LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

ORNL-6606
Distribution Category UC-401

ORNL--6606

Contract No. DE-AC05-84OR21400

DE90 012024

ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

For Period Ending December 31, 1989

W. D. Shults, Director

Date Published - April 1990

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

INTRODUCTION

W. D. Shults, Director

The Analytical Chemistry Division of Oak Ridge National Laboratory (ORNL) is a large and diversified 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 program 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 four major sections, each of which may carry out any of the three types of work mentioned above. Chapters 1 through 4 of this report highlight progress within the four sections during the period January 1 to December 31, 1989. A brief discussion of the division's role in an especially important environmental program is given in Chapter 5. Information about quality assurance, safety, and training programs is presented in Chapter 6, along with a tabulation of analyses rendered. Publications, oral presentations, professional activities, educational programs, and seminars are cited in Chapters 7 and 8. Approximately 69 articles, 41 proceedings, and 31 reports were published, and 151 oral presentations were given during this reporting period. Some 308,981 determinations were performed.

HIGHLIGHTS

This year we began a series of experiments in ultrasensitive detection that use an electrodynamically levitated microparticle or droplet as the sample. The areas of interest include single molecule detection, laser ablation mass spectroscopy of microparticles, and photoemission spectroscopy of analyte molecules adsorbed on particulates. A sample volume of less than 1 pL can be obtained with levitated microdroplets and measuring time is limited by the photochemical lifetime of the analyte. First experiments (with rhodamine-6G) indicate a fluorescent sensitivity of better than 100 molecules per droplet. We also modified a commercial electrodynamic ion trap to allow for introduction of charged particles and for illumination and observation of them. Because the trap can be used for mass spectrometric analysis, we now have the possibility of trapping a particle, ablating ions from its surface, and generating a mass spectrum of the ions in the trap. For photoemission studies, a purely electrostatic Millikan levitator was constructed and used to study charge scavenging by a polystyrene sphere, the charge being introduced by laser pulsing. This new work has many exciting possibilities.

Construction and successful operation of a high intensity positron source at the Oak Ridge Electron Linear Accelerator was reported in the last Annual Report (ORNL-6547). During this year two regimes of positron mass spectrometry have been studied. In the first, mass spectra of several compounds were obtained using 3 keV slow positrons. The spectra were comparable qualitatively to those obtained with 70 and 2700 eV electrons. In the second mode, the 3 keV positron beam was remoderated and contained in a small Penning trap at low energies (0.2 to 10 eV). Some twenty large organic compounds were studied with these low energy positrons and it was found that in all cases ionization occurs when the kinetic energy of the positrons is less than the ionization potential of the compound. This is attributed to the formation of positronium.

One of the most exciting developments this year has been the coupling of electrospray ionization with ion trap mass spectrometry (ESI/ITMS) via our atmospheric sampling glow discharge ionization source (ASGDI). The ASGDI actually functions as an interface between an electrospray and an ion trap, the "electrospray" of ions being directed at the orifice of the ASGDI. Using this ESI/ITMS system we successfully injected both negative and positive ions into the trap and performed MS and MS/MS experiments on them. Biomolecules with molecular weights well beyond the normal range of the ITMS have been studied. They form multiply charged species. To date, the largest molecule that has been detected has been bovine albumin, molecular weight 66,000.

The first unit of our new mass spectrometry laboratories was completed this year and much of the organic MS instrumentation and corresponding staff were moved from Y-12 to X-10. Funds for the second unit have been approved and the building is scheduled to be constructed during CY 1990. It will house instrumentation and staff interested in inorganic MS.

One of the most challenging analytical projects that we have faced in recent years is the characterization of the contents of approximately 25 inactive (unused) tanks at ORNL. "Characterization" entails chemical, physical, and radiochemical measurements. These tanks contained low-level waste that had been collected from the late 1940s to the early 1970s. The material varied from contaminated rainwater to complex mixtures that contained aqueous, organic, and sludge phases. EPA methodology was used insofar as possible. This study was essentially completed this year and a report has been issued. Characterization of material in active tanks -- wastes collected since the early 1970s -- has now begun. This work has involved many people and many groups working together.

Asbestos has become a very important material at the Laboratory because of its health implications. We evaluated our capabilities in polarized light microscopy (PLM) and transmission electron microscopy (TEM), against the growing demand for asbestos analysis. PLM is used for bulk sample analysis and TEM is used for "clearance" analysis after cleanup is complete. During 1989 we established facilities, equipment, procedures, and personnel for both methodologies in preparation for the National Voluntary Laboratory Accreditation Program (NVLAP).

Laser desorption Fourier transform mass spectrometry (FTMS) has been demonstrated to be well suited for the direct detection and identification of compounds on thin layer chromatography plates. The laser provides high spatial resolution and can be used to ionize compounds directly from TLC plates with virtually no sample preparation. Best ion signals were obtained via desorption from modified (C18) silica gel plates and detection limits were in the low nanogram region. The effects of laser wavelength and power are being investigated.

We were able to generate and study aluminum cluster ions (negatively charged clusters of 3 to 50 Al atoms) by laser ablation of a flat aluminum target and trapping the ions in an FTMS. Cluster ions were observed ranging continuously from Al-3 (m/z 81) to Al-50 (m/z 1349). Al-13 was the most intense ion and the odd numbered clusters were more abundant than even numbered. We examined the electron affinities of these clusters, their structures and fragmentation mechanisms, and their reactivity to small gaseous molecules. Laser ablation FTMS proved to be extremely useful for this type of study.

Real progress was made this year in our development of methodology for prompt detection and analysis of organics in environmental and physiological matrices. Direct sampling mass spectrometry using ion trap or glow discharge mass spectrometry is the approach. Many organic compounds in water can be determined by purging them with helium directly into an ITMS, for example. Parts-per-billion levels can be determined in about two minutes. Volatile compounds in soil can be determined by making an aqueous slurry and purging it for about five minutes. Ambient air can be monitored by blending helium with air as it is drawn into the spectrometer. We believe this approach to organic analysis has great potential.

Major initiatives this year have involved the development and application of new analytical methods for explosives and their metabolites, in biological tissues, ordnance materials, and compost. This work is sponsored by the U.S.Army and some of it is done in collaboration with staff of the Environmental Sciences Division. The objective is to determine if animals near ammunition plants take up significant amounts of explosives and their derivatives and if composting is a viable method for disposing of explosives wastes. Two high performance liquid chromatography (HPLC) methods were developed specifically for these studies. One of them allows both ionic and neutral compounds to be retained and well separated in a single HPLC experiment. This work has provided the division with rather unique capabilities.

One of the most satisfying accomplishments of the year has been the restructuring and revitalizing of our Organic Services Group. This group performs qualitative and quantitative determinations of organic compounds in a wide variety of sample types. Virtually all of the work is environmental in origin, supporting Laboratory programs and external Work for Others activities. Most methods are multicomponent in nature and operate in the low parts-per-billion range. This group has added instrumentation, staff, procedures, and capabilities to become a strength within the division.

The physico-chemical properties of the surface of ceramic powders may hold the key to the success of the molding and firing processes used to prepare specialty ceramic products. These surface properties are not differentiated well by tests that are common to the ceramic industry. Accordingly, we have initiated development of tests based on the determination of the adsorption isotherms for a series of probe compounds. From the isotherms, we hope to derive the energy distribution function and the energy of formation of monolayers of the probe compounds. This is an extension of previous work on the theory of nonlinear chromatography. The goal is to correlate these chemical surface properties with the performance of samples of the corresponding material in actual production.

