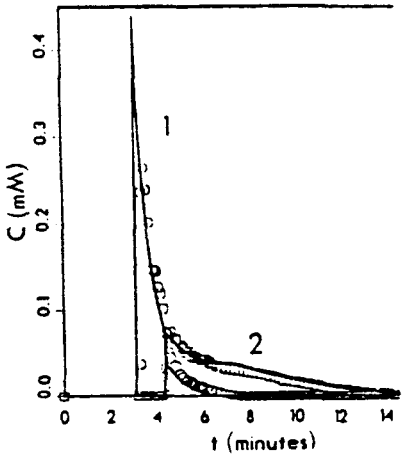


Figure 3. Elution Profile of the Racemic Mixture of N-benzoyl-alanine

In Figure 4, we compare the experimental (symbols) and calculated (lines) band profiles for 2-phenylethanol and 3-phenylpropanol. The two sets of lines are calculated using Langmuir isotherms. The parameters of the isotherms for the dotted lines are measured with frontal analysis, those for the solid lines with a new method, based on the simple wave theory.

In Figure 5, we compare the profiles obtained under linear (small peaks) and nonlinear (large bands) conditions for cis- and trans-androsterone. Both experimental and calculated profiles exhibit a reversal of the elution order with increasing sample size. This phenomenon cannot be explained by the Langmuir isotherms but requires the use of the Levan-Vermeulen isotherm which takes into account the difference in column saturation capacities (i.e., of the molecular "footprints").

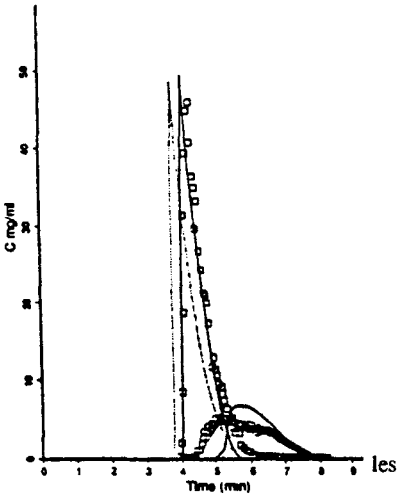


Figure 4. Comparison of Calculated and Experimental Profiles for a Mixture of 2-phenylethanol and 3-phenylpropanol

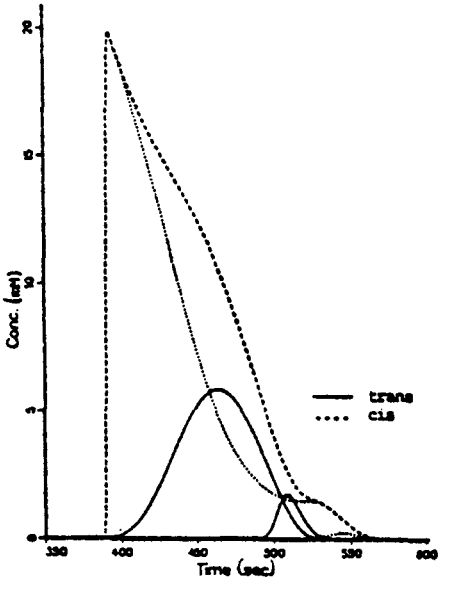


Figure 5. Inversion of the Elution Order of Cis- and Trans-androsterone at High Concentration

Finally, in Figure 6, we compare the profiles obtained for 2-phenylethanol (loading factor, 20%) eluted with a linear concentration gradient of acetonitrile (2%/min). Although it is more difficult to obtain a proper representation of the isotherm to account for band profiles in gradient elution, because the maximum concentrations of the bands are higher, the agreement between theory and experiment is again excellent.

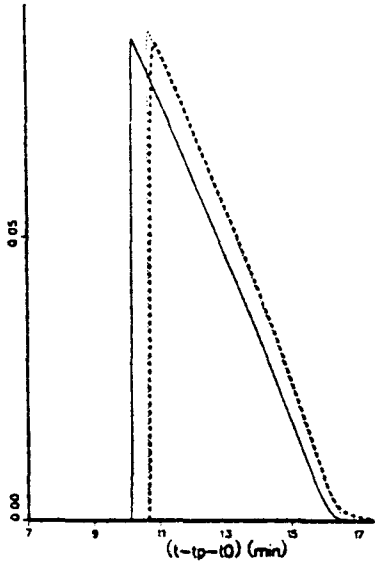


Figure 6. Calculated and Experimental Profile of 2-phenylethanol in Gradient Elution

B. Optimization of Experimental Conditions

We have shown that, provided all the experimental conditions are optimized, the maximum production rate is proportional to $\sqrt{P}$ (P, pressure under which the column can be operated), and to $[(1-\alpha)/\alpha]^3$ (α, relative retention of the two components). We demonstrated how to calculate the optimum experimental conditions for maximum production rate. Under the experimental conditions giving the maximum production rate, the recovery yield is usually low. We have calculated the possible trade-offs between production rate and yield. A typical example (α=1.2, k'_1=3, ΔP = 10 MPa) is given in Table I.

Table I. Trade-offs between Yield and Production Rate

Yield (%)	N_0 Plate	L (cm)	Production Rate
60	550	8.5	0.46
80	650	9.7	0.41
90	825	11.	0.36
95	1050	12.5	0.32
99	1800	17.3	0.23
99.9	3000	23.5	0.17
100	3200	24.5	0.07

These theoretical results, confirmed by some application studies, allow the easy selection of experimental conditions.

C. Study of Phase Equilibria

Our theoretical studies of nonlinear chromatography have shown the extreme importance of an accurate determination of the equilibrium isotherm for an exact

prediction of the band profile. The non-linear Scatchard plot (Fig. 7) shows experimental data for N-benzoyl phenylalanine on immobilized BSA and proves that the isotherm does not follow the Langmuir model.

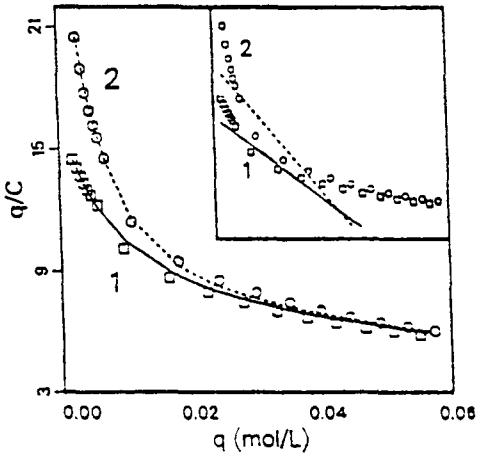


Figure 7. Scatchard Plot of the Isotherm of N-benzoylphenylalanine on Immobilized BSA

In Figure 8, the experimental chromatogram (symbols) of the racemic mixture is compared with the individual profiles calculated with the bilangmuir and the Langmuir

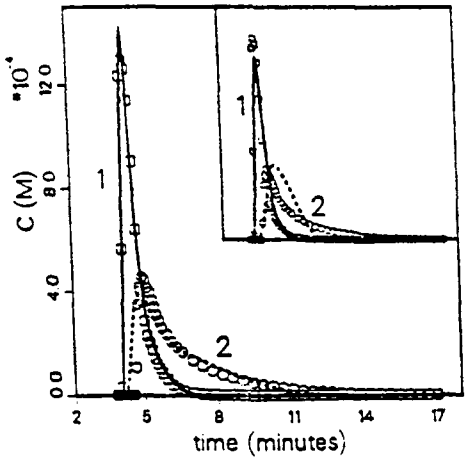


Figure 8. Experimental and Calculated Chromatograms of a Racemic Mixture of N-benzoylphenylalanine

(inset) isotherms.

The two terms of the bilangmuir isotherms of enantiomers adsorbed on a chiral selective phase correspond to the chiral and achiral interactions, respectively. This has been demonstrated in the three cases studied on BSA. A bilangmuir model requires 4 parameters for each adsorbate. For enantiomers, 5 parameters are needed instead of 8 because the isotherm parameters corresponding to the achiral interactions are identical for both isomers and their saturation capacities on the chiral selective sites are identical: this site seems to be the hydrophobic cavity of the BSA molecule. Because they present themselves as rather pure binary (racemic) mixtures, have identical properties except those concerned with the chiral interactions, and because the chiral sites are usually easily saturated, in a low range of concentrations where deviations from Langmuir adsorption behavior are minimal, the study of the adsorption isotherms of enantiomers and the band profiles of racemic mixtures is clean from a theoretical viewpoint. Pairs of less similar isomers raise more complex problems. This is also a problem of great practical importance since the pharmaceutical properties of the two enantiomers are often different.

Competitive isotherms are needed for any successful prediction of multicomponent

band profiles. With enantiomers on BSA, the competitive bilangmuir model gave good results. For cis- and trans-androsterone, which have different conformations, the column saturation capacity ratio is 1.3. We previously determined the competitive equilibrium isotherms on silica and showed that the single component isotherms are well accounted for by the Langmuir model and the competitive isotherms by the Levan-Vermeulen model (Fig. 5). Experiments on chemically bonded phases lead to different conclusions.

A fit of the experimental single component isotherm data of 2-phenylethanol and 3-phenylpropanol to the Langmuir isotherm is only good. Not surprisingly, the competitive Langmuir isotherm fits the multicomponent data only approximately. A new method of determination of isotherms much faster than frontal analysis and potentially at least as accurate was developed and used to study the isotherms in this system. The individual elution profiles of a wide rectangular injection pulse are determined (Fig. 9) and the concentration of one component is plotted versus the concentration of the other (Fig. 10). The experimental points define two lines from which the isotherm parameters can be derived. However, experimental data are rarely consistent with a Langmuir competitive model: the parameters derived depend on the feed composition.

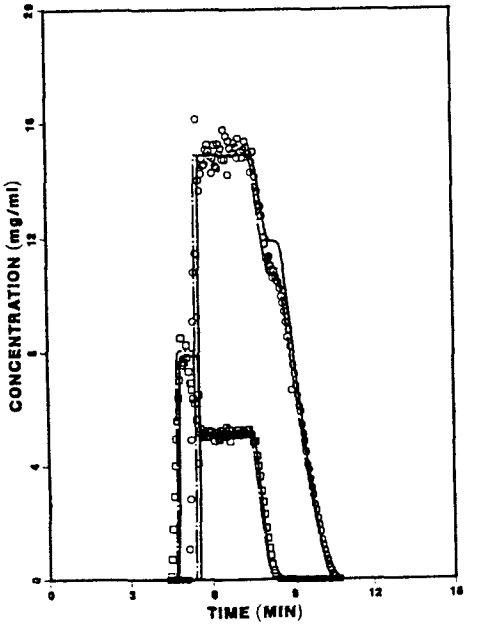


Figure 9. Elution Profile of a Wide Injection Pulse of a Mixture of 2-phenylethanol and 3-phenylpropanol

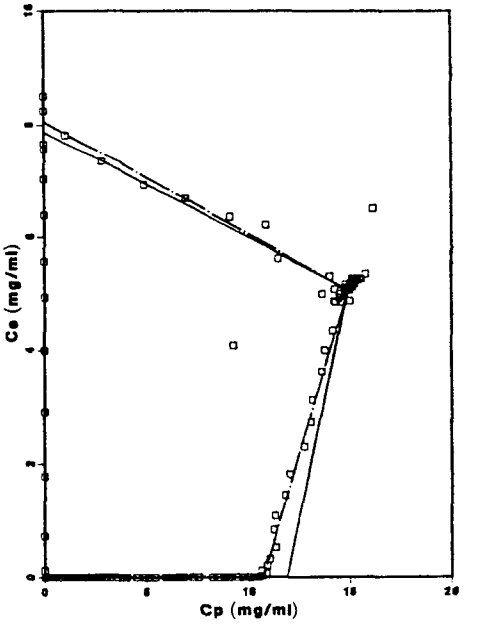


Figure 10. Hodograph Plot of the Elution Profile in Fig. 9

Recent measurements on this pair, with the same phase system, suggest that the data would follow a competitive Fowler model.

Adsorption data measured on other compounds suggest a great variability of the isotherm model for single component data (e.g., bilangmuir for cholesteryl formate and lysozyme on C18 bonded silica, Langmuir plus linear term for cholesterol on C18 bonded silica, bilangmuir for cholesterol on silica). Methods for the selection of isotherm models to fit single component experimental data and models permitting the prediction of competitive adsorption data from single component isotherms are needed for any systematic investigation of the influence of the chromatographic system on the production rate, recovery yield and cost in preparative chromatography. Conversely, as shown in our study of enantiomers, isotherm data may give new information regarding the separation mechanism.

G. A. Guiochon, M. Diack[*], *E. V. Dose*[*], *M. Z. El Fallah*[*], *A. Felinger*[*], *S. Golshan-Shirazi*[***], *S. Jacobson*[**], *P. Jandera*[***], *Z. Ma*[***], *J. Zhu*[***],

[*] UT Postdoctoral Program

[**] UT Predoctoral Program

[***] University of Tennessee

Capillary Zone Electrophoresis

We have developed a new procedure for the calculation of band profiles in capillary zone electrophoresis. We use new methods of managing time and space increments in solving the mass balance equation and segment the column in active and inactive regions. This method permits important savings in computer time. The peak shapes obtained in linear CZE experiments match the shapes, areas and widths expected from theory. The numerical solutions are very stable. Simulations demonstrate the feasibility of simulating practical experiments with realistically low dispersion.

The amount of analyte actually injected into an open capillary by hydrodynamic siphoning or electromotive force is modified by two effects, diffusion and inadvertent hydrodynamic flow. Diffusion causes net flow into or out of the capillary whenever there exists a concentration gradient at the capillary inlet. It is most important for small molecules, for short injection zones, and for slow injection sequences. Inadvertent hydrodynamic flow, most likely caused by a difference in levels of the liquids in the two reservoirs, is most important for liquid level differences of a few millimeters or more, for short

inside diameter. Computer simulations of the first millimeters of capillary length show how concentration profiles can develop rapidly.

A new method of internal standardization was found in the linear relation between each ion's effective volume injected and its inherent mobility. The use of two internal standards allows the analyst to establish this relation quantitatively for each sample and to correct the analyte concentrations for variations in each injection. The computational method given is simple, and we demonstrated experimentally that it can give reproducibilities for manual CZE hydrodynamic and electrostatic injections of under 1% relative standard deviation.

*G. A. Guiochon, E. V. Dose**

---

* UT Postdoctoral Program

Study of the Surface Properties of Ceramic Materials by Chromatography

We have developed a practical method which permits the detailed study of the chemical properties of nonhomogeneous surfaces. This method is based on the determination of the adsorption isotherms of a series of carefully selected probe components on the surface of the studied material. From these isotherms, we can derive the energy distribution function and the energy of formation of a monolayer of these probe compounds. The probes are chosen after consideration of the nature of the surface studied and of the other products involved in the relevant process.

The characteristics of the adsorption energy distribution functions and the monolayer formation energies of probe compounds on a given surface can be related to the performance of the corresponding material in actual production. If the distribution function differs for products which perform well and for those which behave poorly, the method can be used for quality control.

The measurements were made with a Perkin Elmer gas chromatograph on which we have moved the pressure sensor to just upstream of the injector, to control better the column inlet pressure, hence the flow rate. The experimental conditions are extremely stable and the results have been highly reproducible, which has contributed markedly to the success of our work.

A. Column Preparation

Porous Layer Open Tubular (PLOT) columns with an inner wall coated with a

homogeneous thin layer of very small particles are made by evenly filling a 15 m long section of 0.53 mm ID fused silica with a stable slurry of these particles at low concentration (ca. 1% w/w in a dibromoethane/triethylene glycol mixture) and removing the solvent without the settling of the particles. The filled column, closed at one end, is drawn vertically, at a constant rate, into a heated convection oven, through a long metal tube providing a smooth, linear thermal gradient (Fig. 11).

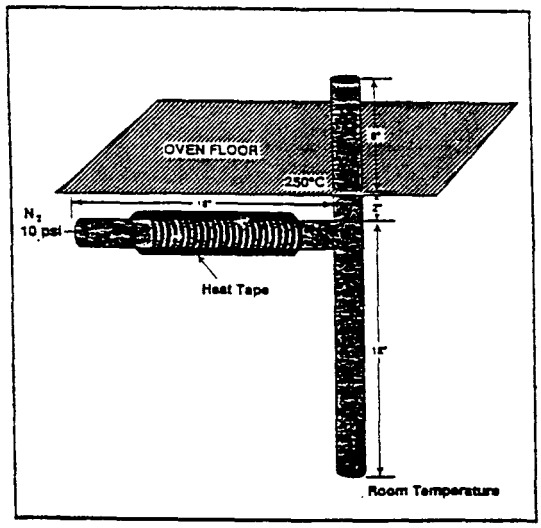


Figure 11. Schematics of the Equipment Used to Prepare the Columns

The column is coiled on a support frame that will be used inside the GC oven, thus eliminating unnecessary handling. The temperature of the slurry-filled column yet to be drawn into the oven must be kept constant, since any expansion or contraction of the solvent will change the effective rate of feed of the solvent-vapor meniscus into the oven.

Conditioning the PLOT column first in the convection oven and then at 350°C in the GC oven removes residual solvent and additives. This treatment improves the mechanical stability of the coating and removes the additives or impurities introduced during the filling and drying steps. All the details of the fabrication procedure have been described.

B. Reproducibility of the Experimental Results

Considerable attention was paid to the development of an accurate method of determination of the adsorption isotherms of the probe compounds. The sources of errors in the acquisition of overloaded elution profiles in gas chromatography have been carefully studied. The experimentation procedure has been designed to reduce as much as possible the magnitude of the errors. Quality control of the experimental results begins with the application of a new procedure which gives the distance between two different experimental profiles and permits the

calculation of this distance. The normalized profiles are defined by arbitrarily setting the peak height equal to 1, the retention time of the band maximum equal to 0 and that of the last data point different from base line equal to 1 (Fig 12a).

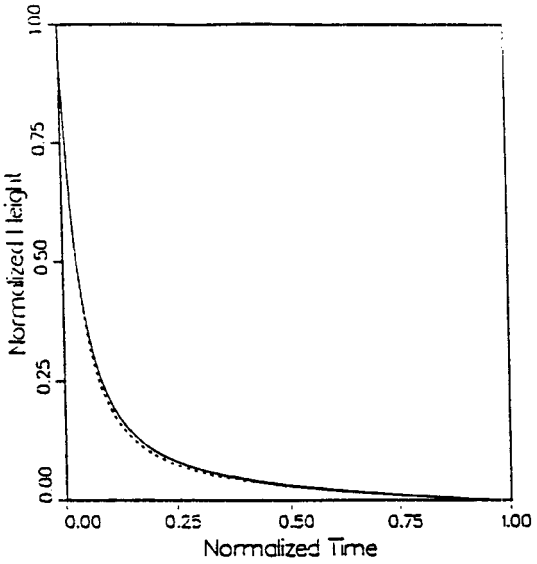


Figure 12a. An Elution Profile

The profile is integrated from the origin (Fig. 12b). Plotting the integral I(τ) for one profile in Figure 12c versus the other one gives the first bisector if the two profiles differ only by a translation and/or a similitude (e.g., two Gaussian curves). When the two profiles are different, a curve such as in Figure 12d (corresponding to the comparison between a Gaussian and a Poisson curve) is obtained.

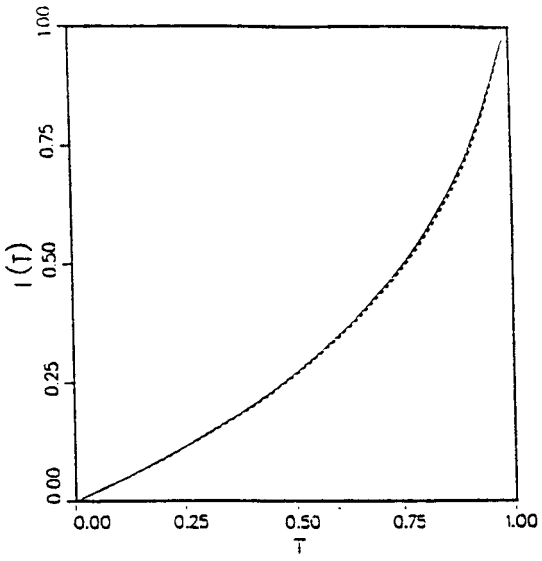


Figure 12b. Indefinite Integral of the Profile

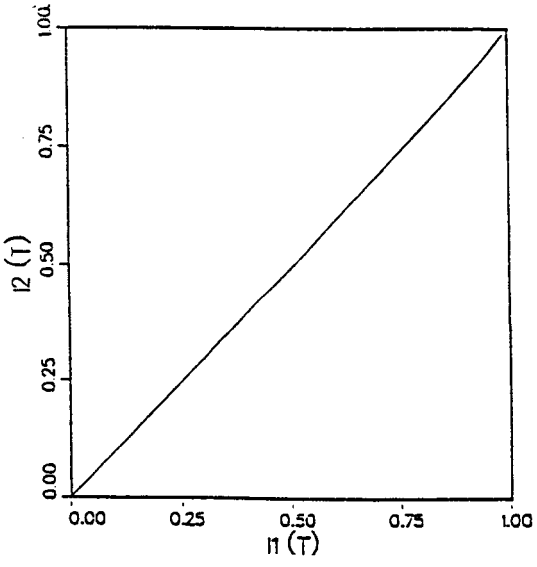


Figure 12c. Plot of the Integral of One Profile Versus the Integral of the Other One. Case of Two Gaussian Curves

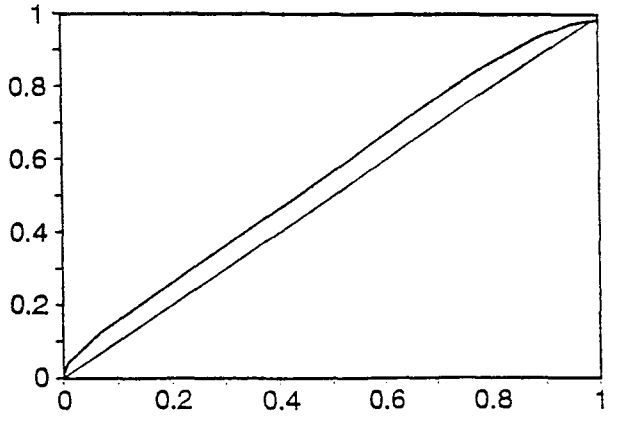


Figure 12d. Same as Fig. 12c, but Poisson Versus Gaussian Curve

The distance between the profiles in a series of successive experiments carried out on the same column should not exceed a threshold determined by the reproducibility of the gas chromatograph. The distance between chromatograms obtained with the same probe compounds, under the same experimental conditions, with different columns is larger than this threshold and determines the precision of the determination of the isotherm. For diethylether on alumina, the adsorption isotherm is well accounted for by an equation summing two Langmuir terms. The relative standard deviation on the coefficients of this equation is slightly less than 0.5%. The process used to manufacture the PLOT columns gives columns which have very reproducible properties.

C. Experimental Design and Data Estimation

The PLOT column is connected to a Perkin Elmer 8500 gas chromatograph and operated isothermally, usually at 40°C with 1-chlorobutane and 60°C with diethylether. Helium is used as carrier gas. A large size sample is injected and the adsorption isotherm is derived from the rear part of the band profile. In all cases so far, the isotherms are strongly convex upward, so the overloaded elution profiles have a steep front, or shock layer, and a diffuse rear. The critical steps of the procedure are the transformation of the chromatogram (time profile of the detector response) into a profile of the partial pressure of the probe at column exit as a function of the gas volume passed, the quantitation of the probe recovery, and the determination of the isotherm.

It is important to determine the exact detector response and to verify that it is linear in the range of concentrations used. Most calibration methods, however, relate the amount injected to the peak area. We need to relate the detector signal at a certain time to the actual concentration of the probe compound in the carrier gas. We developed several procedures for this direct determination, depending whether the detector is

linear or not.

Using the classical calibration procedure, we proved that the detector is linear under our experimental conditions. The calibration curve for the FID is constrained to proportionality of the instantaneous response and the probe concentration in the detector. Only three or four chromatographic peaks are required for calibration. If necessary, other calibration curve shapes could be substituted and their parameters determined by the same method.

Early experiments with alumina suggested that quasi-irreversible adsorption could occur when a probe compound is injected onto a column. An unknown but minor portion of the probe is eluted very slowly. When a temperature programmed run is performed at the end of each experiment, and started after the signal has returned to baseline for about ten minutes, a peak containing a part of the injected probe appears. Detailed analysis of the phenomenon showed, however, that the size of this peak decreases rapidly with increasing time, if the start of the temperature programmed run is delayed. There is no peak if we wait for over 45 minutes before starting the temperature programmed run.

This result is in agreement with the adsorption isotherm determined. Part of the probe sample is bound quite strongly to high energy sites and does not elute readily. The analytical retention time would be very long. Since the amount of high energy sites is small, however, the partial pressure of the probe becomes very low and the signal is lost in the noise. However, the strongly bound solute elutes as a peak during high temperature column conditioning.

Since knowledge of the amount of solute corresponding to a given test peak is essential, we determine it for each injection. The flow out of the injector is split, one portion passing into a calibration column, whose stationary phase causes no irreversible adsorption. The other portion enters the test column. Using the calibration curve, we can assign a concentration to each point on the chromatogram and determine the amount of probe sample bound to the very high energy sites. Further comparison with the isotherm data indicates whether the amount apparently lost is accounted for by the isotherm measured or not. We found that it was in all the determinations we have made so far.

A new method of isotherm determination was developed. It is based on the use of the semi-ideal model of chromatography and on the procedures of calculation of numerical solutions of this

model that we developed and tested in other works (see first part). Experimental band profiles are in excellent agreement with the results of these calculations.

This work demonstrates that small isotherm perturbations are magnified to substantial and easily measured changes in the shape of the elution profiles. Trial isotherm adjustments which improve the agreement between experimental and simulated chromatograms yield better estimates of the experimental isotherm. When the difference between the experimental and simulated chromatograms is minimized, all the available isotherm information is extracted. The key to use of the method is in the choice of a sound isotherm equation for the calculation. For this purpose, we use the bilangmuir isotherm model equation which assumes two independent adsorption sites on the adsorbing surface and a Langmuir isotherm corresponding to each of them. In some cases a more complex model was used. The bilangmuir isotherm is written:

$$q = \frac{a_1 P}{1 + b_1 P} + \frac{a_2 P}{1 + b_2 P} \qquad (6)$$

where q is the amount adsorbed at equilibrium, P is the probe partial pressure and a_1, a_2, b_1 and b_2 are numerical coefficients.

As shown in the results described above (see Figs. 13 and 14), the procedure yields equilibrium isotherms which are in excellent agreement with the raw experimental data, as illustrated by the agreement between the two chromatograms shown in Fig. 13, an experimental chromatogram and the chromatogram calculated from the best isotherm derived using our method. This result demonstrates that the model of nonlinear chromatography used in our work is correct and does not neglect any significant contribution to the band profile.

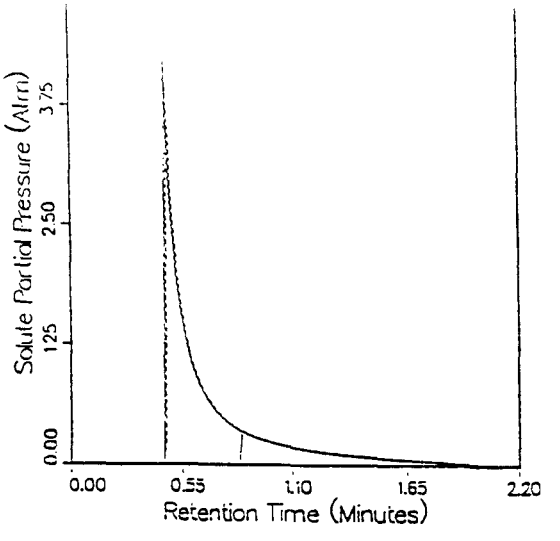


Figure 13. Overloaded Elution Profile of Diethylether on Alumina

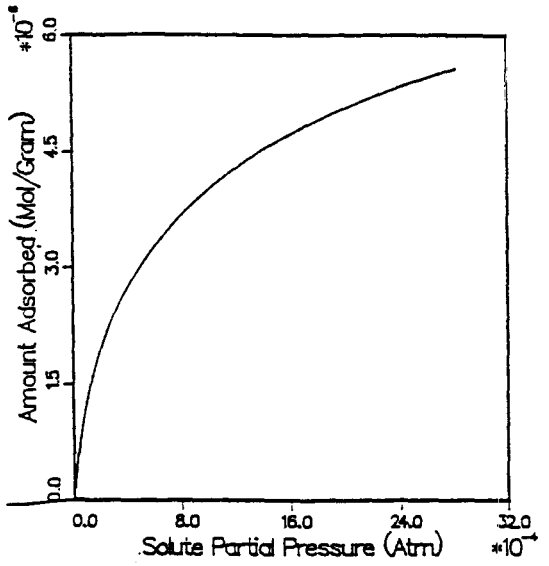


Figure 14. Adsorption Energy Distribution Derived from the Chromatogram in Fig. 13

D. The Adsorption Isotherm and the Energy Distribution Function

First, we derived a theoretical model of the surface which permits the determination of the adsorption energy distribution of a probe component on this surface when the adsorption isotherm is measured. This model assumes that the local adsorption isotherm follows the Langmuir model. Then, we developed a calculation procedure to derive the energy distribution function of a probe on a sample surface.

The apparent or measured adsorption isotherm, q(P), is related to the local isotherm, $\Theta(E,P)$, and to the energy distribution, f(E), by a linear, first kind Fredholm integral equation:

$$q(P) = \int_{\Omega} \Theta(E,P) f(E)\, dE \qquad (7)$$

In this equation, E is the adsorption energy, Ω the range of adsorption energy considered, and f(E) is the amount of probe adsorbed on the surface with an adsorption energy between E and E+dE. $\Theta(E,P)$ is the local adsorption equilibrium isotherm of the probe, and gives the amount adsorbed by the adsorption sites having an energy within the interval (E, E+dE). Only q(P) is accessible experimentally. Provided that the local isotherm, $\Theta(E,P)$, is known or that some reasonable assumption can be made regarding its functional dependence on the probe partial pressure and its adsorption energy, it should be possible to compute the energy distribution function from the global isotherm. We assume that $\Theta(P)$ is a Langmuir isotherm ($q = aP/[1+bP]$) whose coefficients are a function of E.

We have shown how a robust numerical solution can be obtained, by replacing the experimental isotherm in a first stage by a smooth function, which is the sum of several Langmuir terms. The values of the numerical coefficients a_k and b_k of this function are obtained by fitting it to the experimental data. Usually, a bilangmuir isotherm equation suffices to account for the experimental

isotherm in this first step. In some cases, a trilangmuir equation may become necessary. A numerical procedure using the iterative improvement scheme of Adamson and Ling and an algorithm adapted from House et al. has been developed. This procedure usually reveals a multi-modal energy distribution. The minimization of the distance between the experimental isotherm and the isotherm calculated by integration of equation 4 is improved in the second stage of optimization in which each mode of the energy distribution is represented by a Gaussian distribution, if the mode appears symmetrical; by an exponentially modified Gaussian if it is moderately unsymmetrical; and by a Gamma function if it is strongly unsymmetrical. A Simplex routine is used. Convergence is rapid, and the method is robust.

We discussed in detail the precision and accuracy of the energy distribution obtained following our procedure. The precision is studied by determining the influence of the fluctuations of the experimental conditions on the distance between the energy distributions calculated. The accuracy is studied by comparing the experimental isotherm to the isotherm calculated as a direct solution of Equation 4. The confidence intervals for three determinations of the monolayer capacity of an energy mode, its average energy and its variance are 12%, 1.6% and 130%, respectively. The confidence interval on the variance may seem large, but from mode to mode and sample to sample, the variance of an energy mode can change by up to five orders of magnitude, so this precision is quite sufficient in practice. A change in the column temperature of 12° C does not cause a significant change in the energy distribution.

The fundamental Equation 1 illustrates the limit of the method. We determine the distribution of adsorption energy for selected probe compounds, not the distribution of the surface energy at the solid surface, which would be difficult to define without reference to the probe used in the measurement. It will be possible to account for the features of the adsorption energy distributions of probe solutes only when enough data have been collected and detailed information is available regarding the chemical properties of the adsorbent studied.

Nevertheless, the adsorption energy distribution for a series of probe compounds could yield valuable information regarding the energetic heterogeneity of the surface. This information permits, for example, a relative comparison between solid samples of the same chemical nature but of various origins.

First, we determine the experimental isotherm from the rear profile of an overloaded elution band, using the fundamental equation which relates the retention time of a concentration, $t_R(C)$, and the isotherm: where t_0 is the dead time and F the phase ratio.

$$t_R(C) = t_0(1 + F\frac{dq}{dC}) \qquad (8)$$

Using the numerical procedure described above, we fit the experimental isotherm data to the bilangmuir equation. If the result is satisfactory, this isotherm is used in the first step of the determination of the adsorption energy distribution, based on the iterative improvement scheme of Adamson and Ling. Otherwise, a trilangmuir equation is used (e.g., 1-chlorobutane data). A second optimization stage minimizes the distance between the experimental isotherm and the isotherm derived from the adsorption energy distribution.

E. Example of Application

We have applied the whole experimental and computation procedure just described to several groups of alumina samples, (i) a series of high quality α-alumina powders for ceramics; (ii) a series of three lots of α-alumina powders for ceramic of different quality; and (iii) an adsorbent alumina for liquid chromatography. We show in this report the experimental data obtained with 1-chlorobutane for three samples of a similar Coors alumina which have been found to behave well, satisfactorily and poorly in the firing process. The adsorption energy distributions obtained with diethylether on these three samples are nearly identical.

The three chromatograms are shown in Fig. 15. They are quite similar. The three adsorption energy distributions derived from these chromatograms are shown in Fig. 16. The characteristics of the adsorption energy distributions are summarized in Table II. We see that the monolayer capacities of the two high energy modes of the three samples are quite different.

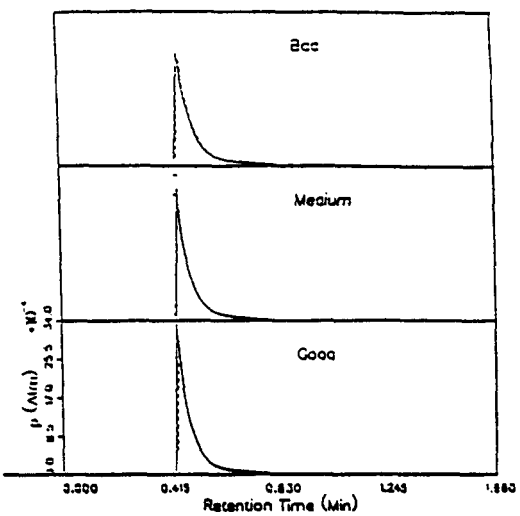


Figure 15. Elution Profiles of 1-chlorobutane on Three Different Alumina Samples

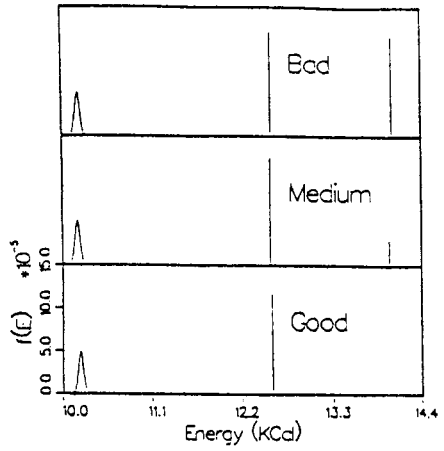


Figure 16. Adsorption Energy Distributions of the Three Alumina Samples Derived from the Chromatograms in Fig. 15

Table II Adsorption Energy Distribution of 1-C_4H_9Cl on Three Alumina samples.

Peak	Adsorbent	q_m μmole/g	E_{AVG} (Kcal/mole)	Variance (Kcal²/mole²
Low Energy Peak	Coors: Good	3.52	10.21	1000
	Medium	4.06	10.18	1010
	Bad	3.94	10.20	1040
Medium Energy Peak	Coors: Good	0.29	12.57	1.0
	Medium	0.31	12.55	1.0
	Bad	0.92	12.56	1.0
High Energy Peak	Coors: Good	0.0133	14.00	1.0
	Medium	0.0722	14.01	1.0
	Bad	0.290	14.03	1.0

The relative confidence limit on this parameter is 12%. Within this limit, the capacity of the second energy mode for the bad sample is three times as large as the capacity of this energy mode for the other two samples. The monolayer capacity of the third mode is four times as high for the bad sample as for the intermediate and twenty times as high as for the good sample.

This result compares favorably with the interpretation currently given for the failures of bad samples. Too large an amount of organic compounds is adsorbed too strongly on the particles of the green bodies. During firing, the kinetics of pyrolysis is faster than the kinetics of vaporization and carbon is deposed inside the ceramic part where it is trapped during the shrinkage accompanying the 40% decrease in volume due to the loss of porosity. This carbon, identified in the parts with poor performance, is responsible for their failure.

The salient conclusions of this work are:

- A correlation was found between the ceramic firing process behavior of a series of alumina samples for ceramic and the adsorption energy distribution of 1-chlorobutane, with a plausible explanation for this correlation;

- The observation of systematic variations of the adsorption energy distributions of the two probes with the hydration degree of the surface of porous alumina was made.

*G. A. Guiochon, J. L. Roles**

* UT Predoctoral Program.

4. OPERATIONS

W. R. Laing

Staffing for the division's Quality Assurance/Quality Control program was completed with the addition of two staff members and a Quality Assurance Specialist from the Quality Department.

Surveillances were conducted on five areas of operations within the division. There were eight external reviews and audits this year. Of the nineteen corrective actions which were open at the beginning of the year, all but two have been closed. All corrective actions on occurrence reports have been closed.

The internal QC effort was supplemented by single-blind controls from five Environmental Protection Agency programs, one DOE program, and monthly samples from a commercial laboratory.

The division continued its excellent safety record this year.

The training officer completed a training needs overview for ACD input into the ORNL training database. Records of needed and completed training will be available. Retraining will be scheduled also.

The Analytical Improvement Council addressed communications, new employee orientation, and procurement and disposal of materials.

The conduct of operations matrix was completed and the ACD manual is being written.

QUALITY ASSURANCE/ QUALITY CONTROL

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

A significant achievement during the past year was the self-assessment of the implementation and effectiveness of the division quality assurance program. The director, each section head, and every group leader made contributions to produce an assessment that was thorough and representative of all division activities. The process revealed areas where the current program could be improved to better fit the organization.