1. ANALYTICAL SPECTROSCOPY

J. A. Carter

The Analytical Spectroscopy Section was reorganized this year. It is presently comprised of four groups: Optical Spectroscopy, Inorganic Mass Spectrometry, Organic Mass Spectrometry, and Secondary Ion Mass Spectrometry. Special research and development projects in radiochemistry are also carried out in this section. Research and development efforts in each group are directed toward enhancing analytical capabilities and reaching a clearer understanding of fundamental processes that can be exploited for application to energy-related analytical problems. Highlights of this year's work include: development of microparticle techniques that combine laser and mass spectroscopies and promise to yield unprecedented sensitivities in some areas; initiation of a collaborative project with staff of the Metals and Ceramics and Fusion Energy Divisions to investigate the fundamental processes affecting chemical vapor deposition; use of positrons to ionize various compounds for subsequent mass analysis; and development of the apparatus necessary to use electrospray ionization with an ion trap mass spectrometer, an advance that has far-reaching implications for future mass spectrometric research in relevant areas.

This year marked our occupation of the first building in our move from antiquated Y-12 facilities to modern ones at the ORNL site. The first occupants are researchers in organic mass spectrometry; their increasing involvement with people associated with universities and industry will be substantially eased by these new, more accessible accommodations. The rest of the section at Y-12 is scheduled to move sometime during the early 1990s.

About 50% of the section's research and development activities are supported by the Division of Chemical Sciences of the Office of Energy Research, U. S. Department of Energy. These efforts are broad in scope and provide the technical base upon which future advances will be founded. Another 30% of the section's research and development funding is about equally distributed among DOE's Office of Safeguards and Security, the Office of Arms Control, and the Office of Health and Environmental Research. The balance of our work is funded by other ORNL divisions and programs, with additional support coming from Y-12 and K-25, through various interagency agreements (FAA, State Department, IAEA), and other work-for-others contracts.

OPTICAL SPECTROSCOPY

J. M. Ramsey

The projects in this group cover a broad range of topics and include instrumentation development as well as fundamental studies. Most of these activities involve laser-based instrumentation. Multiphoton ionization spectroscopy was emphasized, using several different excitation schemes, sampling techniques, and detection devices. Two new areas of study include analysis of microparticles (i.e., diameter < 100 μm) and fundamental studies of chemical vapor deposition processes. We have continued to investigate the use of photorefractive barium titanate optical elements in laser cavities. In addition, instrumentation concepts were developed for the measurement of stable isotope ratios by rotational spectroscopy and the probing of advanced absorption heat pumps by laser-based measurements. Work in the area of counterfeit deterrence was also completed.

Resonant Multiphoton Ionization with Flame Sampling

We are investigating the use of resonant [2+1] multiphoton ionization (MPI) for the sensitive detection of metals from aqueous solutions aspirated into flames. Material from the flame is expanded through an orifice into a low-pressure cell where the laser analysis is performed. Photoelectrons or ions are collected by a biased probe electrode within the cell as the laser wavelength is varied. Earlier experiments showed that significant cooling occurs during the expansion into the cell. It was found that the [2+1] MPI signals through Rydberg states of potassium, rubidium and cesium show a quadratic dependence on the metal concentration. This implies an ionization mechanism for these atoms that involves a collision between them. This is known to be the case in photoexcitation in alkali metal vapors. However, our flame sampling cell provides an environment in which the metal-atom density is quite low--typically ca. 10^9 atoms/cm^3, far below a pascal of pressure. Yet the total pressure inside the cell is on the order of a few hundred pascal, so a metal-metal collision is a rare event.

Comparison was made of the ionization signals from the [2+1] ionization of sodium through the 5s state and of potassium through the 5d state using yellow light from the Nd:YAG-pumped dye laser. All such ionization of sodium through Rydberg states was shown to have a linear concentration dependence, while potassium was always quadratic. The photoionization cross-section is known to be larger for excitation schemes that terminate close to the ionization threshold than for those far above threshold. Experiments were therefore conducted using pulses of the YAG fundamental at 1064 nm to increase the photoionization of the prepared Na 5s and K 5d states. Under our experimental conditions, the Na 5s signal was seen to increase 3-4 fold with the admission of the infrared pulses but the K 5d signal was essentially unchanged. Thus even for these lower energy photons, potassium ionization is dominated by some process (collisional) other than photoionization.

We have also recently verified that the [1+1] ionization of cesium through the 7p state is quadratic with concentration. This adds generality to these observations in the heavy alkalis since the results hold for s, p and d states and do not depend on the order of the ionization process. In contrast, non-resonant two-photon ionization of sodium and potassium are both linear. This is as expected as no long-lived excited state is prepared which survives to collide with another atom. Signals from potassium are much smaller than those from sodium, consistent with a lower photoionization yield. Rubidium and cesium yield even less signal under the same circumstances. A mystery remains in this problem, as calculations indicate that the most likely ionization route for an atom that doesn't photoionize is by an energetic collision with the background gas. This discrepancy is still unexplained.

Other experiments have attempted to investigate further the state distributions of the atoms in the cell. In particular, we have searched for transitions from triplet and metastable levels in strontium to determine if they may survive the expansion into the cell. Different nozzles were employed to alter the sampling characteristics of, and density distributions in, the cell.

Two-color ionization of sodium using the Nd:YAG and YAG-pumped dye laser in combination with our high-resolution ring-dye laser has been performed. Signals from the sodium 3p and 6d states show a Doppler-broadening in the cell of 3-4 GHz. No signals have been seen using the ring-dye laser to drive two-photon transitions. Calculations suggest that the combination of low laser power from the ring laser together with the low species concentration in the sampling cell give rise to a situation where few atoms can be excited.

(P. R. Blazewicz[*]*, W. B. Whitten, J. M. Ramsey)*

Photoionization in an Ion Trap Mass Spectrometer

A Finnigan ion trap detector (ITD) was recently acquired for studies of laser induced photoionization followed by mass analysis. The operating conditions of the ion trap permit several measurement techniques that would be very difficult in conventional resonance ionization mass spectroscopy. The presence of a buffer gas within the trap makes possible collisional ionization from excited atomic and molecular levels, bypassing the photoionization step that requires very high laser intensity. Thus, low-power lasers could be used for resonance excitation with high spectral resolution. The ion trap should also integrate favorably with our low-pressure sampling of analytical flames and other atmospheric pressure atomization sources. The commercial ITD was modified by drilling two opposing holes of ≈ 5-mm diameter in the vacuum chamber. Corresponding holes (≈ 3-mm diameter) were drilled in the ring electrode of the trap. Quartz windows were epoxied over the holes in the vacuum chamber. These modifications allowed introduction of laser light into the trapping region.

Nitric oxide (NO) was the analyte in our first experiments. A Nd:YAG-pumped dye laser was used to excite a four photon (2+2) photoionization process involving the $A^2\Sigma^+(v=1) \leftarrow X^2\Pi_{1/2}(v=0)$ transition (430 nm). Spectra were measured with total NO concentrations between 1% and 6 ppm in the helium buffer gas used in the ion trap. After data treatment the $P_{11} + 0_{21}$ two-photon bandhead is identifiable for the three major isotopes with NO, $^{14}N^{16}0$ (99.4%), $^{15}N^{16}O$ (0.4%), and $^{14}N^{18}O$ (0.2%). At 6 ppm total NO, the $^{14}N^{18}O$ concentration in the trap is 12 ppb and considered the detection limit in our experiment. The position

---

[*] ORAU Post-Doctoral Research Associate

of the three bandheads match the literature values to within the bandwidth of our measurements (0.014 nm). Within the confines of the ion trap electrodes, there are 6 attomoles or less than 4 x 10^6 molecules of $^{14}N^{18}O$. On average, less than 100 molecules are in the laser beam at any instant and only ten of these molecules are in rotational levels that can be excited by the laser beam when tuned to the bandhead. In theory, all of the molecules in the trap could eventually be ionized, given sufficient time.