During 1991 seven standard operating procedures (SOPs) and two standard analytical methods (SAMs) were issued. The ACD was also able to reap further benefits from the intensive efforts made in 1990 in writing and updating SOPs and SAMs. Quality assurance plans for at least eight of the 19 corrective actions were completed in order to satisfy the requirements of external projects relying on data supplied by the ACD.

Nevertheless, of the corrective actions still open, over half depend on either developing more or revising existing procedures, methods, or QA plans. A new measure which will make completion of these types of corrective actions easier was the institution of a more formalized system for scheduling and tracking the development of needed procedures and methods.

Of the outside assessments which touched the ACD during the year, two were annual reviews, two were revisits checking the progress made on corrective actions from the original audits, one was an appraisal of nuclear safety performance, one evaluated environmental compliance, and one was an assessment of the QA applied to software development. The only outside evaluation to focus exclusively on ACD functions was a DOE audit of the neutron activation analysis method to determine if the results for soil samples from the East Poplar Creek project could meet the requirements equivalent to the contract laboratory program (CLP). The deficiencies included sample handling techniques which could lead to cross-contamination and a lack of sample homogeneity; inadequate documentation in areas of sample preparation, neutron flux monitoring, and technician training; and the lack of fully developed procedures.

Six category IV occurrences were attributed to the ACD over the year. These included salvage materials being tagged

incorrectly, mistaken handling of PCBs as RCRA wastes, a missed weekly inspection of a satellite accumulation area, and an unexpected vigorous oxidation reaction. Corrective actions have been completed in all cases.

Quality issues within the division found a new forum when the director initiated monthly quality assurance meetings between himself, the quality assurance coordinator, and the quality assurance specialist. Topics covered quality accomplishments, concerns, evaluations, procedures, and other areas which influence quality.

The ACD began a quality control project with the Nuclear Regulatory Commission (NRC) to support the evaluation of nonradiological water chemistry at nuclear power reactors. The project involves providing standards for licensee analysis, analyzing split samples from primary and secondary coolant systems of nuclear power plants, being "on-call" to assist regional inspectors with technical questions, and controlling the statistical evaluation of all analytical data. The final details were decided at the 1991 meeting of the NRC Regional Inspections which ACD hosted.

One hundred and fifty quality control solutions were distributed by the QC laboratory to the ACD organic, inorganic and radiochemical analysis laboratories in 1991. Of the 3990 results reported, 96.7% were acceptable. Monthly inorganic control solutions were purchased from Analytical Products Group and statistically evaluated with 30-plus laboratories throughout the country. All DOE analytical chemistry laboratories operated by Martin Marietta Energy Systems participate in this monthly program. Of the 800 inorganic results reported during 1991, 99% were acceptable. The ACD organic group also participated in the program. Of the 500 results reported, 97% were acceptable.

The double-blind spiking program continued in which quality control samples were prepared by the QC officer and submitted to ACD by the customer alongside routine environment samples. A total of 67 samples spiked with metals, organics, and radioisotopes were submitted during the year. The average recovery of spiked material was 96.9%.

---

*Quality Department

SAFETY PROGRAM

S. D. Wright

An Environmental Safety & Health Action Plan was implemented as a guide toward better safety in the Analytical Chemistry Division during 1991. The division experienced three (3) first aid cases against four (4) 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 - 26; total attendance - 589.
2. Training guide updates for our facilities at Buildings 2026 and 7920 continue.
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.

During a time of increased activity in areas of environmental safety and health, ORNL experienced a sharp increase in job-related injuries while ACD experienced a small decrease in reported accidents requiring investigation and/or first aid attention. This further exemplified ACD employees' dedication to safe work habits.

As a result of ORNL's emphasis on its environmental, safety and health upgrade program, our 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 among our personnel.

TRAINING

H. H. Ross

The most significant single training project in the division this year was the completion of the "Training Needs Overview" that was initiated in 1990. The objectives of this project were to analyze compliance-based training requirements from appropriate DOE orders and associate each of these with individual personnel in the division. In the first and second phases of this project, generic training needs were cross-correlated with specific work functions within the division. Phase Three required that the training matrix be further characterized to each and every staff member at the job and badge number level. This task was completed within the division; the database that was generated was sent to the Training and Development Department for compilation with other Laboratory divisions and subsequent loading on the TMIS database. When the output of this project is fully implemented, the system will provide timely information to the division about the status of our compliance training and will inform the division training manager (DTM) of needed training updates or training deficiencies. It will also allow the DTM to quickly implement new, required training for personnel whose specific job assignments have changed.

During the past year, division staff have participated in approximately 1100 hours of on-site training. This time includes compliance, personal development, and on-the-job/performance-based training. Additionally, some staff have participated in off-site programs that have included instruction for certain instrument operations, QA and QC procedures, and special requirements for handling work-for-others projects. In each case, attendance and satisfactory completion are documented in the TMIS system as well as the division database.

The Analytical Improvement Council (AIC) has considered for the past several months the adequacy of new employee training in the division. A major finding was that although the general employee training (GET) given to new staff is excellent, the AIC felt there was much additional, division-specific information that would be desirable for a new ACD employee. Sophie Bobrowski, a member of the AIC, formed an ad hoc committee to develop such a supplementary training package for ACD. Three key directives for this endeavor are 1) that the information be supplied as a

personal "hard-copy" item, 2) that the format be sufficiently accommodating so that information can be quickly and easily updated, and 3) that the product be beneficial to both new employees and present staff. The committee has already identified pertinent information and is in the process of completing the initial draft for review and comment.

ANALYTICAL IMPROVEMENT COUNCIL

C. E. Higgins

The major projects of the Analytical Improvement Council (AIC) were concerned with improvement of communication within ACD and the orientation of new employees. A survey of ACD personnel on "how to improve communication in ACD" was conducted with excellent participation by division personnel. Responses were overwhelmingly in favor of the GRAPEVINE, the division newsletter. Communication between employee and supervisor was felt to be excellent, and the brown bag luncheon meetings with the division director were considered to be informative. A large majority of responders indicated that they would like to be apprised of the budget, particularly of that for their own group and section, and they would like to see their performance appraisal before it leaves their section. This latter feature has been included in this year's performance appraisal system. The Orientation Committee came into being because a need was discerned for a more uniform method of orienting new divisional employees. An orientation booklet, modeled after that of Metals and Ceramics, is being assembled and modified to fit division needs.

AIC also perceives a need to reduce the red tape involved with the procurement (and disposal) of materials. Difficulty is frequently experienced in obtaining materials already on site. A need for streamlining the system exists; therefore, AIC is hopeful that new procedures can be generated which will accelerate delivery.

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, and special undergraduates from the Great Lakes Colleges Association. A newer program involves students from the service academies. In addition, graduate programs are maintained with U. T. and Clemson.

Doug Goeringer served as University Relations Coordinator for student guests and faculty during 1991.

OAK RIDGE ASSOCIATED UNIVERSITIES

Postgraduate Research Program. Michael D. Barnes began work with Mike Ramsey on new techniques for ultrasensitive detection of organic and biological molecules.

David M. Chambers began research with Gary Glish on explosives detection projects.

Kevin Hart's appointment was renewed to pursue further research and development projects in mass spectrometry under the direction of Gary Glish.

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

Jun Xu began his research with L. D. Hulett in slow positron research, studying interaction of slow positrons with surfaces.

Eric Kerley completed research with Michelle Buchanan on the development of an external ionization source for FTMS to enable investigation of molecular weight biomolecules.

Graduate Research Program. Rick Flurer (Indiana University) completed his work in the Analytical Spectroscopy Section with Scott McLuckey and Gary Glish.

Professional Intern Program. Patrick Limbach (Ohio State University) began his appointment with Michelle Buchanan on a DOE-sponsored project to develop a new means of injecting ions into a Fourier transform mass spectrometer.

Faculty Research Participation Program. M. Judith Charles (University of North Carolina at Chapel Hill) assisted Gary Glish in research in mass spectrometry.

Kin C. Ng (California State University at Fresno) worked with Mike Ramsey to develop high-resolution, ultrasensitive laser spectroscopic techniques.

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 1991, postdoctoral researchers at ORNL included M. Diack, E. V. Dose, M. Z. El Fallah and A. Fellinger; S. Jacobson, a predoctoral student, completed the group. J. L. Roles, a predoctoral student, completed his appointment in 1991.

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

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

R. T. Short completed his research on organic imaging mass spectrometry with Peter Todd.

C. C. Grimm completed research on organic secondary ion emission with Peter Todd.

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

Science Alliance. 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 continued his work with Jack Young on the magnesium sensors program.

Laboratory Graduate Participation Program. Mona Shahgholi, UTK graduate student, began her appointment with Michelle Buchanan and Robert Hettich in the Organic Chemistry Section.

GREAT LAKES COLLEGES ASSOCIATION

James Wendel (Wabash College) participated in the study of gas phase ion chemistry using mass spectrometry with Gary Glish.

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

Renee Kirk (Denison University) conducted research on laser-induced fluorescence spectroscopy of labeled DNA oligimers with Mike Ramsey.

Jinghai Xu (Denison University) worked with Michelle Buchanan to develop methods for rapid detection of environmental contaminants in water.

CLEMSON UNIVERSITY

Predoctoral Research. Douglas C. Duckworth continued his research with D. L. Donohue and D. H. Smith on the development of radio frequency glow discharge in mass spectrometry.

SERVICE ACADEMIES RESEARCH ASSOCIATES

Nathan Ives (U. S. Naval Academy) did research on single molecule detection by laser-induced fluorescence in microdroplets with Mike Ramsey.

CO-OP PROGRAM

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

DEPARTMENT OF ENERGY

DOE/TRAC Appointments. Scott Lykens (Caesar Rodney High School, Camden, Delaware) studied gas-phase ion chemistry/physics using mass spectrometry with Wayne Griest.

Linda Sinclair (Lexington High School, Lexington, Kentucky) worked with Wayne Griest in the area of separation science and applications to biological media.

Carla Brown (Karns High School, Knoxville) worked with P. J. Todd preparing samples for organic ion imaging.

DOE Fellowship. Julie A. Graudons worked with Frank Dyer measuring ^{129}I in mixed ion exchange resins from LWR primary coolant to establish limits on ^{129}I source term in LWR primary coolant.

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 1991 Advisory Committee was composed of:

D. D. Bly, Central Research, E. I. du Pont de Nemours, Wilmington, Delaware

I. H. Warner, Emory University, Atlanta, Georgia

E. S. Yeung, Iowa State University, Ames, Iowa

CONSULTANTS

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

Stephen Arnold, Polytechnic Institute of New York, Brooklyn, New York

Michael D. Barnes, Rice University, Houston, Texas

Mark E. Bier, Finnigan Corporation, San Jose, California

James E. Butler, Naval Research Laboratory, Washington, D.C.

Jean Cadet, Laboratoire des Lesions des Acides, Grenoble. Cedex, France

Mark A. Cappelli, Stanford University, Stanford, California

Ziyun Chen, Pennsylvania State University, University Park, Pennsylvania

Gregory Downing, National Institute of Standards and Technology, Gaithersburg, Maryland

William D. Ehmann, University of Kentucky, Lexington, Kentucky

Casey C. Grimm, Chestnut Street, New Orleans, Louisiana

Mee Yoo Hahn, University of Pennsylvania, Philadelphia, Pennsylvania

Barry Hogan, Iowa State University, Ames, Iowa

Ashley L. McCormack, University of Virginia, Charlottesville, Virginia

Raymond E. March, Trent University, Peterborough, Ontario, Canada

Robert A. Osteryoung, State University of New York, Buffalo, New York

James P. Reilly, Indiana University, Bloomington, Indiana

Steven W. Rynders, University of Illinois, Urbana, Illinois

Stephen N. Schauer, Arizona State University, Tempe, Arizona

Anthony G. Thompson, University of Illinois, Urbana, Illinois

Vicki H. Wysocki, Virginia Commonwealth University, Richmond, Virginia

Mo Yang, Indiana University, Bloomington, Indiana

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

G. M. Begun, Retired, Martin Marietta Energy Systems, Oak Ridge, Tennessee

K. D. Cook, University of Tennessee, Knoxville, Tennessee

D. C. Duckworth, Clemson University, Clemson, South Carolina

A. L. Harrod, Retired, Martin Marietta Energy Systems, Oak Ridge, Tennessee

W. M. Holland, University of Tennessee, Knoxville, Tennessee

E. L. Kerley, Comstock, Inc., Oak Ridge, Tennessee

W. S. Lyon, Retired, Martin Marietta Energy Systems, Oak Ridge, Tennessee

Gleb Mamantov, University of Tennessee, Knoxville, Tennessee

R. K. Marcus, Clemson University, Clemson, South Carolina

Alan G. Marshall, Ohio State University, Columbus, Ohio

Bryce Philpot, Retired, Martin Marietta Energy Systems, Oak Ridge, Tennessee

R. L. Walker, Retired, Martin Marietta Energy Systems, Oak Ridge, Tennessee

32nd ORNL/DOE CONFERENCE
ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

The 32nd Annual Conference was held in Gatlinburg at the Park Vista Hotel, October 1-3, 1991. Attendance was 385, with representatives from foreign countries, academia, industrial institutions, DOE contractors, and other government agencies. There were 24 exhibits. Major topics included planning, management and technical developments in environmental restoration programs, trapped ion mass spectrometry, ICP/MS, automation and remote sensing, and new techniques for measuring radionuclides.

S. D. Wright and A. L. Harrod were Arrangements Chairmen, W. R. Laing was Technical Program Chairman, and C. C. Overbey was Treasurer. D. E. Freshour and D. C. Smith were Conference secretaries. Other conference committee members were J. G. Dorsey (Y-12), D. W. Green (ANL), M. P. Maskarinec, S. A. McLuckey, W. D. Shults, J. R. Stokely, and J. W. Wade.

SEMINAR PROGRAM

Speaker	Title of Talk	Date
Stephen N. Schauer Arizona State U. Tempe, Ariz.	"Suppression of Molecular Species in SIMS Using Extra Energy Filtering"	2/11/91
Robert A. Osteryoung State U. of New York Buffalo, N.Y.	"Pulse Polarographic Techniques in Electroanalytical Chemistry"	3/1/91
Steven W. Rynders U. of Illinois Urbana, Ill.	"Plasma-Enhanced Chemical Vapor Deposition of Hydrogenous Silicon Carbide Films from Novel Precursors"	3/5/91
Ashley Lee McCormack U. of Virginia Charlottesville, Va.	"Tandem Mass Spectrometry Applied to Protein Sequencing"	3/13/91

Vicki H. Wysocki Virginia Commonwealth U. Richmond, Va.	"Structural Characterization by Surface-Induced Dissociation Tandem Mass Spectrometry"	4/19/91
James E. Butler Naval Research Lab. Washington, D.C.	"Studies of Diamond Chemical Vapor Deposition"	5/17/91
Ziyun Chen Pennsylvania State U. University Park, Pa.	"Photodissociation and Photofragment Dynamics in Probing the Structures of Cluster Ions"	6/20/91
Jean Cadet Laboratoire des Lesions des Acides, Grenoble Cedex, France	"DNA Base Lesions Produced by Oxidation and Photochemical Reactions: Methods of Measurement"	6/28/91
James P. Reilly Indiana U. Bloomington, Ind.	"Laser Ionization Mass Spectrometry and Photoelectron Spectroscopy"	6/28/91
William D. Ehmann U. of Kentucky Lexington, Ky.	"Nuclear Methods of Analysis Applied to the Study of Neurological Diseases"	7/20/91
Michael D. Barnes Rice U. Houston, Texas	"Spectroscopy of Transition States in Biomolecular Reactions"	7/26/91
Anthony G. Thompson U. of Illinois Urbana, Ill.	"Analytical High Speed Countercurrent Chromatography and FAB Mass Spectrometry	8/12/91
Mo Yang Indiana U. Bloomington, Ind.	"UV Laser-Induced Surface Ionization"	8/16/91
Mark A. Cappelli Stanford U. Stanford, Calif.	"Overview of Diamond Research Activities at Stanford University"	8/23/91
Raymond E. March Trent U. Peterborough Ontario, Canada	"The Quadrupole Ion Trap: A Computer-Controlled Electric Test Tube"	9/12/91

Mee Yoo Hahn U. of Pennsylvania Philadelphia, Pa.	"Resonant Two-Photon Ionization Studies of Molecular Clusters"	9/27/91
Barry L. Hogan Iowa State U. Ames, Iowa	"Cellular Analysis with Indirect Detection in Capillary Electrophoresis"	9/30/91
Mark E. Bier Finnigan Corp. San Jose, Calif.	"Recent Developments in Coupling External Ionization with a Quadrupole Ion Trap Mass Spectrometer"	9/30/91
Gregory Downing NIST Gaithersburg, Md.	"Development of the NIST Analytical Beam Techniques"	10/24/91

PATENTS

Cyril A. Thompson was issued a patent February, 1991, for "Soil Sampling Kit and a Method of Sampling Therewith".

AWARDS AND HONORS

Michelle Buchanan was named North American Editor of *Biological Mass Spectrometry.*

R. A. Jenkins was appointed to the Editorial Board of the *Journal of Smoking Related Disorders.*

Norm Teasley received a Martin Marietta Energy Systems President's Award for Performance Improvement for a program to print National Fire Protection Association hazard labels for chemical containers.

Bryce Philpot was awarded the Analytical Chemistry Division Distinguished Service Award.

Harley Ross has been selected for a two-year assignment at the International Atomic Energy Agency (IAEA) in Vienna.

Energy Systems Awards Night

W. D. Shults received the 1991 Management Achievement Award for superior leadership of the ORNL Analytical Chemistry Division and for numerous management contributions to the Laboratory and to Energy Systems.

Barry C. Grant received a Technical Achievement Award for preeminent operation and technical support relating to explosive detection projects and for outstanding contributions toward compliance with OSHA chemical laboratory regulations.

Peter J. Todd received a Technical Achievement Award for design, construction and general development of an organic secondary ion probe for obtaining micrographs of biological tissue.

ADDITIONAL PROFESSIONAL ACTIVITIES

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

J. A. Carter

Chairman	DOE/ISA Laboratory Advisory Group for Effluent Research (LAGER)
Laboratory Coordinator	ISPO Programs

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	University Relations
Member	Energy Systems Ph.D. Recruiting Team

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*
	Journal of Chromatographic Science
	Chromatographia
Member	HPLC Permanent Committee of the International Symposia on Column Liquid Chromatography
	ACS Board, Chromatography Subdivision, ACS Division of Analytical Chemistry

H. J. Hall

ACD Representative	Waste Management

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

Chairman	Analytical Improvement Council

G. B. Hurst

Member	Analytical Improvement Council
	ACD Safety Committee
	ACD Seminar Committee
	East Tennessee ACS Chemistry Olympiad Committee

R. H. Ilgner

Secretary	East Tennessee Mass Spectrometry Discussion Group

R. A. Jenkins

Editorial Board	*The Journal of Smoking Related Disorders*
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
Member	Liquid Low-Level Waste Solidification Project Operational Readiness Team

W. R. Laing

Chairman	ASTM Committee C-26, Nuclear Fuel Cycle
ACD Coordinator	Energy Conservation
ACD Coordinator	Quality Assurance
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 Disposal
	ISO Technical Committee 85, Subcommittee 5
	ORNL Pregrievance Committee

S. A. McLuckey

Chairman	East Tennessee Mass Spectrometry Discussion Group Group
Consultant	Finnigan MAT, San Jose, Calif.
Member	National Cancer Institute SBIR Review
	ASMS Program Review Board

M. P. Maskarinec

Member	EPA Working Group on Improvement of TIC Identification
	ASTM Committee D-34

T. R. Mueller

ACD Representative	Energy Systems Office of Technology Assessment
	Energy Systems User Advisory Committee for Computing Technology
	Classification Officer
ACD Manager	Training
ACD Presenter	Ethics Awareness
Member	ACS Audit Committee
	ACD Seminar Committee

J. C. Price

ACD Representative	Classification Officer

J. M. Ramsey

Chairman	Program Advisory Committee, ACS Division of Analytical Chemistry
Editorial Advisory Board	*Progress in Analytical Spectroscopy*
Co-organizer	18th Federation of Analytical Chemistry and Spectroscopy Societies Meeting
Technical Program Committee	3rd Optical Society of America Topical Meeting on Laser Applications to Chemical Analysis
Member	Energy Systems Publication Award Selection Committee
	DOE/ISA Laboratory Advisory Group for Effluent Research (LAGER)
	ORNL Laser Safety Committee
	International Technology Programs Special Projects Advisory Group

J. R. Ramsey

Member	ACS East Tennessee Section, Lind Lecture Series Selection Committee
	ORAU Traveling Lecture Program
ACD Coordinator	Laser Safety Officer
Consultant	Ames Laboratory
	Center for Indoor Air Research

R. S. Ramsey

Consultant	National Cancer Institute SBIR Reviews
	Center for Indoor Air Research

L. Robinson

President	Oak Ridge Chapter, NAACP
Member	ASTM Task Group on Nuclear Methods of Chemical Analysis
ACD Coordinator	Radiation Control

H. H. Ross

Assignment	International Atomic Energy Agency, Vienna, Austria
Consultant	Savannah River Site, Aiken, S. C.
	GPU Nuclear, Three Mile Island, Unit-2, Middletown, Pa.
Member	Canvassing Committee, ACS Award for Nuclear Chemistry
	Fellowship Committee, ACS Division of Analytical Chemistry
ACD Manager	Training

T. M. Rosseel

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

Chairman	ACS East Tennessee Section
	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, 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. H. Stewart, Jr.

Member	ASTM Committee D-34, Waste Disposal
	International Working Group, "Analytical Standards of Minerals, Ores, and Rocks"
	ASTM Committee C-26, Nuclear Fuel Cycle
ACD Representative	Environmental Protection
	Waste Minimization Officer

J. R. Stokely

Chairman	DOE Site Survey Program RAD Committee
	DOE Technical Safety Appraisal Team
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 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

Chairman	ACD Seminar Committee

M. B. Wise

Coordinator	ASMS Environmental Interest Group
Session Chairman	American Society for Mass Spectrometry
Member	ACD Safety Committee

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
Member	Program Advisory Committee, ACS Division of Nuclear Chemistry and Technology
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	Chemistry Olympiad Committee, ACS East Tennessee Section

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 nonnnuclear energy, new instrumentation and its application, and environmental problems such as monitoring and cleanup 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

Author	Author(s), Title, Where Published
Asano, K. G.	Asano, K. G.; McLuckey, S. A.; Glish, G. L; J. E. Bartmess*, "'Spontaneous' Cluster Ion Decomposition in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1497.
	Glish, G. L.; Troutman, M. R.; Asano, K. G.; McLuckey, S. A., "Effects of Time-Scale on MS/MS Dissociations", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1558.

Buchanan, M. V.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Las Vegas, February 12-14, 1991, p. 273.

Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1677.

Buchanan, M. V.; Hettich, R. L.; Ma, C. Y.; Guerin, M. R., "Crude Oil Characterization by Direct Sampling Ion Trap Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1093.

Hettich, R. L.; Buchanan, M. V., "Investigation of Matrix-Assisted Laser Desorption FTMS for Biomolecules", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 929.

Kerley, E. L.; Buchanan, M. V.; Cook, K. D.*; Shahgholi, M., "Development of an Electrostatic Ion Injection Device for Fourier Transform Ion Cyclotron Research Studies of Electrosprayed Ions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1175.

Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Rapid Recovery of Biological Compounds from Electrophoretic Gel Slices for Subsequent Analysis by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 13.

Buckley, B. T. — Ramsey, J. M.; Whitten, W. B.; Goeringer, D. E.; Buckley, B. T., "Collisional and Electric-Field Ionization of Laser-Prepared Rydberg States in an Ion Trap Mass Spectrometer", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 6, p. 301 (1991).

Carter, J. A. — Carter, J. A.; Glish, G. L.; McLuckey, S. A.; McKenney, S. A.*, "Oak Ridge Vapor Detection Identification System", *Proceedings of the 31st Annual Meeting of the Institute of Nuclear Materials Management (INMM)*, Los Angeles, July 15-18, 1990, p. 775.

Caton, J. E. — Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1677.

Dale, J. M. — Whitten, W. B.; Dale, J. M.; Ramsey, J. M., "Laser Ablation of Microparticles in an Ion Trap Mass Spectrometer", *Proceedings of the Workshop on Laser Ablation Mechanisms and Applications*, Oak Ridge, April 8-10, 1991, p. 112.

Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 534.

Dunphy, J. C. — Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Rapid Recovery of Biological Compounds from Electrophoretic Gel Slices for Subsequent Analysis by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 13.

Dyer, F. F. — Robinson, L.; Dyer, F. F.; Emery, J. F., "Proposed Neutron Activation Analysis Facilities in the Advanced Neutron Source", *Proceedings of the 7th Symposium on Measurements and Applications*, Ann Arbor, Mich., May 20-25, 1990.

Flurer, R. A.

Flurer, R. A.; Glish, G. L.; McLuckey, S. A., "Theoretical and Experimental Studies of the Gas-Phase Ion Chemistry of Freon 113", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 516.

Glish, G. L.

Carter, J. A.; Glish, G. L.; McLuckey, S. A.; McKenney, S. A.*, "Oak Ridge Vapor Detection Identification System", *Proceedings of the 31st Annual Meeting of the Institute of Nuclear Materials Management (INMM)*, Los Angeles, July 15-18, 1990, p. 775.

Glish, G. L.; Troutman, M. R.; Asano, K. G.; McLuckey, S. A., "Effects of Time-Scale on MS/MS Dissociations", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1558.

Glish, G. L.; McLuckey, S. A., "Formation of Substituted Benzene Radical Cations Via Ion/Molecule Reactions with Iodobenzene", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1602.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 536.

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength R2PI/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 771.

Asano, K. G.; McLuckey, S. A.; Glish, G. L; J. E. Bartmess*, "'Spontaneous' Cluster Ion Decomposition in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1497.

Glish, G. L.

Flurer, R. A.; Glish, G. L.; McLuckey, S. A., "Theoretical and Experimental Studies of the Gas-Phase Ion Chemistry of Freon 113", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 516.

Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Enhancement of Mass Resolution in the Quadrupole Ion Trap Via Resonance Ejection", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 532.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Analysis of Metals in Solution Using Electrospray Ionization Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 292.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., ""Methods for Preforming Ions in Solution From Compounds Not Normally Amenable to Electrospray Ionization", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1237.

Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 166.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Effects of Experimental Parameters on Ion Storage in a Quadrupole Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1495.

Glish, G. L.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Application of Substructure Identification Rules to MS^n Spectra Obtained on an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 773.

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Reactive Collisions of Multiply Charged Ions Derived from Electrospray", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 901.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "MS/MS and MS^n Studies of Multiply Charged Oligonucleotides Using a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 981.

Goeringer, D. E.

Ramsey, J. M.; Whitten, W. B.; Goeringer, D. E.; Buckley, B. T., "Collisional and Electric-Field Ionization of Laser-Prepared Rydberg States in an Ion Trap Mass Spectrometer", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 6, p. 301 (1991).

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength R2PI/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 771.

Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Enhancement of Mass Resolution in the Quadrupole Ion Trap Via Resonance Ejection", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 532.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 536.

Goeringer, D. E. — Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 166.

Grant, B. C. — Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 166.

Grimm, C. C. — Short, R. T.; Todd, P. J.; Grimm, C. C., "Kinetic Energy Distribution of Ions After Surface Collisions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 825.

Todd, P. J.; Grimm, C. C.; Short, R. T., "Organic Ion Imaging", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1689.

Guerin, M. R. — Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Las Vegas, February 12-14, 1991, p. 273.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1205.

Buchanan, M. V.; Hettich, R. L.; Ma, C. Y.; Guerin, M. R., "Crude Oil Characterization by Direct Sampling Ion Trap Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1093.

Guerin, M. R. — Guerin, M. R., "Environmental Tobacco Smoke", *Organic Chemistry of the Atmosphere*, Lee D. Hansen, Delbert J. Eatough, eds., CRC Press, Inc., p. 79, 1991.

Guiochon, G. A. — Katti, A. M.; Guiochon, G. A., "Fundamentals of Non-Linear Chromatography: Prediction of Experimental Profiles and Band Separations", *Advances in Chromatography*, J. C. Giddings, E. Grushka, P. R. Brown, Eds., M. Dekker, New York, Vol. 31, p. 1, 1991.

Hart, K. J. — Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Effects of Experimental Parameters on Ion Storage in a Quadrupole Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1495.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Application of Substructure Identification Rules to MS^n Spectra Obtained on an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 773.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. L.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 536.

Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 166.

Hettich, R. L. — Hettich, R. L.; Buchanan, M. V., "Investigation of Matrix-Assisted Laser Desorption FTMS for Biomolecules", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 929.

Hettich, R. L.

Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1677.

Buchanan, M. V.; Hettich, R. L.; Ma, C. Y.; Guerin, M. R., "Crude Oil Characterization by Direct Sampling Ion Trap Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1093.

Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Rapid Recovery of Biological Compounds from Electrophoretic Gel Slices for Subsequent Analysis by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 13.

Hurst, G. B.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Las Vegas, February 12-14, 1991, p. 273.

Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Wise, M. B., "Direct-Sampling MS Measurement of Volatiles in Environmental Samples", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1199.

Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1677.

Hurst, G. B. — Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1205.

Katti, A. M. — Katti, A. M.; Guiochon, G. A., "Fundamentals of Non-Linear Chromatography: Prediction of Experimental Profiles and Band Separations", *Advances in Chromatography*, J. C. Giddings, E. Grushka, P. R. Brown, Eds., M. Dekker, New York, Vol. 31, p. 1, 1991.

Kerley, E. L. — Kerley, E. L.; Buchanan, M. V.; Cook, K. D.*; Shahgholi, M., "Development of an Electrostatic Ion Injection Device for Fourier Transform Ion Cyclotron Research Studies of Electrosprayed Ions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1175.

Laing, W. R. — Laing, W. R., *Abstracts of Papers*, 32nd ORNL-DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., October 1-3, 1991.

McLuckey, S. A. — Carter, J. A.; Glish, G. L.; McLuckey, S. A.; McKenney, S. A.*, "Oak Ridge Vapor Detection Identification System", *Proceedings of the 31st Annual Meeting of the Institute of Nuclear Materials Management (INMM)*, Los Angeles, July 15-18, 1990, p. 775.

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Reactive Collisions of Multiply Charged Ions Derived from Electrospray", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 901.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "MS/MS and MS" Studies of Multiply Charged Oligonucleotides Using a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 981.

McLuckey, S. A.

Glish, G. L.; Troutman, M. R.; Asano, K. G.; McLuckey, S. A., "Effects of Time-Scale on MS/MS Dissociations", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1558.

Glish, G. L.; McLuckey, S. A., "Formation of Substituted Benzene Radical Cations Via Ion/Molecule Reactions with Iodobenzene", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1602.

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength R2PI/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 771.

Asano, K. G.; McLuckey, S. A.; Glish, G. L; J. E. Bartmess*, "'Spontaneous' Cluster Ion Decomposition in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1497.

Flurer, R. A.; Glish, G. L.; McLuckey, S. A., "Theoretical and Experimental Studies of the Gas-Phase Ion Chemistry of Freon 113", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 516.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 536.

Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Enhancement of Mass Resolution in the Quadrupole Ion Trap Via Resonance Ejection", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 532.

McLuckey, S. A.

Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 166.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Effects of Experimental Parameters on Ion Storage in a Quadrupole Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1495.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Application of Substructure Identification Rules to MS^n Spectra Obtained on an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 773.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Analysis of Metals in Solution Using Electrospray Ionization Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 292.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Methods for Preforming Ions in Solution from Compounds Not Normally Amenable to Electrospray Ionization", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1237.

Ma, C. Y.

Ma, C. Y.; Bayne, C. K.*; Maskarinec, M. P., "Differentiation of Aroclors in Environmental Samples Using Negative Ion Chemical Ionization (NICI) Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 700.

Buchanan, M. V.; Hettich, R. L.; Ma, C. Y.; Guerin, M. R., "Crude Oil Characterization by Direct Sampling Ion Trap Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1093.

Maskarinec, M. P.

Ma, C. Y.; Bayne, C. K.*; Maskarinec, M. P., "Differentiation of Aroclors in Environmental Samples Using Negative Ion Chemical Ionization (NICI) Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 700.

Lewis, T. E.*; Camerson, R. E.*; Crockett, A. B.*; Gerlach, C. L.*; Maskarinec, M. P.; Mason, B. J.*; Ramsey, C.*; Schroedl, S. R.*; Siegrist, R. L.*; Uchrin, C. G.*; Wilson, L. B.*; Zarrabi, K.*, "Soil Sampling and Analysis for Volatile Organics Compounds", *EPA Superfund Ground Water Issue*, January 1991.

Ramsey, J. M.

Whitten, W. B.; Ramsey, J. M.; Arnold, S.*; Bronk, B. V.*, "Progress in the Detection of Single Molecules in Levitated Microdroplets", *Proceedings of the U. S. Army 1990 Scientific Conference on Obscuration and Aerosol Research*, June 25-27, 1990, p. 139.

Ramsey, J. M.; Whitten, W. B.; Goeringer, D. E.; Buckley, B. T., "Collisional and Electric-Field Ionization of Laser-Prepared Rydberg States in an Ion Trap Mass Spectrometer", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 6, p. 301 (1991).

Whitten, W. B.; Dale, J. M.; Ramsey, J. M., "Laser Ablation of Microparticles in an Ion Trap Mass Spectrometer", *Proceedings of the Workshop on Laser Ablation Mechanisms and Applications*, Oak Ridge, April 8-10, 1991, p. 112.

Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 534.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M.; Heatherly, L.*, "Fundamental Studies of Chemical Vapor Deposition Diamond Growth Processes", *Proceedings of the 1991 International Symposium on Optical and Optoelectronic Applied Science and Engineering*, San Diego, Calif., July 21-26, 1991, p. 170.

Robinson, L. — Robinson, L.; Dyer, F. F.; Emery, J. F., "Proposed Neutron Activation Analysis Facilities in the Advanced Neutron Source", *Proceedings of the 7th Symposium on Measurements and Applications*, Ann Arbor, Mich., May 20-25, 1990.

Ross, H. H. — Ross, H. H., "Photon Scattering Effects in Heterogeneous Scintillator Systems", *Liquid Scintillation Counting and Organic Scintillators*, Lewis, 1991, p. 195.

Shahgholi, M. — Kerley, E. L.; Buchanan, M. V.; Cook, K. D.*; Shahgholi, M., "Development of an Electrostatic Ion Injection Device for Fourier Transform Ion Cyclotron Research Studies of Electrosprayed Ions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1175.

Shaw, R. W. — Young, J. P.; Shaw, R. W.; Smith, D. H., "Application of Diode Lasers to Resonance Ionization Mass Spectrometry", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 5, p. 227 (1991).

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M.; Heatherly, L.*, "Fundamental Studies of Chemical Vapor Deposition Diamond Growth Processes", *Proceedings of the 1991 International Symposium on Optical and Optoelectronic Applied Science and Engineering*, San Diego, Calif., July 21-26, 1991, p. 170.

Short, R. T. — Short, R. T.; Todd, P. J.; Grimm, C. C., "Kinetic Energy Distribution of Ions After Surface Collisions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 825.

Todd, P. J.; Grimm, C. C.; Short, R. T., "Organic Ion Imaging", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1689.

Smith, D. H. — Young, J. P.; Shaw, R. W.; Smith, D. H., "Application of Diode Lasers to Resonance Ionization Mass Spectrometry", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 5, p. 227 (1991).

Theobald, D. L.

Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Wise, M. B., "Direct-Sampling MS Measurement of Volatiles in Environmental Samples", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1199.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1205.

Thompson, C. V.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Las Vegas, February 12-14, 1991, p. 273.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1205.

Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Wise, M. B., "Direct-Sampling MS Measurement of Volatiles in Environmental Samples", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1199.

Todd, P. J.

Todd, P. J., "Origin of Secondary Ions Emitted from Liquids", *Proceedings of the 7th International Conference on Secondary Ion Mass Spectrometry*, Wiley and Sons, 1990, p. 25.

Todd, P. J.; Grimm, C. C.; Short, R. T., "Organic Ion Imaging", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1689.

Todd, P. J. — Short, R. T.; Todd, P. J.; Grimm, C. C., "Kinetic Energy Distribution of Ions After Surface Collisions", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 825.

Troutman, M. R. — Glish, G. L.; Troutman, M. R.; Asano, K. G.; McLuckey, S. A., "Effects of Time-Scale on MS/MS Dissociations", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1558.

Van Berkel, G. J. — Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Analysis of Metals in Solution Using Electrospray Ionization Mass Spectrometry", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 292.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., ""Methods for Preforming Ions in Solution From Compounds Not Normally Amenable to Electrospray Ionization", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1237.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 536.

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Reactive Collisions of Multiply Charged Ions Derived from Electrospray", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 901.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "MS/MS and MS^n Studies of Multiply Charged Oligonucleotides Using a Quadrupole Ion Trap", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 981.

Whitten, W. B.

Whitten, W. B.; Ramsey, J. M.; Arnold, S.*; Bronk, B. V.*, "Progress in the Detection of Single Molecules in Levitated Microdroplets", *Proceedings of the U. S. Army 1990 Scientific Conference on Obscuration and Aerosol Research*, June 25-27, 1990, p. 139.

Ramsey, J. M.; Whitten, W. B.; Goeringer, D. E.; Buckley, B. T., "Collisional and Electric-Field Ionization of Laser-Prepared Rydberg States in an Ion Trap Mass Spectrometer", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 6, p. 301 (1991).

Whitten, W. B.; Dale, J. M.; Ramsey, J. M., "Laser Ablation of Microparticles in an Ion Trap Mass Spectrometer", *Proceedings of the Workshop on Laser Ablation Mechanisms and Applications*, Oak Ridge, April 8-10, 1991, p. 112.

Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 534.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M.; Heatherly, L.*, "Fundamental Studies of Chemical Vapor Deposition Diamond Growth Processes", *Proceedings of the 1991 International Symposium on Optical and Optoelectronic Applied Science and Engineering*, San Diego, Calif., July 21-26, 1991, p. 170.

Wise, M. B.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, Las Vegas, February 12-14, 1991, p. 273.

Buchanan, M. V.; Wise, M. B.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1677.

Wise, M. B.

Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Wise, M. B., "Direct-Sampling MS Measurement of Volatiles in Environmental Samples", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1199.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, Tenn., May 19-24, 1991, p. 1205.