We have also observed resonance ionization of rubidium atoms in the ion trap. The rubidium atoms were evaporated from a rhenium filament inserted in place of the electron gun. The atomic beam was excited to a series of Rydberg levels by two-photon transitions from the ground state followed by photo or collisional ionization. The Quanta-Ray YAG-pumped dye laser was again used as the excitation source. For intermediate Rydberg levels of low n (less than 30), the ionization signal from the nD levels predominates over the nS. As the n-value increases, however, the signal from nS levels becomes increasingly larger than from the nD. The nature of the ionization process from the Rydberg levels is currently being explored.

(D. E. Goeringer, J. M. Ramsey, W. B. Whitten)

Resonance Ionization Mass Spectroscopy

Last year, we described a 1 + 1 + 1 resonance ionization mass spectroscopic (RIMS) method that utilized an inexpensive diode laser to promote the first optical step of a three-photon resonance ionization process for lanthanum. Unlike other lasers that have been used for RIMS, semiconductor diode lasers possess simple operating characteristics while maintaining the desirable properties of tunability, narrow bandwidth (down to 25 MHz for off-the-shelf devices), and spatial coherence. In the earlier study, we positioned the diode laser wavelength on a lanthanum transition and scanned a dye laser (that provided the second and third photons of the RIMS process) to record spectra. Since then we have discovered that if the experiment is reversed, i. e., the diode laser is scanned over a narrow spectral range (≈ 15 GHz) with the dye laser wavelength stationary (at 584.8 nm), very sharp spectra result. The hyperfine structure of the La-139 atom produces these sharp resonances. The high resolution of this technique has import for isotopically selective RIMS measurements.

Spectral linewidths as narrow as 150 MHz have been measured, well below the expected Doppler limit of 1 GHz. Some process that effects sample atom beam collimation must be operative; the most likely is collection of photoions only from a restricted spatial region. The resolution is not as yet limited by the linewidth of the scanning diode laser; further improvements in resolution (and isotopically selective ionization) may be possible by changes in the ion optics of the mass spectrometer.

Sub-Doppler resolution spectra were acquired for both the $^2D_{3/2}$ and $^2D_{5/2}$ to $^4F^o{}_{3/2}$ transitions at 753.9 and 819.0 nm, respectively. Atomic hyperfine structure constants were determined for the heretofore unanalyzed 13260 cm^{-1} $^4F^o{}_{3/2}$ state. A computer program was written to perform this analysis. Both the 754 and 819-nm spectra yield the same values for the nuclear magnetic dipole and electric quadrupole constants (A and B, respectively) within experimental error:

$$A = -350 \pm 4 \text{ MHz}$$
$$B = 54 \pm 12 \text{ MHz}$$

In addition, 6J symbol calculations have been performed to compare the observed hyperfine line intensities with theoretical values. Those values agree within ±15%, so no significant optical pumping appears to be occurring in our CW experiment.

Isotopically selective resonance ionization was also achieved for a natural abundance lanthanum (0.089% La-138) sample. The 754 nm La-138 spectrum is very similar to that for La-139, but the lines extend both to higher and lower frequencies. The spectral offset of the lowest frequency lines (670 MHz) was used to attempt isotopically selective ionization. Preliminary ion counting results indicate that the apparent La-139/La-138 isotope ratio of a natural abundance lanthanum sample can be changed from about 30 to over 22,000 by judicious selection of diode laser excitation frequency. Narrow bandwidth laser-derived isotopic selectivity can be used to reduce the dynamic range required of a mass spectrometer for isotope ratio measurements of elements with widely differing isotopic abundances; the selectivity due to the diode laser can serve to skew the apparent abundances toward equality. Recall that the isotopic selectivity achieved here was accomplished with a simple and inexpensive diode laser.

Although this study utilized a diode laser for only the first excitation step of a three-photon process, the obvious extension is to employ diode lasers for all of the optical steps. The last step, excitation to the continuum, has a much lower cross section and a method such as electric field or carbon dioxide laser ionization will be required. Counterpropagating beam methods for Doppler-free linewidths will permit isotopic selectivity in many cases, and a practical instrument for isotope ratio determinations can be envisioned. The feasibility of such an instrument is currently under investigation.

The development of a disposable graphite furnace as an atom source for mass spectrometry continues. As has been pointed out, such a source offers potential advantages over existing thermal sources. The work function of carbon promotes the generation of neutrals, as opposed to ions; the shape of the furnace will yield a directed beam of atoms; and the presence of carbon will minimize metal oxide ion formation. A prototype graphite furnace has operated as a thermal ionization source with either lanthanum or gadolinium loading; the samples were loaded as aqueous solutions. These tests were performed with the graphite furnace opening directed toward a hot rhenium metal filament that ionized the species effusing from the furnace. Both La and Gd ions in expected isotopic distribution were seen during the operation of the furnace; no evidence of LaO^+ or GdO^+ was observed.

(R. W. Shaw, J. P. Young, D. H. Smith, J. M. Dale)

Microparticle Techniques

We have begun a series of experiments in ultrasensitive detection that use an electrodynamically levitated microparticle or droplet as the sample. The areas of interest include single molecule detection, laser ablation mass spectroscopy of microparticles, and photoemission spectroscopy of analyte molecules adsorbed on particulates.

Detection limits for molecules in solution by laser-induced fluorescence have been limited historically to about 10^{-12} molar by solvent fluorescence and Raman scattering. Improvements in detection through the past decade have been either through reduction of sample volume or increase in measurement time. With levitated microdroplets, we can attain a sample volume of less than 1 pL with a measuring time limited by the photochemical lifetime of the analyte. If historically detectable concentrations can be achieved with levitated droplets, detection of single molecules should be possible.

We have constructed an electrodynamic trap consisting of three electrodes in the form of a hollow sphere for these measurements. With this trap and a commercial piezoelectric pipette, it is possible to generate and levitate charged droplets with diameters in the micrometer range. A combination of a graded refractive index lens and a microscope objective collects the fluorescence from the droplet and focuses it through several filters onto a photomultiplier tube. Fluorescence is excited by an argon-ion laser beam, 514.5-nm wavelength, with an intensity from 500 to 1000 W cm^{-2}. Calculations of the expected signal and Raman and Mie scattering contributions to the background indicate that a detection limit approximating one analyte molecule per droplet should be attainable.

Our first experiments have been with a solution of rhodamine-6G dye in glycerol-water with 5 μM concentration. The peak fluorescence intensity-to-background ratio is about 10^4 for droplets with diameters in the 10-μm range, so the present sensitivity is better than 10^2 molecules per droplet. Some of the background signal varies with droplet size, probably due to solvent Raman emission. Our sensitivity can therefore be increased by reducing the size of the trapped droplets.

For the photoemission studies, a purely electrostatic Millikan levitator has been constructed. This device uses scattered light from a He-Ne laser to generate a position error signal so that the levitating field can be feedback-stabilized. The apparatus is sensitive to a very small change in electric charge on the suspended particle. We have used the apparatus to measure charge scavenging by a levitated polystyrene sphere when a focused dye laser pulse produces ions within the trap volume.

For laser-ablation mass spectroscopy, the electrodes of a commercial electrodynamic ion trap were modified to allow for the introduction of charged particles and for illumination and observation of the particles. The trap is a three-dimensional quadrupole made up of three electrodes with hyperbolic surfaces having rotational symmetry. A vacuum chamber was constructed to contain the trap and a new power supply was constructed to provide the electric field for levitating the particles. Particles of polystyrene, 24 microns in diameter, have been levitated in the trap under both vacuum and atmospheric pressure. The trapped particles are illuminated with a helium-neon laser and observed with a twenty power telescope.

A charged particle, from hundreds of microns in diameter to as small as a single ion, can be confined in the small volume of the trap. Because the trap can also be used for mass spectrometric analysis, this leads to the exciting possibility of trapping the particle, ablating ions from the particle, and then generating a mass spectrum of these ions in the trap. Ions can be sequentially ejected from the trap in order of low to high mass-to-charge ratios (m/e) by increasing the AC electric field. The ejected ions are detected with high sensitivity with an electron multiplier. The radio frequency supply for storing and measuring the mass spectrum of the ablated ions is under development.

(W. B. Whitten, J. M. Ramsey, J. M. Dale, S. Arnold, B. V. Bronk**)*

---

*Polytechnic Institute of New York
**U. S. Army CRDEC

Continuous Wave Lasers with Photorefractive Elements

The refractive index of BaTiO$_3$ can be modified by exposure to light through a combination of photoconductivity and the Pockels effect. Of particular interest to us, a holographic diffraction grating can be produced when two laser beams interfere within a single-domain crystal. We have been exploring for several years how these photorefractive crystals can be used as intracavity optical elements in CW lasers. In one configuration, light scattered from such a grating is reflected around a triangular path so that it is one of the beams writing the grating. The other beam comes from the pump laser. Since the optical path around the ring is in general a nonintegral number of half wavelengths, the new interference pattern may be spatially displaced with a consequent but delayed revision in the holographic grating. As this process unfolds continuously, the frequency of the light circulating in the ring can be slightly different from the pump laser. We also observed that the transverse mode pattern of the ring beam undergoes a complicated but cyclical evolution from the lowest TEM$_{00}$ mode through as many as 10 higher order modes until the pattern repeats. We have recently catalogued the cyclical mode patterns in terms of Laguerre-Gaussian modes of laser theory. It is especially intriguing that the mode succession proceeds first through six patterns described by the real part of the Laguerre-Gaussian modes followed by five (one is identically zero) of the imaginary parts of the same series before repeating. We are currently evaluating two possible explanations for the mode succession - either spatial gain depletion due to charge displacement by the moving gratings, or variations in the optical path length around the ring that produce a series of transverse mode changes for each longitudinal mode jump.

In another experimental study, a BaTiO$_3$ crystal was placed within the cavity of an argon-ion laser to see if mode selection effects similar to those for CW dye lasers could be observed. Without the crystal, the laser oscillated with a bandwidth of 4.5 GHz and a longitudinal mode spacing of 63 MHz. With the crystal in place, the overall bandwidth was the same but the number of oscillating modes was reduced to give a mode spacing of c/2L where L is the distance from the crystal to the front mirror. This behavior is consistent with our earlier observations that holographic feedback restricts oscillation to those modes whose interference patterns are coincident within the crystal.

(J. A. Howell, J. M. Ramsey, W. B. Whitten)*

---

*Earlham College, ORAU Faculty Research Program

Fundamental Studies of Chemical Vapor Deposition Materials Growth Processes

We have recently begun a program to apply several spectroscopic and materials characterization techniques to foster a fundamental understanding of film growth by chemical vapor deposition (CVD) processes. Although many technologically important materials are synthesized by this general family of techniques, including semiconducting and insulating films, hydrogenated amorphous silicon for solar cells, high-temperature superconducting films, and diamond films for wear hardening, little is known about the details of the chemical and physical mechanisms involved in the processes of film growth. The experiments to be conducted will be used to develop a fundamental understanding of the materials growth process at the atomic (molecular) level. The goal is to learn how to control the material growth process for desirable film properties, not to optimize a given preparation technique. This study is a collaborative effort with staff from the ORNL Metals and Ceramics and Fusion Energy Divisions; it was initiated with Director's R&D Fund support in October 1989.

For our initial studies we have selected the growth of diamond films. The details of their growth processes will be studied by a battery of plasma diagnostic and materials characterization techniques. The current and expected applications of diamond films are tied to the unique physical properties of diamond: excellent thermal conductivity, extreme hardness, chemical inertness, high resistivity, and semiconducting character when doped. Current commercial applications include heat sinks for electronic components, optical windows for harsh environments, transparent coatings for optical disks, and wear-resistant coatings for cutting tools. Semiconductor applications are expected to be the largest growth area, particularly for high-power applications where high thermal loads are encountered. For semiconductor applications, diamond films must exhibit low-defect-density structures and very high purity.

Diamond films are currently prepared via several growth techniques, and the commercial potential of all of these methods would be enhanced if lower substrate temperatures were possible and if film growth rate and spatial uniformity for large area deposits could be improved. The purity, microstructure, and substrate adhesion of the resulting films are highly dependent on the method selected. The details of these growth processes are only poorly understood.

Initial studies will be performed using a hot filament CVD reactor. Growth of diamond films in this reactor involves placing a tungsten filament < 1 cm from a substrate in a 95/5, H_2/CH_4 atmosphere at ≈ 5 kPa. The diagnostics to be developed involve collection of information from three different regions of the reactor and correlation of these data with the quality and properties of the material grown. The three different regions are the bulk reactor volume or plasma region, the skin layer (the gas phase species within a few molecular diameters of the surface), and the molecular layer on the growing surface. Such a comprehensive examination of the overall deposition process is necessary because a combination of gas phase and surface chemistry is probably operating. Laser induced fluorescence, ionization-detected absorption spectroscopy, and non-linear optical surface spectroscopy will be emphasized.

The bulk plasma is probably the easiest region to investigate. Techniques that allow three dimensional species-and temperature-mapping of the volume will be used. For the investigation of the skin layer or gas-solid boundary layer, we propose the use of a technique developed in our laboratory for combustion diagnostics: orifice sampling into a high vacuum. Once process-intermediate species are extracted into vacuum, various types of optical spectroscopy and mass spectroscopy will be used to identify them. The final region is the material at the surface of the substrate itself. For an understanding of growth processes, we feel that only the monolayer of material on the surface should be examined. Two interesting new approaches to probing the surface layer of materials are second-harmonic generation and sum-frequency generation. These are optical probes of the surface that are quite sensitive to interfacial phenomena while not requiring ultra-high vacuum conditions. Information collected using these techniques would be correlated with the quality of the material that is actually grown, using Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy.

Assembly of a hot filament diamond film growth reactor is underway in the laser laboratory. Initial experiments will involve orifice sampling of reaction intermediates from methane-hydrogen pyrolysis and resonantly enhanced multiphoton ionization mass spectroscopic detection.

(J. M. Ramsey, R. W. Shaw, and W. B. Whitten)

Spectroscopy of Plasmas Used for Thin Film Deposition

The goal of a Director's R&D Fund project under the direction of J. B. Bates, Solid State Division, is the development of thin film batteries and sensors. These devices consist of thin layers of conductors, electrolytes, and ceramics. The entire assembly is less than 10 microns thick. These films are prepared by magnetron sputtering, a RF plasma technique that removes material from a target and deposits it as a thin film on a substrate. The chemical reactions that occur during this process are essentially unknown; consequently, film preparation techniques are determined empirically. We are examining optical diagnostic methods in an attempt to understand the thin film preparation processes.