Young, J. P.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Application of Diode Lasers to Resonance Ionization Mass Spectrometry", Proceedings of RIS-90 Conference, Varese, Italy, September 1990, *Inst. Phys. Conf.*, Ser. 114, Sect. 5, p. 227 (1991).

JOURNAL ARTICLES

Author	Author(s), Title, Where Published
Buchanan, M. V.	Buchanan, M. V.; Hettich, R. L.; Wise, M. B., "Rapid Analysis Using Direct Sampling Mass Spectrometry", *Preprints of the Fuel Chemistry Division, American Chemical Society.*
	Hettich, R. L.; Buchanan, M. V., "Investigation of UV Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry for Peptides", *J. Am. Soc. Mass Spectrom.* 2, 22 (1991).
	Hettich, R. L.; Buchanan, M. V., "Structural Characterization of Normal and Modified Oligonucleotides by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", *J. Am. Soc. Mass Spectrom.* 2, 402 (1991).
Christie, W. H.	Golanski, A.*; Christie, W. H.; Galloway, M. D.*; Park, J. L.*; Pennycook, S. J.*; Poker, D. B.*; Moore, J. L.*; Harmon, H. E.*; White, C. W.*, "Ion Beam Induced Diffusion and Crystallization in High-Dose Er Implanted Si", *Nucl. Instrum. Methods Phys. Res.*, B59/60, 444 (1991).
Czok, M.	Czok, M.; Guiochon, G. A., "Comparison of the Results Obtained with Different Models for the Simulation of Preparative Chromatography", *Comput. Chem. Eng.* 14, 1435 (1990).
	Czok, M.; Katti, A. M.; Guiochon, G. A., "The Effect of Sample Viscosity in High Performance Size Exclusion Chromatography and Its Control", *J. Chromatogr.* 550, 705 (1991).
	Czok, M.; Guiochon, G. A., "Pitfalls in the Choice of Isotherms for the Simulation of Band Profiles in Preparative Chromatography", *J. Chromatogr.* 537, 497 (1991).

Czok, M.

Katti, A. M.; Czok, M.; Guiochon, G. A. "Prediction of Single and Binary Profiles in Overloaded Elution Chromatography Using Various Semi-Ideal Models", *J. Chromatogr.* 556, 205 (1991).

Dai, Sheng

Dai, Sheng; Young, J. P.; Mamantov, Gleb, "A New Sample Cell for Diffuse Reflectance IR Spectroscopy of Air-Sensitive Solid Samples", *Appl. Spectrosc.* 45, 1056 (1991).

Diack, M.

Diack, M.; Guiochon, G., "The Adsorption Isotherm of Phenyldodecane on Porous Carbon and the Elution Profile of Its Bands in High Concentration Chromatography", *Anal. Chem.* 63, 2608 (1991).

Donohue, D. L.

Donohue, D. L.; Petek, M.*, "Isotopic Measurements of Palladium Metal Containing Protium and Deuterium by Glow Discharge Mass Spectrometry", *Anal. Chem.* 63, 740 (1991).

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*, "Slow Positron Beam Extraction and Manipulation Using a Pulsed Gap Accelerator Technique", *Bulletin of the American Physical Society* 35, No. 8, 1733 (1990).

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*, "A Quadratic Potential Time-of-Flight Mass Spectrometer for Use with Slow Positron Ionization Sources and Other Large-Volume Ion Sources", *Rev. Sci. Instrum.* 62, 2131 (1991).

Dose, E. V.

Dose, E. V.; Jacobson, S.; Guiochon, G. A., "Determination of Isotherms from Chromatographic Peak Shapes", *Anal. Chem.* 63, 833 (1991) (invited).

Dose, E. V.; Guiochon, G. A., "High Resolution Modelling of Capillary Zone Electrophoresis and Isotachophoresis", *Anal. Chem.* 63, 1063 (1991).

Dose, E. V.; Guiochon, G. A., "Internal Standardization Technique for Capillary Zone Electrophoresis", *Anal. Chem.* 63, 1154 (1991).

Dose, E. V. — Katti, A. M.; Dose, E. V.; Guiochon, G. A., "Comparison of the Performance of Overloaded Elution and Displacement Chromatography with a Given Column", *J. Chromatogr.* 540, 1 (1991).

Eckenrode, B. A. — Eckenrode, B. A.; McLuckey, S. A.; Glish, G. L., "Comparison of Electron Ionization and Chemical Ionization Sensitivities in an Ion Trap Mass Spectrometer", *Int. J. Mass Spectrom. Ion Proc.* 106, 137 (1991).

El Fallah, M. Z. — El Fallah, M. Z.; Guiochon, G. A., "Comparison of Experimental and Calculated Results in Overloaded Gradient Elution Chromatography for a Single-Component Band", *Anal. Chem.* 63, 859 (1991).

El Fallah, M. Z.; Guiochon, G. A., "Gradient Elution Chromatography at Very High Column Loading: Effect of the Deviation from the Langmuir Model on the Band Profile of a Single Component", *Anal. Chem.* 63, 2244 (1991).

Golshan-Shirazi, S.*; El Fallah, M. Z.; Guiochon, G. A., "Effect of the Intersection of the Single Component Isotherms in Displacement Chromatography", *J. Chromatogr.* 541, 195 (1991).

Glish, G. L. — McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L.; Huang, E. C.*; Henion, J. D.*, "Ion Spray Liquid Chromatography/Ion Trap Mass Spectrometry Determination of Biomolecules", *Anal. Chem.* 63, 375 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Electrospray Ionization of Porphyrins Using a Quadrupole Ion Trap for Mass Analysis", *Anal. Chem.* 63, 1098 (1991).

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength Laser Ionization/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Anal. Chem.* 63, 1186 (1991).

Glish, G. L.

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Charge Determination of Product Ions Formed from Collision-Induced Dissociation of Multiply Protonated Molecules Via Ion/Molecule Reactions", *Anal. Chem.* 63, 1971 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Preforming Ions in Solution via Charge-Transfer Complexation for Analysis by Electrospray Ionization Mass Spectrometry", *Anal. Chem.* 63, 2064 (1991).

Cooks, R. G.*; Glish, G. L.; McLuckey, S. A.; Kaiser, R. E., Jr.*, "Ion Trap Mass Spectrometry", *Chem. Eng. News* 69, 26 (1991) (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Multiple Stages of Mass Spectrometry in a Quadrupole Ion Trap Mass Spectrometer: Prerequisites", *Int. J. Mass Spectrom. Ion Proc.* 106, 213 (1991).

Eckenrode, B. A.; McLuckey, S. A.; Glish, G. L., "Comparison of Electron Ionization and Chemical Ionization Sensitivities in an Ion Trap Mass Spectrometer", *Int. J. Mass Spectrom. Ion Proc.* 106, 137 (1991).

McLuckey, S. A.; Goeringer, D. E.; Glish, G. L., "Selective Ion Isolation/Rejection Over a Broad Mass Range in the Quadrupole Ion Trap", *J. Am. Soc. Mass Spectrom.* 2, 11 (1991).

Goeringer, D. E.

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength Laser Ionization/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Anal. Chem.* 63, 1186 (1991).

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Resonance Enhanced Multiphoton Ionization in an Ion Detector", *Int. J. Mass Spectrom. Ion Proc.* 106, 175 (1991).

McLuckey, S. A.; Goeringer, D. E.; Glish, G. L., "Selective Ion Isolation/Rejection Over a Broad Mass Range in the Quadrupole Ion Trap", *J. Am. Soc. Mass Spectrom.* 2, 11 (1991).

Grimm, C. C.

Grimm, C. C.; Short, R. T.; Todd, P. J., "A Wide-Angle Secondary Ion Probe for Organic Ion Imaging", *J. Am. Soc. Mass Spectrom.* 2, 362 (1991).

Short, R. T.; Grimm, C. C.; Todd, P. J., "Monitor for Displaying Real-Time Images of Low Energy Ion Beams", *J. Am. Soc. Mass Spectrom.* 2, 226 (1991).

Guiochon, G. A.

Katti, A. M.; Guiochon, G. A., "Fundamentals of Non-Linear Chromatography: Prediction of Experimental Profiles and Band Separation", *Adv. Chromatogr.* 31, 1 (1991).

Golshan-Shirazi, S.*; Guiochon, G. A., "Optimization in Preparative Liquid Chromatography", *Am. Biotech. Lab.* 8, 26 (1990).

Jacobson, S.; Golshan-Shirazi, S.*; Guiochon, G. A., "Isotherm Selection for Band Profile Simulations in Preparative Chromatography" *AIChE J.* 37, 836 (1991).

Guiochon, G. A.; Sepaniak, M. J.*, "Data Acquisition for Chromatographic Peaks", *Anal. Chem.* 63, 73 (1991).

Dose, E. V.; Jacobson, S.; Guiochon, G. A., "Determination of Isotherms from Chromatographic Peak Shapes", *Anal. Chem.* 63, 833 (1991).

El Fallah, M. Z.; Guiochon, G. A., "Comparison of Experimental and Calculated Results in Overloaded Gradient Elution Chromatography for a Single-Component Band", *Anal. Chem.* 63, 859 (1991).

Dose, E. V.; Guiochon, G. A., "High Resolution Modelling of Capillary Zone Electrophoresis and Isotachophoresis", *Anal. Chem.* 63, 1063 (1991).

Golshan-Shirazi, S.*; Huang, J. K.*; Guiochon, G. A., "Comparison of an Experimental Competitive Isotherm and the Levan-Vermeulen Model and Prediction of Band Profiles in a Case of Selectivity Reversal", *Anal. Chem.* 63, 1147 (1991).

Guiochon, G. A.

Dose, E. V.; Guiochon, G. A., "Internal Standardization Technique for Capillary Zone Electrophoresis", *Anal. Chem.* 63, 1154 (1991).

El Fallah, M. Z.; Guiochon, G. A., "Gradient Elution Chromatography at Very High Column Loading: Effect of the Deviation from the Langmuir Model on the Band Profile of a Single Component", *Anal. Chem.* 63, 2244 (1991).

Diack, M.; Guiochon, G., "The Adsorption Isotherm of Phenyldodecane on Porous Carbon and the Elution Profile of Its Bands in High Concentration Chromatography", *Anal. Chem.* 63, 2608 (1991).

Zhu, J.*; Katti, A. M.; Guiochon, G. A., "The Effect of Impurities in the Displacer on the Chromatographic Profiles Obtained in Displacement Chromatography", *Anal. Chem.* 63, 2183 (1991).

Katti, A. M.; Huang, J. -X.*; Guiochon, G. A., "Prediction of Single Component Profiles of Proteins in Overloaded Elution Chromatography", *Biotechnol. Bioeng.* 36, 288 (1990).

Golshan-Shirazi, S.*; Guiochon, G. A., "Practical Optimization of the Experimental Conditions in Preparative Liquid Chromatography", *Chromatographia* 30, 613 (1990).

Jacobson, S.; Golshan-Shirazi, S.*; Guiochon, G. A., "Influence of the Mobile Phase Composition on the Adsorption Isotherms of an Amino-Acid Derivative on Immobilized Bovine Serum Albumin", *Chromatographia* 31, 323 (1991).

Czok, M.; Guiochon, G. A, "Comparison of the Results Obtained with Different Models for the Simulation of Preparative Chromatography", *Comput. Chem. Eng.* 14, 1435 (1990).

Ma, Z.*; Guiochon, G. A., "Application of Orthogonal Collocation on Finite Elements in the Simulation of Non-Linear Chromatography", *Comput. Chem. Eng.* 15, 415 (1991).

Guiochon, G. A.

Huang, J. X.*; Schudel, J. V. S.; Guiochon, G. A., "Adsorption Behavior of Some Proteins on TSK-DEAE 5PW Anion Exchanger", *J. Chromatogr. Sci.* 29, 122 (1991).

Golshan-Shirazi, S.*; Guiochon, G. A., "Optimization of the Experimental Conditions in Preparative Liquid Chromatography. Trade-Offs Between Production Rate and Recovery Yield", *J. Chromatogr.* 536, 57 (1991).

Czok, M.; Guiochon, G. A., "Pitfalls in the Choice of Isotherms for the Simulation of Band Profiles in Preparative Chromatography", *J. Chromatogr.* 537, 497 (1991).

Katti, A. M.; Dose, E. V.; Guiochon, G. A., "Comparison of the Performance of Overloaded Elution and Displacement Chromatography with a Given Column", *J. Chromatogr.* 540, 1 (1991).

Golshan-Shirazi, S.*; El Fallah, M. Z.; Guiochon, G. A., "Effect of the Intersection of the Single Component Isotherms in Displacement Chromatography", *J. Chromatogr.* 541, 195 (1991).

Lin, B.*; Ma, Z.*; Guiochon, G. A., "Influence of the Boundary Conditions on the Results of the Dynamic Chromatography Model", *J. Chromatogr.* 542, 1 (1991).

Golshan-Shirazi, S.*; Guiochon, G. A., "On the Use of the Levon-Vermeulen Isotherm Model for the Calculation of Individual Elution Band Profiles in Preparative Liquid Chromatography", *J. Chromatogr.* 545, 1 (1991).

Zhu, J.*; Katti, A. M.; Guiochon, G. A., "Comparison of Various Isotherm Models for Predicting Competitive Adsorption Data", *J. Chromatogr.* 552, 71 (1991) (invited).

Katti, A. M.; Czok, M.; Guiochon, G. A. "Prediction of Single and Binary Profiles in Overloaded Elution Chromatography Using Various Semi-Ideal Models", *J. Chromatogr.* 556, 205 (1991).

Guiochon, G. A.

Czok, M.; Katti, A. M.; Guiochon, G. A., "The Effect of Sample Viscosity in High Performance Size Exclusion Chromatography and Its Control", *J. Chromatogr.* 550, 705 (1991).

Moreau, M.*; Valentin, P.*; Vidal-Madjar, C.*; Lin, B. C.*; Guiochon, G. A., "Adsorption Isotherm Model for Multicomponent Adsorbate-Adsorbate Interactions", *J. Colloid. Interface Sci.* 141, 127 (1991).

Roles, J.; Guiochon, G. A., "Determination of the Surface Energy Distribution Using Adsorption Isotherm Data Obtained by Inverse Gas-Solid Chromatography", *J. Phys. Chem.* 95, 4098 (1991).

Golshan-Shirazi, S.*; Guiochon, G. A., "Combined Effects of Finite Axial Dispersion and Slow Adsorption/Desorption Kinetics on Band Profiles in Non-Linear Chromatography", *J. Phys. Chem.* 95, 6390 (1991).

Hettich, R. L.

Buchanan, M. V.; Hettich, R. L.; Wise, M. B., "Rapid Analysis Using Direct Sampling Mass Spectrometry", *Preprints of the Fuel Chemistry Division, American Chemical Society.*

Hettich, R. L.; Buchanan, M. V., "Investigation of UV Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry for Peptides", *J. Am. Soc. Mass Spectrom.* 2, 22 (1991).

Hettich, R. L.; Buchanan, M. V., "Structural Characterization of Normal and Modified Oligonucleotides by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", *J. Am. Soc. Mass Spectrom.* 2, 402 (1991).

Hulett, L. D.

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*, "Slow Positron Beam Extraction and Manipulation Using a Pulsed Gap Accelerator Technique", *Bulletin of the American Physical Society*, 35, No. 8, 1733 (1990).

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*, "A Quadratic Potential Time-of-Flight Mass Spectrometer for Use with Slow Positron Ionization Sources and Other Large-Volume Ion Sources", *Rev. Sci. Instrum.* 62, 2131 (1991).

Jacobson, S.

Jacobson, S.; Golshan-Shirazi, S.*; Guiochon, G. A., "Isotherm Selection for Band Profile Simulations in Preparative Chromatography" *AIChE J.* 37, 836 (1991).

Dose, E. V.; Jacobson, S.; Guiochon, G. A., "Determination of Isotherms from Chromatographic Peak Shapes", *Anal. Chem.* 63, 833 (1991).

Jacobson, S.; Golshan-Shirazi, S.*; Guiochon, G. A., "Influence of the Mobile Phase Composition on the Adsorption Isotherms of an Amino-Acid Derivative on Immobilized Bovine Serum Albumin", *Chromatographia* 31, 323 (1991).

Katti, A. M.

Katti, A. M.; Guiochon, G. A., "Fundamentals of Non-Linear Chromatography: Prediction of Experimental Profiles and Band Separation", *Adv. Chromatogr.* 31, 1 (1991).

Zhu, J.*; Katti, A. M.; Guiochon, G. A., "The Effect of Impurities in the Displacer on the Chromatographic Profiles Obtained in Displacement Chromatography", *Anal. Chem.* 63, 2183 (1991).

Katti, A. M.; Huang, J. -X.*; Guiochon, G. A., "Prediction of Single Component Profiles of Proteins in Overloaded Elution Chromatography", *Biotechnol. Bioeng.* 36, 288 (1990).

Katti, A. M.; Dose, E. V.; Guiochon, G. A., "Comparison of the Performance of Overloaded Elution and Displacement Chromatography with a Given Column", *J. Chromatogr.* 540, 1 (1991).

Katti, A. M.; Czok, M.; Guiochon, G. A. "Prediction of Single and Binary Profiles in Overloaded Elution Chromatography Using Various Semi-Ideal Models", *J. Chromatogr.* 556, 205 (1991).

Zhu, J.*; Katti, A. M.; Guiochon, G. A., "Comparison of Various Isotherm Models for Predicting Competitive Adsorption Data", *J. Chromatogr.* 552, 71 (1991).

Katti, A. M.

Czok, M.; Katti, A. M.; Guiochon, G. A., "The Effect of Sample Viscosity in High Performance Size Exclusion Chromatography and Its Control", *J. Chromatogr.* 550, 705 (1991).

McLuckey, S. A.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L.; Huang, E. C.*; Henion, J. D.*, "Ion Spray Liquid Chromatography/Ion Trap Mass Spectrometry Determination of Biomolecules", *Anal. Chem.* 63, 375 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Electrospray Ionization of Porphyrins Using a Quadrupole Ion Trap for Mass Analysis", *Anal. Chem.* 63, 1098 (1991).

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength Laser Ionization/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", *Anal. Chem.* 63, 1186 (1991).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Charge Determination of Product Ions Formed from Collision-Induced Dissociation of Multiply Protonated Molecules Via Ion/Molecule Reactions", *Anal. Chem.* 63, 1971 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Preforming Ions in Solution via Charge-Transfer Complexation for Analysis by Electrospray Ionization Mass Spectrometry", *Anal. Chem.* 63, 2064 (1991).

Cooks, R. G.*; Glish, G. L.; McLuckey, S. A.; Kaiser, R. E., Jr.*, "Ion Trap Mass Spectrometry", *Chem. Eng. News* 69, 26 (1991).

Eckenrode, B. A.; McLuckey, S. A.; Glish, G. L., "Comparison of Electron Ionization and Chemical Ionization Sensitivities in an Ion Trap Mass Spectrometer", *Int. J. Mass Spectrom. Ion Proc.* 106, 137 (1991).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Multiple Stages of Mass Spectrometry in a Quadrupole Ion Trap Mass Spectrometer: Prerequisites", *Int. J. Mass Spectrom. Ion Proc.* 106, 213 (1991) (invited).

McLuckey, S. A. — McLuckey, S. A.; Goeringer, D. E.; Glish, G. L., "Selective Ion Isolation/Rejection Over a Broad Mass Range in the Quadrupole Ion Trap", *J. Am. Soc. Mass Spectrom.* 2, 11 (1991).