Initial studies involved measuring the spatially resolved spontaneous emission spectrum from the discharge. Exploratory studies were conducted with an intensified linear diode array detector coupled to a spectrograph. The light collection system consists of a fiber optic with a spherical lens positioned at the launch end of the fiber; the fiber optic exits the vacuum chamber via a vacuum feedthrough. The vertical resolution of the emission collected by the optical fiber is about 4 mm.

Emission spectra were collected for several targets (Li_4SiO_4, Li_3PO_4, Li_2CO_3 at different mole ratios), different plasma gases (argon, oxygen, and mixtures of argon and oxygen), gas pressure, and magnetron powers. In the 475 to 690 nm region, the observed emissions were assigned to neutral lithium emission and O_2^+ molecules. The intensity of the neutral lithium emission increased with RF power and plasma gas pressure. In a pure oxygen plasma, emission from neutral oxygen atoms was also observed. Emission from phosphorous or silicon was not observed.

(L. N. Klatt, R. W. Shaw, and J. M. Ramsey)

Microwave Spectroscopy

We are developing a microwave spectroscopic technique for the determination of stable isotope ratios for clinical studies. The microwave rotational transitions of small molecules are generally shifted substantially compared to the spectral linewidth by isotopic substitution. It is therefore comparatively easy to obtain the necessary specificity with microwave techniques. For clinical tracer studies, minor isotopes must be determined with high sensitivity as well.

Our microwave spectrometer uses supersonic expansion to rotationally cool the analyte molecules. The molecules can thus absorb strongly at the frequency of the lowest rotational transition. The sample interacts with the microwaves in a Fabry-Perot cavity formed from two diamond-turned copper mirrors. The microwave frequency is locked to a resonant frequency of the cavity and can be scanned by translating one of the mirrors slightly with a piezoelectric pusher. Superheterodyne detection is used, followed by a lock-in amplifier referenced to the pulsed expansion nozzle. To test our sensitivity, we have measured the microwave absorption of a mixture of 1% carbonyl sulfide in argon. We observe a signal-to-noise ratio of 25 for the 12.1238-GHz line of $^{16}C^{13}C^{32}S$ that has a natural abundance 1.05%. Carbonyl sulfide may be an important analyte for clinical tracer studies because of its substantial dipole moment and because it can be generated from breath CO_2 by a reaction with H_2S.

(W. B. Whitten, J. M. Ramsey)

Two-Photon Excitation of Actinide Fluorescence

Two-photon excitation of actinide (or lanthanide) ion fluorescence in the solid state is being evaluated. This study is being carried out in cooperation with personnel of the Transuranium Research Laboratory at ORNL. Two-photon excitation schemes have been reported for Tb(III) in CaF_2 (Maknet, A. G. and Skripto, G. A., *Phys. Status Solids*, 53, 243, 1979) but no mention of actinides is given. From a sample of $CmBr_3$ we have observed anti-stokes emissions that correspond to a number of levels up to 9000 cm^{-1} above the photon energy of the exciting laser beam, 16800 cm^{-1}. Three of these are transitions from known excited states to the ground state that have not been observed in fluorescence before. The mechanism for the excitation is not yet proven, but is believed to be due to two-photon excitation into the several levels of Cm(III) in the vicinity of 33600 cm^{-1}. This method of fluorescence excitation should be generally applicable to actinides and may lead to new methods of actinide identification and determination in the environment.

(J. P. Young and G. M. Murray)

Hot-Cell Spectrophotometer System

The Chemical Technology Division (CTD) is embarking on a program to separate large amounts of curium from americium at the Radiochemical Engineering Development Center (REDC). L. M. Toth of CTD is leading the effort to develop the separation scheme. An oxidant will be added to the solution containing Am and Cm to oxidize all of the Am to Am(VI). The Am(VI) is then selectively reduced to Am(V) and the separation performed in dilute nitric acid media with an ion exchange column; the Cm(III) is retained on the column. A high concentration of nitric acid is used to strip the Cm(III) from the column. Because of the high Cm alpha activity, which produces hydrogen peroxide resulting in the reduction of Am(V) to Am(III), the concentration of oxidant, reductant, oxidation state of Am, and the speed of the ion exchange separation are important parameters. Since all of the relevant oxidation states of Am and Cm have absorption bands in the visible spectrum, spectrophotometry is ideally suited to monitor this process. Our task is to assemble and install a hot-cell spectrophotometer at REDC.

The hot-cell spectrophotometer system being assembled and tested is patterned after the in-line spectrophotometer system developed at the USDOE Savannah River Laboratory (SRL) (D. R. Van Hare and W. S. Prather, "Fiber Optic Modification of a Diode Array Spectrometer, DP-1714, January, 1986). The system is based on a HP8452A Diode Array Spectrometer (Hewlett-Packard, Palo Alto, CA). It is controlled by an IBM compatible computer. Quartz optical fibers are used to transmit the output of a 75 watt xenon arc lamp from the measurement cell, located in the hot cell, to the spectrometer, located in the control room of REDC. A high precision linear translation stage is used to multiplex the source and spectrometer optical fibers to eight different measurement points.

For in-line measurements, flow-through cells constructed from Swagelok components will be used. The hot-cell end of the optical fibers is terminated in a specially designed and fabricated connector that fits into a standard 1/4 inch Swagelok reducer and is secured with a stainless steel ferrule and nut. A custom designed lens, which collimates the light emerging from the fiber, is sealed in the tubing end of the Swagelok reducer. This lens also provides the optical interface to the process solution.

Equipment for the system has been received. The HP8452A required several modifications for use with fiber optics and an external light source; these were completed. Software to operate the spectrometer was obtained from SRL, and the modifications required for this application were completed. Initial noise and stability studies were made. Short term noise, expressed in terms of detector signal, is better than 0.4%; long term drift (greater than 8 hrs.) is about 1.5%. A mock-up of the fiber optic cables with the anticipated number of splices planned for the REDC installation was completed. Light loss across the multiplexer and one butt joint averages -1.5 dB; the theoretical reflective loss for the same number of quartz air interfaces is about -0.6 dB.

Multivariate modeling techniques will be used to deconvolute the observed spectra into the individual components. Software to accomplish this was also obtained from SRL. Modeling of the spectra will be undertaken after the system is installed and spectra of Am and Cm solutions at the process solution concentrations can be measured.

(L. N. Klatt)

Instrumentation for Absorption Fluid Studies

The objective of the Chemical Heat Pump Program, managed by the Energy Division, is to identify and develop potential heat pump systems capable of recovering energy from industrial waste heat. Operating temperatures of these proposed systems are as high as 200°C. The proposed fluids are aqueous ternary mixtures of salts with total salt concentrations ranging from 55 to 85 w/w%. Very little physicochemical data are available for these systems. Assistance is being provided to the Chemical Heat Pump Program in instrumentation and computer-based data acquisition.

Two experimental loops were assembled for these studies. One loop is being used to obtain density and vapor pressure data as a function of temperature and solute concentration. The second loop is a complete absorption heat pump system that is being used to obtain heat and mass transfer information from the test fluids so comparisons with existing fluids can be made.

Data acquisition and processing are accomplished with an IBM compatible computer. The data acquisition system consists of a high resolution digital voltmeter and multiplexer unit (Models 3456A and 3497A, Hewlett-Packard, Palo Alto, CA) interfaced to the computer with an IEEE-488 bus. Data acquisition and processing software were written as a series of GW-Basic subroutines, which are merged into the program required to accomplish the tasks specified by each experiment. Sensors installed on the system include 12 Type K thermocouples, three pressure transducers, two density monitors, two mass flow monitors, and one volumetric flow meter.