Ma, C. Y. — Faison, B. D.*; Clark, T. M.*; Ma, C. Y.; Sharkey, D. M.*; Woodward, C. A.*, "Degradation of Organic Sulfur Compounds by a Coal-Solubilizing Fungus", *Appl. Biochem. Biotechnol.* 28/29, 237 (1991).

Mamantov, G. — Dai, Sheng; Young, J. P.; Mamantov, Gleb, "A New Sample Cell for Diffuse Reflectance IR Spectroscopy of Air-Sensitive Solid Samples, *Appl. Spectrosc.* 45, 1056 (1991).

Ramsey, J. M. — Whitten, W. B.; Ramsey, J. M.; Arnold, S.*; Bronk, B. V.*, "Single Molecule Detection in Levitated Microdroplets", *Anal. Chem.* 63, 1027 (1991).

Whitten, W. B.; Ramsey, J. M., "Laser Analysis in an Electrodynamic Trap", *Bulletin of the American Physical Society* 35, 1512 (1990).

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Resonance Enhanced Multiphoton Ionization in an Ion Trap Detector", *Int. J. Mass Spectrom. Ion Proc.* 106, 175 (1991).

Arnold, S.*; Liu, C. T.*; Whitten, W. B.; Ramsey, J. M., "A Microparticle Based Spectral Hole Burning Memory", *Optics Lett.* 16, 420 (1991).

Roles, J. — Roles, J.; Guiochon, G. A., "Determination of the Surface Energy Distribution Using Adsorption Isotherm Data Obtained by Inverse Gas-Solid Chromatography", *J. Phys. Chem.* 95, 4098 (1991).

Rosseel, T. M. — Rosseel, T. M.; Young, J. P.; Vane, C. R.*; Zuhr, R. A.*; Peterson, R. S.*, "High-Resolution Heavy-Ion-Induced X-ray Satellite Emission Study of Implanted Sulfur as a Probe of Co-Implanted Oxygen in an Oxide Substrate", *Nucl. Instrum. Meth.* B56/B57, 41 (1991).

Schudel, J. V. S. — Huang, J. X.*; Schudel, J. V. S.; Guiochon, G. A., "Adsorption Behavior of Some Proteins on TSK-DEAE 5PW Anion Exchanger", *J. Chromatogr. Sci.* 29, 122 (1991).

Short, R. T. — Short, R. T.; Grimm, C. C.; Todd, P. J., "Monitor for Displaying Real-Time Images of Low Energy Ion Beams", *J. Am. Soc. Mass Spectrom.* 2, 226 (1991).

Grimm, C. C.; Short, R. T.; Todd, P. J., "A Wide-Angle Secondary Ion Probe for Organic Ion Imaging", *J. Am. Soc. Mass Spectrom.* 2, 362 (1991).

Brostrom, L.*; Larsson, M.*; Mannervik, S.*; Short, R. T.; Sonnek, D.*, "Photodissociation of Ne^{2+*}" *J. Chem. Soc. Faraday Trans.* 87(6), 797 (1991).

Todd, P. J. — Todd, P. J., "Solution Chemistry and Secondary Ion Emission from Amine-Glycerol Solutions", *J. Am. Soc. Mass Spectrom.* 2, 33 (1991).

Short, R. T.; Grimm, C. C.; Todd, P. J., "Monitor for Displaying Real-Time Images of Low Energy Ion Beams", *J. Am. Soc. Mass Spectrom.* 2, 226 (1991).

Grimm, C. C.; Short, R. T.; Todd, P. J., "A Wide-Angle Secondary Ion Probe for Organic Ion Imaging", *J. Am. Soc. Mass Spectrom.* 2, 362 (1991).

Van Berkel, G. J. — McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L.; Huang, E. C.*; Henion, J. D.*; "Ion Spray Liquid Chromatography/Ion Trap Mass Spectrometry Determination of Biomolecules", *Anal. Chem.* 63, 375 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Electrospray Ionization of Porphyrins Using a Quadrupole Ion Trap for Mass Analysis", *Anal. Chem.* 63, 1098 (1991).

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Preforming Ions in Solution via Charge-Transfer Complexation for Analysis by Electrospray Ionization Mass Spectrometry", *Anal. Chem.* 63, 2064 (1991).

Van Berkel, G. J.

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Charge Determination of Product Ions Formed from Collision-Induced Dissociation of Multiply Protonated Molecules Via Ion/Molecule Reactions", *Anal. Chem.* 63, 1971 (1991).

Van Berkel, G. J.; Castro, A. J.*; Filby, R. H.*, "Tabulation of Exact Masses and Comparison of Isotope Patterns Expected for Geoporphyrin Molecular Ions in Electron Ionization Mass Spectra", *Appl. Geochem.* 6, 105 (1991).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Multiple Stages of Mass Spectrometry in a Quadrupole Ion Trap Mass Spectrometer: Prerequisites", *Int. J. Mass Spectrom. Ion Proc.* 106, 213 (1991).

Beato, B. D.*; Yost, R. A.*; Van Berkel, G. J.; Filby, R. H.*; Quirke, J. M. E.*, "The Henryville Bed of the New Albany Shale-III: Tandem Mass Spectrometric Analyses of Geoporphyrins from the Bitumen and Kerogen", *Org. Geochem.* 17, 93 (1991).

Vick, D. O.

Young, J. P.; Murray, G. M.*; Ensor, D. D.*; Vick, D. O., "Luminescence Spectrum of Trivalent Terbium Ions Adsorbed on a Single Resin Bead", *Appl. Spectrosc.* 45, 134 (1991).

Whitten, W. B.

Whitten, W. B.; Ramsey, J. M.; Arnold, S.*; Bronk, B. V.*, "Single Molecule Detection in Levitated Microdroplets", *Anal. Chem.* 63, 1027 (1991).

Whitten, W. B.; Ramsey, J. M., "Laser Analysis in an Electrodynamic Trap", *Bulletin of the American Physical Society* 35, 1512 (1990).

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Resonance Enhanced Multiphoton Ionization in an Ion Trap Detector", *Int. J. Mass Spectrom. Ion Proc.* 106, 175 (1991).

Arnold, S.*; Liu, C. T.*; Whitten, W. B.; Ramsey, J. M., "A Microparticle-Based Spectral Hole Burning Memory", *Optics Lett.* 16, 420 (1991).

Wise, M. B. — Buchanan, M. V.; Hettich, R. L.; Wise, M. B., "Rapid Analysis Using Direct Sampling Mass Spectrometry", *Preprints of the Fuel Chemistry Division, American Chemical Society.*

Young, J. P. — Young, J. P.; Murray, G. M.*; Ensor, D. D.*; Vick, D. O., "Luminescence Spectrum of Trivalent Terbium Ions Adsorbed on a Single Resin Bead", *Appl. Spectrosc.* 45, 134 (1991).

Dai, Sheng; Young, J. P.; Mamantov, Gleb, "A New Sample Cell for Diffuse Reflectance IR Spectroscopy of Air-Sensitive Solid Samples", *Appl. Spectrosc.* 45, 1056 (1991).

Rosseel, T. M.; Young, J. P.; Vane, C. R.*; Zuhr, R. A.*; Peterson, R. S.*, "High-Resolution Heavy-Ion-Induced X-ray Satellite Emission Study of Implanted Sulfur as a Probe of Co-Implanted Oxygen in an Oxide Substrate", *Nucl. Instrum. Meth.* B56/B57, 41 (1991).

REPORTS

Laing, W. R. — Laing, W. R., *Analytical Chemistry Division Summary Report: Inorganic Chemistry Section*, ORNL/CF-91/69, February 1991.

McBay, E. H. — Smith, D. H.; Bostick, D. A.; McBay, E. H.; Carter, J. A.; Ehinger, M. H.*, *The Joint PNC-ORNL Tank Calibration Experiment of 1991*, ORNL/TM-12001, November 1991.

McLuckey, S. A. — McLuckey, S. A., *Report of Foreign Travel to Amsterdam*, ORNL/FTR-4023, September 1991.

Ma, C. Y. — Jenkins, R. A.; Nestor, C. W.*; Thompson, C. V.; Gayle, T. M.*; Ma, C. Y.; Tomkins, B. A.; Moody, R. L.*, *Characterization of Rocket Propellant Combustion Products. Chemical Characterization and Computer Modeling of the Exhaust Products from Four Propellant Formulations*, ORNL/TM-11759, December 9, 1991.

Maskarinec, M. P. — Maskarinec, M. P.; Bayne, C. K.*; Johnson, L. H.; Holladay, S. K.; Jenkins, R. A.; Tomkins, B. A., *Stability of Explosives in Environmental Water and Soil Samples*, ORNL/TM-11770, January 1991.

Robinson, L. — Robinson, L., *Response to Accelerators and Radiation Sources Review Committee's Review of the 14-MeV Neutron Generator Facility in Building 2011*, ORNL/CF-91/329, September 1991.

Rosseel, T. M. — Rosseel, T. M., *Report of Foreign Travel to Amsterdam*, ORNL/FTR-4078, October 1991.

Smith, D. H. — Smith, D. H.; Bostick, D. A.; McBay, E. H.; Carter, J. A.; Ehinger, M. H.*, *The Joint PNC-ORNL Tank Calibration Experiment of 1991*, ORNL/TM-12001, November 1991.

Thompson, C. V. — Jenkins, R. A.; Nestor, C. W.*; Thompson, C. V.; Gayle, T. M.*; Ma, C. Y.; Tomkins, B. A.; Moody, R. L.*, *Characterization of Rocket Propellant Combustion Products. Chemical Characterization and Computer Modeling of the Exhaust Products from Four Propellant Formulations*, ORNL/TM-11759, December 9, 1991.

Tomkins, B. A.

Shugart, L. R.*; Griest, W. H.; Tan, E.*; Guzman, C.*; Caton, J. E.; Ho, C. -h; Tomkins, B. A., *TNT Metabolites in Animal Tissues*, ORNL/M-1336, December 1990.

Maskarinec, M. P.; Bayne, C. K.*; Johnson, L. H.; Holladay, S. K.; Jenkins, R. A.; Tomkins, B. A., *Stability of Explosives in Environmental Water and Soil Samples*, ORNL/TM-11770, January 1991.

Jenkins, R. A.; Nestor, C. W.*; Thompson, C. V.; Gayle, T. M.*; Ma, C. Y.; Tomkins, B. A.; Moody, R. L.*, *Characterization of Rocket Propellant Combustion Products. Chemical Characterization and Computer Modeling of the Exhaust Products from Four Propellant Formulations*, ORNL/TM-11759, December 9, 1991.

Young, J. P.

Young, J. P.; Mamantov, Gleb*, *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-1370, February 15, 1991.

Young, J. P.; Mamantov, Gleb*, *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-1484, May 15, 1991.

Young, J. P.; Mamantov, Gleb*, *In-Line Sensors for Electrolytic Magnesium Cells - Annual Report*, ORNL/M-1599, August 1991.

Young, J. P.; Mamantov, Gleb*, *In-Line Sensors for Electrolytic Magnesium Cells - Quarterly Report*, ORNL/M-1783, November 15, 1991.

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.

Speaker	Author(s), Meeting, Date
Asano, K. G.	Asano, K. G.; McLuckey, S. A.; Glish, G. L., "'Spontaneous" Cluster Ion Decomposition in a Quadrupole Ion Trap", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.
Buchanan, M. V.	Buchanan, M. V.; Ilgner, R. H.; Watson, A. P.*, "Determination of Chemical Agent Contamination in Building Materials" American Chemical Society National Meeting, Atlanta, April 14-19, 1991 (invited).
	Buchanan, M. V.; Hettich, R. L.; Caton, J. E.; Hurst, G. B., "Development of New Methods for Rapid Analysis of Drugs in Biological Matrices", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.
	Buchanan, M. V.; Hettich, R. L.; Ma, C. Y.; Guerin, M. R., "Crude Oil Characterization by Direct Sampling Ion Trap Mass Spectrometry", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.
	Buchanan, M. V.; Wise, M. B.; Guerin, M. R.; White, D. C.*; Polumbo, A. C.*, "Direct Sampling ITMS for the Monitoring of Microbial Processes", Symposium on Chromatography and Mass Spectrometry, Lund, Sweden, June 10-13, 1991 (invited).

Buchanan, M. V.

Buchanan, M. V.; Hettich, R. L.; Wise, M. B., "Rapid Analysis Using Direct Sampling Mass Spectrometry", American Chemical Society National Meeting, New York, August 25-30, 1991 (invited).

Buchanan, M. V.; Hettich, R. L., "Investigation of Normal and Modified Oligonucleotides by Matrix-Assisted Laser Desorption FTMS", Eastern Analytical Symposium, Somerset, N. J., November 11, 1991.

Buchanan, M. V.; Wise, M. B.; Hurst, G. B.; Hettich, R. L., "New Approaches for Rapid Trace Analysis Using Quadrupole Ion Traps", 43rd Annual South-East Regional American Chemical Society Meeting, Richmond, Va., November 13, 1991 (invited).

Ceo, R. N.

Ceo, R. N.; Thompson, K. A.*, "Automated Nondestructive Analysis at the Oak Ridge Y-12 Plant", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Christie, W. H.

Christie, W. H., "Progress in Secondary Ion Mass Spectrometry", BES Site Review, Oak Ridge, May 2, 1991.

Christie, W. H., "Isotopic Ratios and Multielement Trace Analysis: Is There a Middle Ground?", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Christie, W. H.; Rosseel, T. M.; Riciputi, L. R., "Analytical Secondary Ion Mass Spectrometry", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Dai, Sheng

Dai, S.; Coffield, J. E.; Begun, G.; Young, J. P.; Mamantov, G., "Development of Raman Fiber Optic Probes for Hostile Environments", American Chemical Society National Meeting, New York, August 25-30, 1991.

Dai, Sheng — Dai, S.; Coffield, J. E.; Begun, G. M.; Young, J. P.; Mamantov, G., "Characterization of the Structure of $MgCl_2$ Species in Several Systems by Raman Spectroscopy", American Chemical Society National Meeting, New York, August 25-30, 1991.

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", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Diack, M. — Diack, M.; Guiochon, G. A., "The Adsorption Isotherms of Long Chain Phenyl Alkanes on Porous Pyrolytic Carbon and the Elution Profiles of Their Bands in High Concentration Chromatography", PREP '91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Dose, E. V. — Dose, E. V.; Guiochon, G. A., "Modelling of High Resolution Capillary Zone Electrophoresis", International Symposium on Capillary Zone Electrophoresis, San Diego, February 4-6, 1991.

Dose, E. V.; Guiochon, G. A., "High-Resolution of Modelling of Nonlinear Electrophoretic Phenomena", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Dose, E. V.; Guiochon, G. A., "Use of Internal Standards in Capillary Electrophoresis", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Duckworth, D. C. — Duckworth, D. C., "Development of an RF Probe for Glow Discharge Mass Spectrometry", BES Site Review, Oak Ridge, May 1, 1991.

Duckworth, D. C.; Marcus, R. K.*; Smith, D. H., "Direct Solids Analysis of Nonconducting Materials by Radio Frequency Powered Glow Discharge Mass Spectrometry", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Dunphy, J. C.

Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Development of Laser Desorption/FTMS for the Analysis of Biological Compounds of Agarose Gels", 42nd Pittsburgh Conference/Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, March 4-8, 1991.

Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Rapid Recovery of Biological Compounds from Electrophoretic Gel Slides for Subsequent Analysis by Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Dyer, F. F.

Dyer, F. F., Robinson, L., Nichols, G., "A Search for Arsenic in Hair and Nail Remains of Former President Zachary Taylor by Neutron Activation Analysis", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

El Fallah, M. Z.

El Fallah, M. Z.; Guiochon, G. A., "Comparison Between Experimental and Theoretical Profiles of a Single Solute in Nonlinear-Gradient Liquid Chromatography", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

El Fallah, M. Z.; Guiochon, G. A., "Effect of the Deviation from the Langmuir Model on the Band Profiles of a Single Component in Overload Gradient Elution Chromatography", PREP '91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Flurer, R. A.

Flurer, R. A.; Glish, G. L.; McLuckey, S. A., "Theoretical and Experimental Studies of the Gas-Phase Ion Chemistry of Freon 113", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Glish, G. L.

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E., "Ion Activation in a Quadrupole Ion Trap", American Society for Mass Spectrometry Symposium on Ion Activation and Dissociation, Sanibel Island, Fla., January 29-February 1, 1991.

Glish, G. L.

Glish, G. L., "The Quest for a High Performance Low Cost Gas Phase Chemical Laboratory", Ohio State University Seminar, February 19, 1991 (invited).

Glish, G. L., "Quadrupole Ion Trap Mass Spectrometry at ORNL", East Tennessee Mass Spectrometry Discussion Group, March 13, 1991 (invited).

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, March 28, 1991 (invited).

Glish, G. L., "The Modern Mass Spectrometer: A Versatile Gas-Phase Chemical Laboratory", Iowa State University Seminar, April 11, 1991 (invited).

Glish, G. L.; McLuckey, S. A., "New Mass Spectrometric Ionization Methods", American Chemical Society National Meeting, Atlanta, April 14-19, 1991 (invited).

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J., "Extending the MS/MS Experiment", American Chemical Society National Meeting, Atlanta, April 14-19, 1991 (invited).

Glish, G. L, "Selected Highlights in Organic Mass Spectrometry", BES Site Review, Oak Ridge, May 2, 1991.

Glish, G. L.; McLuckey, S. A.; Asano, K. G.; Grant, B. C., "A New Ion Source for Continuous Ambient Air Monitoring Using Mass Spectrometry", Symposium on Measurement of Toxic and Related Air Pollutants, Durham, N. C., May 7-10, 1991.

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J.; Hart, K. J., "Ion Activation in a Quadrupole Ion Trap", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Glish, G. L.

Glish, G. L.; McLuckey, S. A., "Formation of Substituted Benzene Radical Cations Via Ion/Molecule Reactions with Iodobenzene", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Glish, G. L., "MS/MS: A New Dimension in Mass Spectrometry", West Virginia Wesleyan College, September 17, 1991 (invited).

Glish, G. L., "Mass Spectrometry in Sciences From A (Astrophysics) to Z (Zoology)", Oak Ridge Science Semester, Oak Ridge, September 18, 1991 (invited).

Glish, G. L.; McLuckey, S. A.; Goeringer, D. E.; Van Berkel, G. J., "The Quadrupole Ion Trap: The Mass Spectrometer of the Future?", North New Jersey Mass Spectrometry Discussion Group, New Brunswick, N. J., September 23, 1991 (invited).

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E., "The Role of MS/MS and Quadrupole Ion Traps in Biomolecule Analysis", Sandoz Research Institute, East Hanover, N. J., September 23, 1991 (invited).

Glish, G. L.; Charles, M. J.; Hart, K. J.; Goeringer, D. E.; McLuckey, S. A., "Fundamentals of Resonant Excitation for Collisional Activation in a Quadrupole Ion Trap", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E., "Fundamental and Analytical Studies of Biomolecules with a Quadrupole Ion Trap", Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, Calif., October 7-11, 1991 (invited).

Glish, G. L.; McLuckey, S. A.; Grant, B. C.; McKown, H. S., "Tandem Mass Spectrometry for Explosives Vapor Detection", FAA Symposium on Explosives Detection, Atlantic City, November 13-15, 1991.

Glish, G. L.

Glish, G. L.; McLuckey, S. A.; Charles, M. J.*, "Fundamentals of the MS/MS Experiment in the Quadrupole Ion Trap", International Workshop on Tandem Mass Spectrometry, Lake Louise, Alberta, Canada, November 21-23, 1991 (invited).

Glish, G. L., "The Mass Spectrometer as a Gas Phase Laboratory", University of North Carolina Seminar, Chapel Hill, December 12, 1991.

Goeringer, D. E.

Goeringer, D. E.; Glish, G. L.; McLuckey, S. A., "Fixed-Wavelength R2PI/Tandem Mass Spectrometry for Mixture Analysis in the Quadrupole Ion Trap", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "Enhancement of Mass Resolution in the Quadrupole Ion Trap Via Resonance Ejection", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Goeringer, D. E.; Whitten, W. B.; McLuckey, S. A.; Glish, G. L., "Experimental and Theoretical Aspects of Enhanced Mass Resolution with the Quadrupole Ion Trap", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Granger, C. C.

Granger, C. C.; Teasley, N. A., "Radioactivity Screening of Deer Harvests from the Oak Ridge Reservation", Canberra Instruments/Nuclear Data Users Group (CINDUG) Meeting, Del Mar, Calif., April 13-19, 1991.

Grant, B. C.

Grant, B. C.; Goeringer, D. E.; Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Performance of an Atmospheric Sampling Glow Discharge Ionization Source with a Triple Quadrupole Mass Spectrometer", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Griest, W. H.

Griest, W. H.; Ho, C. -h.; Guerin, M. R.; Tyndall, R. L.*, "Chemical Comparison of Weathered Spilled Oil and Exxon/Valdez Hold Oil from an Occupational Health Standpoint", 84th Air & Waste Management Association Meeting, Vancouver, British Columbia, June 16-21, 1991 (invited).

Griest, W. H.; Stewart, A. J.*; Tyndall, R. L.*; Ho, C. -h.; Caton, J. E.; Caldwell, W. M.; Ironside, K. S.*, "Chemical and Toxicological Investigation of Composted Explosive-Contaminated Lagoon Soils" U.S. Army Toxic & Hazardous Materials Agency Environmental R & D Symposium, Williamsburg, Va., June 25-27, 1991 (invited).

Griest, W. H., "Oak Ridge National Laboratory Underground Nuclear Waste Storage Tank Characterization", DOE National Tank Waste Characterization Workshop, Hanford, Wash., June 25-27, 1991 (invited).

Griest, W. H.; Schenley, R. L.; Wolfe, P. F.; Caton, J. E.; Moneyhun, J. H., "TCLP Volatile Organics Analyses of Radioactive Mixed Wastes", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991 (invited).

Griest, W. H.; Ramsey, R. S.; Ho, C.-h; Caldwell, W. M., "Supercritical Fluid Extraction and Organic Solvent Microextraction of Chemical Agent Simulants from Soil", U. S. Army Chemical Research Conference on Chemical Defense, Aberdeen Proving Ground, Md., November 19-22, 1991 (invited).

Guiochon, G. A.

Guiochon, G. A., "Comparison Between Experimental and Calculated Band Profiles in Chromatography at High Concentrations", Separations Science Award Address, American Chemical Society National Meeting, Atlanta, April 14-19, 1991 (invited).

Ma, Z.*; Guiochon, G. A., "Comparison Between Experimental and Theoretical Profiles of a Single Solute in Nonlinear-Gradient Liquid Chromatography", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Guiochon, G. A.

Zhu, J.*; Guiochon, G. A., "Practical Problems in Displacement Chromatography", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Newberger, J.*; Guiochon, G. A., "Utility of Sample Self-Displacement as a Routine Preparative Technique", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Golshan-Shirazi, S.*; Guiochon, G. A., "Comparison of the Kinetic Models for Preparative Chromatography", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Golshan-Shirazi, S.*; Guiochon, G. A., "Comparison of the Various Kinetic Models USEDC in Preparative Chromatography", PREP'91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Newberger, J.*; Delange, B.*; Guiochon, G. A., "Sample Self-Displacement Optimization: Borrowing a Tool from Displacement Chromatography", PREP'91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Jandera, P.*; Guiochon, G. A., "Influence of the Sample Solvent on the Band Profiles and Resolution in Preparative Liquid Chromatography", PREP'91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Yang, Y.-B.*; Harrison, K.*; Carr, D.*; Guiochon, G. A., "The Effects of Column Dimension on Loading Capacity in Direct Scale-up Preparative HPLC of Proteins", PREP'91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Guiochon, G. A., "Comparison Between Experimental and Calculated Band Profiles in Chromatography at High Concentrations", HPLC'91, 15th International Symposium on Column Liquid Chromatography, Basel, Switzerland, June 3-7, 1991.

Guiochon, G. A.

Newberger, J.*; Delange, B.*; Guiochon, G. A., "Sample Self-Displacement Optimization: Borrowing a Tool from Displacement Chromatography", HPLC'91, 15th International Symposium on Column Liquid Chromatography, Basil, Switzerland, June 3-7, 1991.

Golshan-Shirazi, S.*; Guiochon, G. A., "Solutions of the Ideal Model of Chromatography for One and Two Components", NATO ASI on Theoretical Advances in Chromatography and Related Separation Techniques, Ferrara, Italy, August 15-29, 1991.

Golshan-Shirazi, S.*; Guiochon, G. A., "The Equilibrium-Dispersive Model of Chromatography", NATO ASI on Theoretical Advances in Chromatography and Related Separation Techniques, Ferrara, Italy, August 15-29, 1991.

Golshan-Shirazi, S.*; Guiochon, G. A., "Review of the Various Models of Linear Chromatography and of Their Solutions", NATO ASI on Theoretical Advances in Chromatography and Related Separation Techniques, Ferrara, Italy, August 15-29, 1991.

Hart, K. J.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Effects of Experimental Parameters on Ion Storage in a Quadrupole Ion Trap Mass Spectrometer", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Hart, K. J.; McLuckey, S. A.; Glish, G. L., "Application of Substructure Identification Rules to MS^n Spectra Obtained on an Ion Trap Mass Spectrometer", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Hettich, R. L.

Hettich, R. L.; Buchanan, M. V., "Applications and Current Limitations of Matrix-Assisted Laser Desorption Fourier Transform Mass Spectrometry for Biomolecules", Workshop on Laser Ablation Mechanisms and Applications, Oak Ridge, April 8-10, 1991 (invited).

Hettich, R. L.

Hettich, R. L., "Ion-Molecule Reactions of Carbon Cluster Anions", Workshop on Laser Ablation Mechanisms and Applications, Oak Ridge, April 8-10, 1991.

Hettich, R. L.; Compton, R. N.*; Ritchie, R. H.*, "Doubly Charged Negative Ions of Bucky Ball - C_{60}^{2-}", Workshop on Laser Ablation Mechanisms and Applications, Oak Ridge, April 8-10, 1991.

Hettich, R. L.; Buchanan, M. V., "Applications of Matrix-Assisted Laser Desorption FTMD for Biomolecules", Workshop on Laser Ablation Mechanisms and Applications, Oak Ridge, April 8-10, 1991.

Hettich, R. L., "Structural Characterization of Biomolecules and Clusters Using Laser Desorption FTMS", East Tennessee Mass Spectrometry Discussion Group, April 25, 1991.

Hettich, R. L.; Buchanan, M. V., "Collision-Induced Dissociation and Ion-Molecule Reactions by FT/ICR", DOE Workshop on Dissociating Large Ions, Seattle, April 29-May 2, 1991.

Hettich, R. L.; Buchanan, M. V., "Investigation of Matrix-Assisted Laser Desorption FTMS for Biomolecules", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Hettich, R. L.; Compton, R. N.*; Ritchie, R. H.*, "Observation and Possible Formation of Mechanisms of Doubly Charged Negative Ions of C_{60} and C_{70}", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Hettich, R. L.; Compton, R. N.*, "Structural Characterization of Fullerenes by Laser Desorption FTMS", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Hettich, R. L.; Buchanan, M. V., "Characterization of Biomolecules and Carbon Clusters by Laser Desorption FTMS", Federation of Analytical Chemists and Spectroscopy Societies, Anaheim, Calif., October 6-11, 1991 (invited).

Hettich, R. L.

Hettich, R. L.; Buchanan, M. V.; Compton, R. N.*, "Characterization of Aluminum and Carbon Cluster Ions by Fourier Transform Ion Cyclotron Resonance Mass Spectrometer", Eastern Analytical Symposium, Somerset, N. J., November 11, 1991 (invited).

Hulett, L. D.

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*; Hayter, J. B.*; Peretz, F. J.*; Montgomery, B. H.*; Misra, A. K.*, "Intense Monoenergetic Positron Beam Production and Applications at Oak Ridge National Laboratory", Japan Atomic Energy Research Institute Workshop on Positron Spectroscopy, Tokyo, February 28-March 1, 1991 (invited).

Hulett, L. D., "Interactions Between Positrons and Molecules: New Results and Instrumentation", BES Site Review, Oak Ridge, May 2, 1991.

Hulett, L. D.; Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Lewis, T. A.*, "Mass Spectrometry Studies of the Ionization of Large Organic Molecules by Slow Positrons", 9th International Conference on Positron Annihilation, Szombathely, Hungary, August 26-31, 1991 (invited).

Hurst, G. B.

Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Wise, M. B., "Direct-Sampling MS Measurement of Volatiles in Environmental Samples", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Hurst, G. B.; Wise, M. B.; Tomkins, B. A.; Thompson, C. V.; Theobald, D. L.; Buchanan, M. V.; Guerin, M. R., "Screening Methods for Volatiles in Environmental Samples Using Direct-Sampling Ion Trap Mass Spectrometry", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Ilgner, R. H.

Ilgner, R. H.; Maskarinec, M. P.; Moneyhun, J. H.; Ho, C.-h., "Toxicity Characteristic Leaching Procedure (TCLP) Implementation: Tricks and Tips", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991 (invited).

Jacobson, S.

Jacobson, S.; Golshan-Shirazi, S.; Guiochon, G. A., "Experimental and Theoretical Study of Enantiomers on Chiral Stationary Phases at High Concentrations", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Jacobson, S.; Guiochon, G. A., "Comparison Between Experimental and Theoretical Band Profiles of Some Enantiomers at High Concentrations", PREP '91, 8th International Symposium on Preparative Chromatography, Arlington, Va., May 13-15, 1991.

Jenkins, R. A.

Jenkins, R. A.; Moody, R. L.; Higgins, C. E.; Moneyhun, J. H., "Nicotine in Environmental Tobacco Smoke (ETS): Comparison of Mobile Personal and Stationary Area Sampling", Environmental Protection Agency/Air Waste Management Association Conference on Measurement of Toxic and Related Air Pollutants", Durham, N. C., May 7-10, 1991 (invited).

Kerley, E. L.

Kerley, E. L.; Buchanan, M. V.; Cook, K. D.*; Shahgholi, M., "Development of an Electrostatic Ion Injection Device for Fourier Transform Ion Cyclotron Research Studies of Electrosprayed Ions", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

McBay, E. H.

Swihart, G. H.*; McBay, E. H.; Smith, D. H.; Stefke, J. W.*, "A Lacustrine Evaporite Borate Deposit as a Record of Long-Term Variations in Geothermal Fluid Boron Isotopic Composition", Geological Society of America, San Diego, October 21-24, 1991.

McLuckey, S. A.

McLuckey, S. A., "Mechanisms of Collisional Activation" American Society for Mass Spectrometry Symposium on Ion Activation and Dissociation, Sanibel Island, Fla., January 29-February 1, 1991 (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Ion/Molecule Reactions of Multiply Charged Ions from Electrospray", University of Georgia Seminar, Athens, February 14, 1991.

McLuckey, S. A.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "Quadrupole Ion Trap Analysis of Biopolymers: Proteins and Oligonucleotides", University of Kent, Canterbury, England, February 21, 1991 (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Mass Spectrometry/Mass Spectrometry of Multiply Protonated Peptides and Proteins, American Chemical Society National Meeting, Atlanta, April 14-19, 1991 (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Reactive Collisions of Multiply Charged Ions Derived from Electrospray", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991 (invited).

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "MS/MS and MS^n Studies of Multiply Charged Oligonucleotides Using a Quadrupole Ion Trap", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E.; Glish, G. L.; Ramsey, R. S., "Recent Developments in Quadrupole Ion Trap Mass Spectrometry of Ions Derived From Electrospray", 8th Montreux Symposium on Liquid Chromatography Mass Spectrometry, Cornell University, Ithaca, N. Y., July 15-19, 1991 (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Ion/Molecule Reactions of Multiply Charged Ions Derived From Electrospray", 12th International Mass Spectrometry Conference, Amsterdam, August 26-31, 1991 (invited).

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "Collision-Induced Dissociation of Multiply Charged Biopolymers in a Quadrupole Ion Trap", 12th International Mass Spectrometry Conference, Amsterdam, August 26-31, 1991 (invited).

Glish, G. L.; McLuckey, S. A., "Ion/Molecule Reactions of Even-Electron Ions Giving Odd-Electron Product Ions", 12th International Mass Spectrometry Conference, Amsterdam, August 26-31, 1991 (invited).

McLuckey, S. A.

Glish, G. L.; McLuckey, S. A.; Donohue, D. L.; Hulett, L. D., "Positron Ionization Mass Spectrometry", 12th International Mass Spectrometry Conference, Amsterdam, August 26-31, 1991 (invited).

Duckworth, D. C.; Marcus, R. K.*; McLuckey, S. A.; Glish, G. L., "Radio-Frequency Glow Discharge/Ion Trap Mass Spectrometry", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

McLuckey, S. A., "From TNT to DNA: Adventures in Ion Trapping", ORNL Showcase Seminar, Oak Ridge, October 9, 1991.

McLuckey, S. A., "From TNT to DNA: Adventures in Ion Trapping", University of Texas Seminar, Austin, October 24, 1991.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L.; Ramsey, R. S., "Tandem Mass Spectrometry of Multiply Charged Oligonucleotides", 43rd Annual South-East Regional American Chemical Society Meeting, Richmond, Va., November 13, 1991 (invited).

McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J., "Chemistry and Physics in an Mass Spectrometer: What Makes a Reaction Analytically Useful?", Pittsburgh Area Mass Spectrometry Discussion Group, Pittsburgh, November 17, 1991.

Ma, C. Y.

Ma, C. Y.; Bayne, C. K.*; Maskarinec, M. P., "Differentiation of Aroclors in Environmental Samples Using Negative Ion Chemical Ionization (NICI) Mass Spectrometry", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Maskarinec, M. P.

Maskarinec, M. P., "Analysis of TCLP Extracts: Problems and Potential Solutions", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Mueller, T. R.

Hasty, Elaine*; Littau, Sara*; Revesz, Robert*; Stewart, J. H.; Mueller, T. R., "Microwave Sample Preparation of Oils with Temperature Feedback Control", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Ondracek, A. L.

Ondracek, A. L., "Determination of Mercury in Soil Using a Planar Detector", GLCA Symposium, ORNL, December 9, 1991.

Ramsey, J. M.

Ramsey, J. M.; Whitten, W. B.; Arnold, S.*; Bronk, B. V*, "Ultrasensitive Fluorescence Measurements in Microdroplets", Optical Methods for Ultrasensitive Detections and Analysis: Techniques and Applications, OE/LASE '91, Los Angeles, January 20-25, 1991 (invited).

Ramsey, J. M.; Whitten, W. B.; Brown, G. M.*; Garrity, M. L.*; Jacobson, K. B.*; Sachleben, R. A.*, "Ultrasensitive Luminescence Detection of Lanthanide Ion Labels for DNA Sequencing and Mapping", DOE Human Genome Workshop, Santa Fe, February 17-21, 1991.

Ramsey, J. M.; Whitten, W. B.; Brown, G. M.*; Arnold, S.*; Bronk B. V.*, "Ultrasensitive Fluorescence Detector in Levitated Microdroplets", Northeastern University Seminar, Boston, March 26, 1991.

Ramsey, J. M.; Dale, J. M.; Whitten, W. B., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", DOE Particle Workshop, Sacramento, Calif., April 8-12, 1991.

Ramsey, J. M., "Lasers and Electrodynamic Traps", BES Site Review, Oak Ridge, May 1, 1991.

Ramsey, J. M.; Dale, J. M.; Whitten, W. B., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", DOE Science and Technology Optics Workshop, Washington, D. C., July 16-17, 1991.

Ramsey, J. M., "Microchip Liquid Chromatograph", DOE LAGER Meeting, Washington, D. C., August 21, 1991.

Ramsey, J. M.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M., "Chemical Vapor Deposition Diagnostics Using Resonance Ionization Mass Spectrometry", Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, Calif., October 6-11, 1991.

Ramsey, J. M.; Whitten, W. B.; Arnold, S.*; Bronk, B. V.*, "Single Molecule Detection in Microdroplets", Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, Calif., October 6-11, 1991.

Ramsey, J. M., "Micro-Spectrochemical Analysis: Single Particles to Single Molecules", University of Delaware Seminar, November 4, 1991.

Ramsey, J. M., "Document Tracking Using Dichroic Fibers", DOE EXPO '91 on Special Operations, Albuquerque, N. M., November 19-21, 1991 (invited).

Ramsey, J. M., "Microinstrumentation for Liquid Phase Analysis", DOE EXPO '91 on Special Operations, Albuquerque, N. M., November 19-21, 1991 (invited).

Ramsey, J. M., "Advanced Techniques for the Chemical Characterization of Microparticles", DOE EXPO '91 on Special Operations, Albuquerque, N. M., November 19-21, 1991 (invited).

Ramsey, R. S.

Ramsey, R. S.; Van Berkel, G. J., "Determining Pyrimidine Photoproducts in UV-Irradiated DNA", American Chemical Society National Meeting, New York, August 25-30, 1991.

Robinson, L.

Robinson, L.; Dyer, F. F., "Status of NAA Facilities in the Advanced Neutron Source", 8th International Conference on Modern Trends in Activation Analysis, Vienna, September 14-19, 1991.

Roles, J.

Roles, J.; Guiochon, G. A., "Characterization of Aluminum Oxides Used in Ceramic Processing by Inverse Chromatography", American Chemical Society National Meeting, Atlanta, April 14-19, 1991.

Roles, J.

Roles, J.; Guiochon, G. A., "Study of the Surface Heterogeneity of Various Materials", 8th Danube Symposium on Chromatography, Warsaw, Poland, September 2-6, 1991.

Shaw, R. W.

Shaw, R. W., "Diode Laser Resonance Ionization Mass Spectrometry", BES Site Review, Oak Ridge, May 1, 1991.

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M.; Heatherly, L.*, "Fundamental Studies of Chemical Vapor Deposition Diamond Growth Processes", 1991 International Symposium on Optical and Optoelectronic Applied Science and Engineering, San Diego, July 21-26, 1991 (invited).

Shaw, R. W.; Whitten, W. B.; Ramsey, J. M., "Laser Spectroscopic Diagnostics for Chemical Vapor Deposition of Diamond Films", American Chemical Society National Meeting, New York, August 25-30, 1991.

Short, R. T.

Short, R. T.; Todd, P. J.; Grimm, C. C., "Kinetic Energy Distribution of Ions After Surface Collisions", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Smith, D. H.

Smith, D. H., "Progress in Inorganic Mass Spectrometry", BES Site Review, Oak Ridge, May 1, 1991.