Procedures to verify the calibration of all the sensors were developed. A design flaw with the density sensors was identified during this phase of the work. The density monitor signal processing electronics require the temperature of the fluid flowing through the sensor as an input signal. We discovered that the temperature sensor is mounted on the outside wall of the fluid line in the sensor module, resulting in an incorrect temperature as input. This caused large errors in the density values. The problem was solved by installing thermocouples inside the fluid lines to obtain the fluid temperature and using a digital-to-analog converter to convert these temperatures to the input voltages required. With this modification to the density monitor, steam table data were reproduced with an average density error of 0.003 g/cm^3 over the temperature range of 15 to 150°C.

A fluid consisting of $LiNO_3$, $NaNO_3$, and KNO_3 (53:19:28 % weight ratio) was completely characterized. A manuscript describing these results has been submitted for publication in J. Chem. Eng. Data. Measurements on a proprietary fluid developed by Trane Company, LaCross, WI were also completed. This fluid is a candidate for the Triple Effect Cycle licensed by ORNL to the Trane Company. Measurements with LiBr-H_2O, a widely used fluid in absorption heat pumps, were completed to serve as a basis for comparison.

(L. N. Klatt)

Program for The Detection of Counterfeit Documents

The U.S. Department of Treasury, Bureau of Engraving and Printing (BEP) has an on-going program to develop new methods to detect and deter the counterfeiting of U.S. currency. As part of this program, BEP is investigating the possibility of introducing taggants into the inks as a covert counterfeiting deterrent system. BEP has issued a solicitation for offerors to submit taggants that can be used in the currency inks.

Phase II of this taggant proposal involves an adversarial analysis to assess the degree of difficulty for detecting the taggants, reproducing the taggants, and simulating the authentication scheme without actually reproducing the taggants. We submitted a work proposal to perform the adversarial analysis and received a contract from BEP. Work is currently in progress to identify the taggants in one set of federal reserve notes and to determine the probable mechanism to be used for detecting the taggants for the authentication process.

As a result of work for BEP for an earlier project, a paper entitled "Principal Component Analysis of Diffuse Near-infrared Reflectance Data from Paper Currency" was written and published in Applied Spectroscopy.

(J. M. Dale, L. N. Klatt, and J. M. Ramsey)

INORGANIC MASS SPECTROMETRY

D. H. Smith

A number of different activities—both support and research—are carried out in this group. Inorganic mass spectrometric research is a major effort, and both isotope ratio and elemental analyses are performed. A glow discharge mass spectrometer is used for the latter, and recently a collaborative effort with staff from Clemson University was begun. Much of the isotope ratio work was directed toward transferring our lutetium double spike method for inventory of tank contents to the international safeguards community. We continue to provide support to the stable isotopes program and to aid in the analysis of gases.

Analytical applications of positrons continues. The intense ORELA beam is being used to explore positron-induced ionization for mass spectrometry. Work has just begun on possible application of positrons for characterization of super-conducting materials.

Heavy ion x-ray satellite emission (HIXSE) is being studied as a method to characterize the chemical state of elements in various solid materials. Results are encouraging. Sulfur and a combination of sulfur and oxygen were implanted in a variety of matrices and analyzed with HIXSE. Fluorescence yields varied in a predictable way with implanted core and matrix. It was shown that impurity oxygen can be observed in an oxygen-rich matrix.

Safeguards-Related Projects

This year we provided a consultant to the International Atomic Energy Agency for developing a training course for inspectors. The goal was to train inspectors, many of whom have little technical experience, to prepare and analyze samples using a Finnigan-MAT THQ mass spectrometer. Consultation was provided on sample preparation chemistry and in overall course content. Active assistance was provided in developing instruction manuals and in teaching the first course. Four inspectors received training.

This concept has implications for the IAEA that transcend the technical questions involved. This is the first project for which a country signatory to the non-proliferation treaty (Japan) has agreed to provide laboratory space in which a permanent IAEA installation could be housed. It is important that the exercise be successful so that future similar installations become a recognized part of international safeguards. Only thus can timely analyses of samples be assured.

A chemical procedure is being developed for separating gadolinium from lutetium. The Japanese use gadolinium as a neutron poison, and its presence in a sample can cause problems in mass spectrometric analysis ($^{160}GdO^{+}$ interferes with $^{176}Lu+$), this is especially true when gadolinium is present at concentrations up to 5000 higher than lutetium. Preliminary studies indicate that lutetium can be separated from gadolinium on a 25-40 um Dowex 50X8 cation exchange column. A synthetic sample solution containing the two rare earth elements (REEs) is loaded onto the ion exchange column. Initially, the cation column is in the hydrogen form to take advantage of the greater affinity of the resin for the REEs in this form and to prevent any loss of REEs due to hydrolysis. The column is then converted to the ammonium form prior to REE elution, using an eluent of 0.25 M alpha-hydroxy-isobutyrate at pH 4.15. REE separation is carried out at 50.5°C to produce a 0.3 mL/min eluent flow rate. As little as 14.3 ng Lu have been separated and collected in the second half-milliliter of eluent; as much as 153 ug Gd have been collected in the fifth through eighth milliliters. ICP analysis of the eluent fractions has been used to determine that the recovery of both metals is quantitative. Mass spectral analysis of the lutetium fraction indicate that traces of gadolinium are present, but its effect at these levels can be eliminated by the proper selection of filament temperature prior to lutetium analysis.

Future work will be directed toward the sample preparation procedures required to remove uranium, plutonium, and fission products from the dissolver tank sample prior to REE separation. Either a liquid extraction or clean-up column procedure will be used to remove uranium and plutonium from the sample. Initial results indicate that the separation of lutetium from alkali and alkali earth metals may be possible by simply washing the metal interferents off the Dowex 50X8 column prior to REE separation. Other REE fission products, such as Ce,Pr, Nd, Pm, and Sm, have elution times greater than gadolinium and should not be present in the initial lutetium fraction. Once the purified lutetium fraction is collected, a concentration step may be required for mass spectral analysis. Sample volume reduction and resin bead loading will be investigated as possible concentration techniques.

(D. H. Smith, R. L. Walker, D. A. Bostick, M. P. May)

Glow Discharge Mass Spectrometry

The VG-9000 Glow Discharge Mass Spectrometer is being modified to run an RF discharge, thus permitting the analysis of non-conducting samples such as glass, ceramic, or geological materials. This work is being carried out in collaboration with Professor R. K. Marcus and D. C. Duckworth of Clemson University. They have made a modified glow discharge ion source to mate with the VG-9000 and have brought their RF power supply and matching network to drive it. Initial results in which a conducting brass sample was analyzed to the 100 ppm level using the Daly detector system have been encouraging. Mass spectra of the various elements including Cu, Zn, Ni, Fe, Sn and Pb were taken. Time constraints prevented an analysis of a non-conducting sample, but a number of important operating parameters were measured and problems such as RF noise interference were identified. More work is scheduled in 1990 to further refine this ion source to the point of routine utility.

(D. L. Donohue, D. H. Smith, W. H. Christie)

Isotope Ratio Mass Spectrometry

Work was initiated this year in collaboration with Professor George Swihart of Memphis State University for isotopic analysis of boron using our VG-354 mass spectrometer. Measurements of this type shed light on the mechanisms of mineral formation. The method being developed will involve measuring the $Cs_2BO_2^+$ at mass positions 308 and 309. Use of these high masses reduces problems associated with isotopic fractionation. This work is in its early stages; we are presently trying to learn how to cope with an interference at mass 308.

A technique has been developed to analyze lutetium using the VG-354. Lutetium is being evaluated in Japan and in Germany as a double spike to help assay the contents of holding tanks for dissolver solutions at reprocessing plants. To make our results directly comparable to those from other laboratories, we decided to obtain them using our VG (most laboratories have similar instruments) rather than our more sensitive ORNL-built mass spectrometers, which are unique. The procedure requires 50 ng of lutetium and yields a 1-volt ion beam that lasts several hours. Typical internal standard deviations range from 0.1 to 0.2 %. This procedure has been communicated to the Japanese staff at their Tokai-mura reprocessing facility.

(E. H. McBay, R. L. Walker, L. K. Bertram, D. H. Smith)

Mass Spectrometric Support Activities

Mass spectrometric support for various actinides programs has continued. The final fuel pin from the joint US-UK actinides program has been received and is presently being dissolved. This pin is crucial to the characterization of various physical parameters for many isotopes. It has undergone very high burn-up and is thus very difficult to dissolve.

We have continued to provide analyses to support work carried out on the ORIGEN code. These specialized measurements allow fine-tuning the predictive ability of the code.

We continue to analyze various water samples for uranium and plutonium on a scheduled basis. We are able to analyze very small quantities (detection limits of about 10^{-16} g/ml) and can usually provide a 235/238 ratio for uranium.

Work has continued in collaboration with Steve Lambert of Sandia. He provides salt brine samples for studies of $^{234}U/^{238}U$ disequilibrium, where the high abundance sensitivity of our instruments and our ability to analyze small samples are major assets. These studies have implications for the use of brines as waste disposal sites.

We have analyzed many gas samples this year. Of particular interest are tritium samples that originate at Savannah River; these are the first to arrive since resumption of activity there. Numerous isotopically enriched krypton and xenon samples have been analyzed, along with our more routine work to characterize gases used in various atmospheres in the Martin Marietta facilities at Oak Ridge.

(R. L. Walker, L. K. Bertram, R. J. Hydzik, J. M. McMahon, M. M. Honaker, C. A. Pritchard, M. P. May, E. G. Miller, R. M. Coleman, D. H. Smith)

The ORNL Positron Source: Improved Positron Moderation

The ORNL positron source makes use of waste gamma radiation produced by the Oak Ridge Electron Linear Accelerator (ORELA). An extended description of this facility is given in the 1988 annual report (ORNL-6547). The gamma radiation is converted to positron-electron pairs by means of an annealed tungsten moderator placed in the path of the gamma bremsstrahlung of the accelerator. After the positrons emerge from the moderator surface they are extracted and transported through an evacuated solenoid to an adjacent experiment room. After about one year of continuous use, which included exposure to corrosive vapors, the surface of our first moderator became damaged to the extent that the yield of slow positrons was reduced by a factor of 10. At that point the decision was made to install a new moderator, and to experiment with different designs.

In designing the new moderator, extensive use was made of the ray tracing program, SIMION. Calculations showed that the yield of positrons might be improved by opening up the moderator configuration such that the electrostatic extraction field could penetrate more efficiently. A V-shaped configuration was used, which involved about 40 straight vanes inclined with respect to the axis along which extraction occurs. The vanes were annealed in the usual fashion to condition the surface for slow positron escape. This new configuration restored the yield of positrons to about the same level as for the old moderator when it was first put in use. About a month after installation a faulty weld in the new moderator housing caused a water coolant leak, which necessitated its removal. The original moderator was re-installed in order that spectroscopic studies could continue.

A third moderator configuration was fabricated, using a reinforced housing. At this time it has been in use for several months with no failure. The present moderator consists of a stack of 40 annular rings of tungsten sheet, 1/2 mm thick, spaced 1 mm apart. The inner and outer diameters of the rings increase continuously from the bottom of the stack to the top, such that the inside surface of the stack is conical. The yield of the slow positrons is only slightly better than that of the first moderator configuration when it was first installed. At this point we conclude that the slow positron yield is somewhat independent of the moderator configuration. The yield is quite high, however, about 1.1 x 10^8 positrons per second, when the accelerator is operating at 30 kW.

Positron beams have a unique feature, compared to ion or electron beams, in that the brightness can be enhanced. This is accomplished by re-moderation. The beam is condensed onto the back side of a tungsten film about 100 nm thick. The positrons are thermalized and diffuse to the front side of the film and are re-emitted. The total number of positrons is reduced by factors of 3-4, but because the energy, divergence angle, and cross section of the beam are also reduced, the brightness of the beam is increased. The beam is better collimated, and smaller in diameter, such that the number of positrons per unit area is much greater.

To accomplish brightness enhancement, the tungsten film must be carefully prepared, which includes a special growing procedure, followed by cleaning and annealing in high vacuum. Many experiments have been done in an attempt to deposit tungsten films at ambient temperatures, but in most cases it assumes a metastable crystal structure, face centered cubic, which reverts to the normal body centered cubic when annealed. This crystal transformation causes the film to disintegrate. Another group, located at the University of Aarhus, Denmark, has perfected a method for growing the films at high temperature, producing a remarkably tough single crystal structure. We have acquired several of the Aarhus films and have developed an electron beam annealing procedure for them. Annealing must be done very carefully, using a special tungsten mounting plate to avoid contamination. It has been found that if the commonly used method of tantalum holder mounting is used the film is contaminated and its remoderation capability destroyed. With the new preparation techniques, effective brightness enhancement films with high yields have been produced.

(L. D. Hulett, Jr., D. L. Donohue, T. A. Lewis)*

---

*I&C Division, ORNL

Positron Ionization Mass Spectrometry

Two regimes of positron ionization mass spectrometry have been studied. The first measurements were made using the 3 keV positron beam as initially extracted from the moderator. In the second work the 3 keV beam was re-moderated and contained in a Penning trap at low energies, ranging between a minimum of about 0.2 eV and an upper limit of 10 eV.

The line-of-sight beam coming from the delivery solenoid contains ions, fast electrons, and fast positrons, as well as the monoenergetic 3 keV slow positrons. To avoid the fast particles, the 3 keV positron beam was diverted 30° from line-of-sight into a collision chamber to which a time-of-flight mass spectrometer was attached. Mass spectra of methane, isobutane, toluene, SF_6, and o, m, and p-xylene were measured, using the 3 keV positron beam for ionization. An electron gun was in place in the ionization chamber so that an immediate comparison to the mass spectra produced by 70 and 2700 eV electron bombardment could be made. It was found that the spectra produced by the high energy electrons and positrons were qualitatively very similar.

For the low energy ionization studies the collision chamber was equipped with a 100 nm tungsten film that intercepted the incoming 3 keV positrons. A large fraction of the thermalized positrons diffused to the exit side of the film where they were ejected with energies ranging from 0 to about 2.4 eV. Using a retarding grid spectrometer, the peak energy of the distribution was found to be at 1-2 eV. By biasing the moderator film with respect to the entrance grid of the collision chamber, the energy of the positrons could be varied from a minimum of about 0.2 eV to a maximum of 10 eV.