Stewart, J. H.

Rettberg, I. H.*; Blair, P. D.*; Stewart, J. H.; Hall, G.*, "Analysis of Wood and Cellulose Materials by Laser Ablation - ICP-MS", FACSS/Pacific Conference, Anaheim, Calif., October 6-11, 1991 (invited).

Hasty, Elaine*; Littau, Sara*; Revesz, Robert*; Stewart, J. H.; Mueller, T. R., "Microwave Sample Preparation of Oils with Temperature Feedback Control", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Teasley, N. A. — Teasley, N. A.; Wade, J. W.; Granger, C. C., "Improvements in Alpha Spectra Calculations in the Low Level Radiochemical Analysis Group", Canberra Instruments/Nuclear Data Users Group (CINDUG) Meeting, Del Mar, Calif., April 13-19, 1991.

Todd, P. J. — Todd, P. J.; Grimm, C. C.; Short, R. T., "Organic Ion Imaging", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Tomkins, B. A. — Tomkins, B. A.; Merriweather, R.; Jenkins, R. A., "Analysis of Eight Organochlorine Pesticides at Low Part-per-Trillion Concentrations in Groundwater", 105th Annual International Meeting and Exposition of Association of Official Analytical Chemists, Phoenix, Ariz., August 12-15, 1991.

Troutman, M. R. — Glish, G. L.; Troutman, M. R.; Asano, K. G.; McLuckey, S. A., "Effects of Time-Scale on MS/MS Dissociations", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Van Berkel, G. J. — Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Analysis of Metals in Solution Using Electrospray Ionization Mass Spectrometry", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Methods for Performing Ions in Solutions from Compounds Not Normally Amenable to Electrospray Ionization", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Whitten, W. B. — Whitten, W. B.; Dale, J. M.; Ramsey, J. M., "Laser Ablation of Microparticles in an Ion Trap Mass Spectrometer", Workshop on Laser Ablation Mechanisms and Applications, Oak Ridge, April 8-10, 1991.

Whitten, W. B., "Fluorescence Spectroscopy in Microspheres", BES Site Review, Oak Ridge, May 1, 1991.

Whitten, W. B.

Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Chemical Characterization of Microparticles by Laser Ablation in an Ion Trap Mass Spectrometer", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Dale, J. M.; Whitten, W. B.; Ramsey, J. M., "Laser Ablation Mass Spectrometry of Microparticles", The Chemical Research & Development Engineering Center (CRDEC) Conference on Obscuration and Aerosol Research, Aberdeen, Md., July 23-26, 1991 (invited).

Whitten, W. B.; Dale, J. M.; Ramsey, J. M., "Detection of Explosives Material on Single Microparticles", Federal Aviation Administration 1st International Symposium on Explosives Detection Technology, Atlantic City, N. J., November 13-15, 1991.

Wise, M. B.

Wise, M. B.; Ilgner, R. H.; Buchanan, M. V.; Guerin, M. R., "Rapid Determination of Drugs and Semivolatile Organics by Direct Thermal Desorption Ion Trap Mass Spectrometry", Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, February 12-14, 1991.

Wise, M. B.; Hurst, G. B.; Thompson, C. F.; Buchanan, M. V.; Guerin, M. R., "Screening Volatile Organics by Direct Sampling Ion Trap and Glow Discharge Mass Spectrometry", Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, February 12-14, 1991.

Wise, M. B.; Hurst, G. B.; Thompson, C. V.; Theobald, D. L.; Guerin, M. R., "Direct Measurement of Volatile Organics in Air Using an Ion Trap Mass Spectrometer", 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, Tenn., May 19-24, 1991.

Wise, M. B. — Wise, M. B.; Guerin, M. R.; Thompson, C. V.; Hurst, G. B.; Buchanan, M. V., "Direct Sampling Ion Trap Mass Spectrometry for Environmental Monitoring Applications", Rocky Mountain Conference on Analytical Chemistry, Denver, July 30, 1991 (invited).

Young, J. P. — Young, J. P.; Shaw, R. W., "Resonance Ionization Mass Spectrometry Utilizing Diode Lasers", 32nd ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, October 1-3, 1991.

Young, J. P.; Shaw, R. W.; Ramsey, J. M., "Resonance Ionization Mass Spectroscopy Using Multiple Diode Lasers", Federation of Analytical Chemistry and Spectroscopy Societies, Anaheim, Calif., October 6-11, 1991.

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
Buchanan, M. V.	5			2	1						4	9		21
Carter, J. A.												23		23
Christie, W. H.		1											2	3
Dale, J. M.												1		1
Dose, E. V.	8								2				1	11
Dyer, F. F.		1											1	2
El Fallah, M. Z.	4								2				1	7
Glish, G. L.	1		2			2		1	1	2	1	6		16
Goeringer, D. E.								1				2		3
Griest, W. H.	4											1		5
Guerin, M. R.												3	2	5
Guiochon, G.	265[a]								17	3		8	9	302
Hettich, R. L.			1		1							1		3
Laing, W. R.													33	33
McLuckey, S. A.		1	3			3	1	3				10		21
Mueller, T. R.		1										1		2

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
Ramsey, J. M.	2											5	3	10
Ramsey, R. S.	2											3		5
Rosseel, T. M.												25		25
Shaw, R. W.												1		1
Smith, D. H.			2									2		4
Stewart, J. H.					1								40	41
Todd, P. J.									2		1	41		44
Tomkins, B. A.	1													1
Van Berkel, G. J.									3			2		5
Whitten, W. B.	1	1										2	2	6
Wise, M. B.			1		1	1		1						4
Young, J. P.	1											2	3	6
TOTALS	294	5	9	2	4	6	1	6	27	5	6	170	88	612

[a]As Associate Editor

SUMMARY OF ANALYTICAL SERVICE WORK

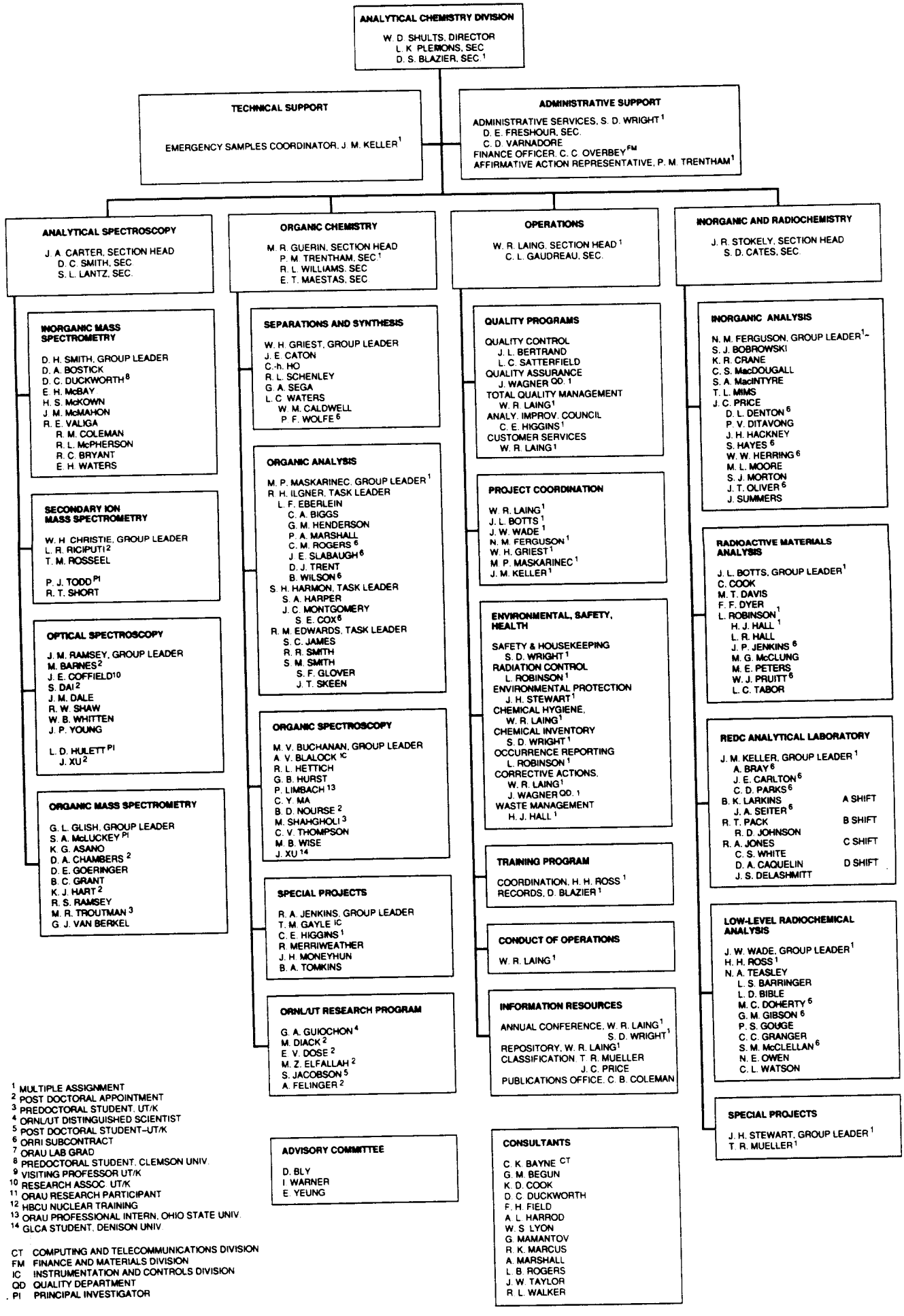
ORGANIZATION	Number of Results Reported By: Analytical Spectroscopy	Inorganic and Radiochemistry	Organic Chemistry	TOTAL
ORNL Unit				
Analytical Chemistry	1,115	978	1,920	4,013
Central Management		7,569	1,444	9,013
Chemical Technology	7,217	11,666	11,669	30,552
Chemistry		794	301	1,095
Energy		1,041	545	1,586
Engineering		60	3,360	3.420
Engineering Physics and Mathematics		481	3,838	4,319
Engineering Technology	80	49	150	279
Environmental Compliance and Documentation		16,772	25,082	41,854
Environmental Sciences		6,631	10,505	17,136
Finance and Materials	1,010	370	3,210	4,590
Fusion Energy		40	480	520
Health and Safety Research	45	495	1,204	1,744
Instrumentation and Controls	100	39	60	199
Laboratory Protection		42	151	193
Metals and Ceramics	3,300	2,993	19,080	25,373
Physics	203	156	541	900
Plant and Equipment		5,998	23,340	29,338
Quality		297	421	718
Research Reactors	55	541	3,360	3,956
Robotics and Process Systems	60	1,614	1,503	3,177
Safety and Health Protection		3,200	901	4,101
Solid State		259	869	1,128
Waste Management and Remedial Action	220	49,751	43,710	93,681
Others				
K-25	80	315		395
Paducah		2,978	18,000	20,978
Y-12	6,206	5,425	6,450	18,081
TOTAL	**19,691**	**120,554**	**182,094**	**322,339**

FY 1991 DIVISIONAL MANPOWER AND FINANCIAL SUMMARY

Source	$K	PY
DOE Programs		
Energy Research		
Basic Energy Sciences	1,742	10.7
Health and Environmental Research	287	1.2
OERWM - Env Restoration & WM-Def	916	4.3
Safeguards and Security	482	3.3
OERWM - Env Restoration & WM-Non-Def	592	3.4
Fossil Energy	57	0.3
Miscellaneous	205	0.7
Total DOE Programs	4,281	23.9
Work for Others - Federal Agencies		
Department of Defense	864	5.0
Nuclear Regulatory Commission	30	0.1
National Cancer Institute	227	1.4
Federal Aviation Administration	518	0.8
National Institutes of Health	15	0.0
NASA	168	0.4
Miscellaneous	582	4.8
Total WFO - Federal Agencies	2,404	12.5
Work for Others - Nonfederal Agencies		
Full Cost Recovery Customers		
Protective Coating Companies	36	0.0
Uranium Ore Testing Companies	14	0.0
Center for Indoor Air Research	24	0.1
Miscellaneous	18	0.0
Total WFO - Nonfederal Agencies	92	0.1
Indirect Staff/Non-Chargers		5.5
Total DOE Programmatic, Federal and Nonfederal Agencies	6,777	36.6
Support/Services (does NOT include overhead)		
ORNL Divisions/Programs	6,050	61.9
Other Clients	2,674	27.4
Intra-division	919	
Subtotal	9,644	89.3
Indirect Staff/Non Chargers		6.6
Total Support/Services	9,644	89.3
TOTAL FINANCIAL PLANS	15,502[a]	125.9

[a]Total ACD cost excludes intra-division charges.

OCTOBER,1991



[1] MULTIPLE ASSIGNMENT
[2] POST DOCTORAL APPOINTMENT
[3] PREDOCTORAL STUDENT, UT/K
[4] ORNL/UT DISTINGUISHED SCIENTIST
[5] POST DOCTORAL STUDENT–UT/K
[6] ORRI SUBCONTRACT
[7] ORAU LAB GRAD
[8] PREDOCTORAL STUDENT, CLEMSON UNIV.
[9] VISITING PROFESSOR UT/K
[10] RESEARCH ASSOC. UT/K
[11] ORAU RESEARCH PARTICIPANT
[12] HBCU NUCLEAR TRAINING
[13] ORAU PROFESSIONAL INTERN, OHIO STATE UNIV.
[14] GLCA STUDENT, DENISON UNIV.

CT COMPUTING AND TELECOMMUNICATIONS DIVISION
FM FINANCE AND MATERIALS DIVISION
IC INSTRUMENTATION AND CONTROLS DIVISION
QD QUALITY DEPARTMENT
PI PRINCIPAL INVESTIGATOR

ORNL-6701
Distribution Category UC-401

INTERNAL DISTRIBUTION

1. H. L. Adair
2. T. D. Anderson
3. B. R. Appleton
4. J. B. Ball
5. V. M. Baylor
6. C. K. Bayne
7. J. L. Bertrand
8. S. J. Bobrowski
9. J. L. Botts
10. M. V. Buchanan
11. R. S. Carlsmith
12. J. A. Carter
13. J. E. Caton
14. W. H. Christie
15-16. C. B. Coleman
17. J. W. Culver
18. J. M. Dale
19. M. T. Davis
20. R. M. Davis
21. J. G. Dorsey
22. D. C. Duckworth
23. B. G. Eads
24. G. G. Fee
25. N. M. Ferguson
26. W. Fulkerson
27. T. M. Gayle
28. R. K. Genung
29. G. L. Glish
30. D. E. Goeringer
31. W. H. Griest
32-35. M. R. Guerin
36. G. Guiochon
37. S. H. Harmon
38. A. L. Harrod
39. F. C. Hartman
40. R. L. Hettich
41. C.-h. Ho
42. R. B. Honea
43. L. D. Hulett
44. G. B. Hurst
45. R. H. Ilgner
46. R. A. Jenkins
47. S. V. Kaye
48. J. M. Keller
49. L. N. Klatt
50. E. H. Krieg
51. W. R. Laing
52. W. S. Lyon
53. C. S. MacDougall
54. S. A. MacIntyre
55. S. A. McKenney
56-59. S. A. McLuckey
60. J. M. McMahon
61. L. E. McNeese
62. C. L. Ma
63. A. P. Malinauskas
64. M. P. Maskarinec
65. J. H. Moneyhun
66. R. W. Morrow
67. T. R. Mueller
68. R. F. Peacher
69. M. L. Poutsma
70. J. C. Price
71. J. M. Ramsey
72. R. S. Ramsey
73. D. E. Reichle

74. J. B. Roberto
75. L. Robinson
76. T. M. Rosseel
77. T. H. Row
78. L. C. Satterfield
79. R. L. Schenley
80. G. A. Sega
81. R. W. Shaw
82. R. T. Short
83-133. W. D. Shults
134. D. H. Smith
135. R. R. Smith
136. J. H. Stewart
137. J. O. Stiegler
138. J. R. Stokely
139. J. H. Swanks
140. N. A. Teasley
141. P. J. Todd
142. B. A. Tomkins
143. R. E. Valiga
144. G. J. Van Berkel
145. R. I. Van Hook
146. D. O. Vick
147. J. W. Wade
148. J. L. Wagner
149. R. C. Ward
150. C. W. Weber
151. W. B. Whitten
152. M. B. Wise
153. S. D. Wright
154. J. P. Young
155. Biology Library
156-158. Central Research Library
159-160. Laboratory Records
161. Laboratory Records RC
162. Laboratory Shift Supervisor
163. ORAU Technical Library
164. ORAU/UPD
165. ORNL Y-12 Library
166. Patent Section
167. PGDP Library

EXTERNAL DISTRIBUTION

168. G. M. Begun, 106 Colby Road, Oak Ridge, TN 37830
169. D. D. Bly, E. I. du Pont de Nemours, Wilmington, DE 19898
170. J. L. Burnett, Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, Washington, DC 20545
171. N. F. Christopher, Analytical Services, Portsmouth Gaseous Diffusion Plant, Portsmouth, OH 45662
172. K. D. Cook, Department of Chemistry, University of Tennessee, Knoxville, TN 37936-1600
173. F. H. Field, 13 Moore Lane, Oak Ridge, TN 37830
174. Gerald Goldstein, Office of Health & Environmental Research, Department of Energy, Washington, DC 20545
175. D. W. Green, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439
176. R. L. Hirsch, Biomedical Research Technical Program/NCRR, Bethesda, MD 20892
177. S. K. Holshouser, Analytical and Technical Services, Paducah Gaseous Diffusion Plant, Paducah, KY 42001
178. R. O. Hultgren, Department of Energy-Oak Ridge Operations, P.O. Box 2008, Oak Ridge, TN 37831-6269
179. Institute for Energy Analysis, P.O. Box 117, Oak Ridge, TN 37830
180. D. H. Lester, Hoechst Celanese Corporation, P.O. Box 32414, Charlotte, NC 28232
181. Gleb Mamantov, Department of Chemistry, University of Tennessee, Knoxville, TN 37936-1600
182. R. K. Marcus, Department of Chemistry, Clemson University, Clemson, SC 29634
183. R. S. Marianelli, Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, Washington, DC 20545
184. A. G. Marshall, 745 Morningside Drive, Sevierville, TN 37862
185. John Phillips, Los Alamos National Laboratory, Los Alamos, NM 87545
186. L. B. Rogers, 219 Rollingwood Drive, Athens, GA 30605
187. W. J. Spetnagel, Laboratory Services and Safety Analysis, Portsmouth Gaseous Diffusion Plant, Portsmouth, OH 45662
188. F. D. Stevenson, Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, Washington, DC 20545
189. J. W. Taylor, Department of Chemistry, University of Wisconsin, Madison, WI 53706
190. U. S. Department of Agriculture, National Agriculture Library, Beltsville, MD 20705
191. R. L. Walker, 17 Clark Place, Oak Ridge, TN 37830
192. I. H. Warner, Department of Chemistry, Emory University, Atlanta, GA 30322
193. R. W. Wood, Office of Health & Environmental Research, Department of Energy, Washington, DC 20545
194. D. J. Wynn, USATHAMA, Aberdeen Proving Ground, MD 21010
195. E. S. Yeung, Department of Chemistry, Iowa State University, Ames, IA 50011
196. C. Yonker, Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, Washington, DC 20545

197-254. Distribution as shown in DOE/OSTI-4500 under Category UC-401