The low energy collision chamber was in the form of a miniature Penning trap. The entrance grid to the trap, held at +5 volts, was placed immediately after the re-moderation film. As the positrons emerged from the film the grid potential was dropped to let them enter a 3 cm drift region, after which the potential was restored to its 5 volt level. Exit from the other side of the drift region was blocked by a grid held at 24 volts. Lateral containment of the positrons was accomplished with a 50 gauss magnetic field running parallel to the drift region. An extraction grid was located at the side of the trap. After a period of 20-30 microseconds, the ions produced were pulsed out of the trap in a direction 90° with respect to the positron entrance, and accelerated to 3000 eV for mass analysis with a time-of-flight mass spectrometer.

Low energy ionization of over 20 large organic molecules has been studied. Among these were straight chain aliphatics, such as butane and decane, alkenes such as hexene and 1,5 hexadiene, and several aromatics such as benzene, aniline and n-butyl benzene. In all cases it has been found that positrons having kinetic energies less than the ionization potentials will effect ionization. This is believed to occur via positronium formation. Positronium is a neutral species consisting of a positron and electron bound together in an atomic orbit. The ionization potential of positronium is 6.8 eV, exactly half that of atomic hydrogen. When a positron passes by an atom or molecule, it is able to 'rob' it of one of its valence electrons, provided the kinetic energy of the positron is above a certain threshold. The threshold for the transfer of the electron to the positron is reached when the sum of the kinetic energy of the positron plus 6.8 eV is greater than the ionization potential of the atom or molecule giving up the electron. For a number of organic molecules used in this study, this threshold condition for the production of ions was observed. The fragmentation behavior of the molecules tended to parallel that induced by electron bombardment for corresponding kinetic energies above the respective thresholds.

The extraction of an electron from a molecule to form positronium is a sudden process, occurring in times less than 0.1 picoseconds. This implies a vertical Franck-Condon transition similar to that for ionization by electrons or photons.

We are currently preparing to investigate very low energy positron attachment to molecules, which presumably can occur only if the positron approaches the molecule at a rather low velocity, such that the electron cloud of the molecule can become polarized and attach the positron before it passes by. For this to occur, the positron kinetic energy must be lower than 0.2 eV. Positrons have been observed to be trapped under conditions for which their kinetic energies should be approaching this value, but possibly it was above the attachment threshold. In our next experiments the magnetic field of the Penning trap will be increased in order to reduce the possibility of positron loss by elastic scattering.

(D. L. Donohue, L. D. Hulett, B. A. Eckenrode, S. A. McLuckey, G. L. Glish)*

Mutagenesis of DNA by Positron Bombardment

The ability to produce mutagenesis of DNA by positron bombardment is being investigated. Low molecular weight DNA (approximately 3 kilobase) was placed on surfaces of annealed tungsten plates and exposed to 3 keV positrons. After doses ranging from 10^7 - 10^9 positrons, the DNA was re-dissolved and instilled in E-coli. Normally, DNA of the particular type used will cause E-coli to become immune to streptomycin, but positron irradiation of the DNA altered this effect. These results are encouraging, indicating that a mild dose of positrons will produce measurable effects. Perhaps by using the bacteria as a biological amplifier, the mutated DNA can be replicated and generated in concentrations sufficiently high for analysis by other techniques. The 3 keV positrons were much higher in energy than the 0 - 10 eV positrons that will be used in future experiments. With the lower energy particles it may be possible to surgically implant mutations in selected areas of the large molecules.

(L. D. Hulett, D. L. Donohue)

High-Resolution HIXSE Studies of the Chemical Environment of Sub-Surface Moieties

The characterization of ion implanted materials, thin films, and film-substrate interfaces is becoming increasingly important to the materials processing industry. Although a wide variety of methods are routinely used to analyze these substances, few techniques can answer questions concerning the local chemical nature of sub-surface moieties. For example, some surface analysis techniques when combined with sputter depth profiling methods yield spatial and chemical information. Unfortunately,

---

*ORAU Post-Doctoral Research Associate

sputtering can significantly alter both the concentration profile of the implant or interface and its chemistry. Other methods, such as backscattering, provide information about concentration profiles of implants but do not reveal chemical speciation or bonding. Heavy-ion-induced X-ray satellite emission (HIXSE), an X-ray fluorescence technique which uses fast (≈ 1 MeV/amu), heavy ions for excitation and yields intense, chemically sensitive satellite lines, is being evaluated as a method which can chemically characterize sub-surface moieties.

We have implanted a series of quartz glass, Si(100) wafers, aluminum, and alumina targets with varying doses of sulfur and sulfur plus oxygen ranging from 0.5 to 10 x 10^{16} / cm^2 at the Surface Modification and Characterization Collaborative Research Center (SMAC/CRC). Rutherford backscattering (RBS) measurements were used to verify the dose, the depth, and the uniformity of the implant. Using a 24 MeV Si ion beam extracted from the EN-tandem accelerator to excite the sub-surface atoms, high-resolution sulfur K_α X-ray measurements were obtained with the HI-PER-X spectrometer. The data show that the relative ion-induced X-ray fluorescence yield of ion implanted sulfur varies both as a function of the implanted dose and the matrix in which it is implanted. These changes can be predicted on the basis of the local valence electron density or chemical environment of the implanted sulfur moiety. In addition, we have shown that co-implanted oxygen has a direct effect on the sulfur X-ray spectrum in silicon and silica matrices. The latter result means that we can indirectly and nondestructively observe impurity oxygen in an oxide matrix. We currently know of no other technique which can yield this information. Potential applications in the field of ceramic materials will be explored.

(T. M. Rossel, J. P. Young, R. A. Zuhr,[*] *C. R. Vane,*[**] *and R. S. Peterson*[***]*)*

---

[*] Solid State Division

[**] Physics Division

[***] University of the South

ORGANIC MASS SPECTROMETRY

Gary L. Glish

Efforts to develop new and improved mass spectrometric and related techniques for the analysis of organic molecules have continued. Progress has been made in several on-going projects and several new projects have been initiated. The research falls into both the fundamental and applied categories. A major focus of the work has been related to our atmospheric sampling glow discharge ionization (ASGDI) source, with continued applications to the detection of organic compounds in ambient air and new applications. Much of the work has been a continuation of the development and application of the quadrupole ion trap. This device is developing into a very powerful mass spectrometer for both analytical applications and fundamental studies. In addition to the work summarized below, we have continued to collaborate with the positron group in studying the ionization of organic molecules by positrons. Also during this year, much of our research experienced a major interruption as we moved most of the instrumentation from Y-12 to the new building at X-10. We are still in the process of getting some of the instruments back up and running.

Electrospray Ionization/ITMS

Probably the most exciting advance in the past year is the successful demonstration of electrospray ionization (ESI) mass spectrometry with the ITMS. The system is based on the ITMS fitted with the atmospheric sampling, glow discharge ionization (ASGDI) source. However, the ASGDI is not used as an ionization source but as the interface between the electrospray, which operates in the atmosphere, and the ITMS. Our current ESI system consists of a dome tipped stainless steel syringe needle (120 µm i.d.) connected to a syringe pump via a short length of 0.5 mm i.d. teflon tubing. A solution of the analyte, dissolved in the appropriate solvents, is pumped through the needle at flow rates of 1-10 µL/min. A voltage of 3-4 kV applied to the needle results in an "electrospray" which is aimed at the 100 µm orifice in the entrance aperture of the ASGDI source. To facilitate positioning of the spray relative to the orifice, the needle is mounted on an X-Y-Z manipulator. The ASGDI source operates as a platform from which to inject the electrospray-generated ions into the trap. That is, it provides the region of differential pumping needed to transfer the ions generated at atmospheric pressure into the lower pressure region of the trap. To facilitate this transfer of ions, the region between the aperture plates of the ASGDI source has been fitted with two focusing lenses. Using this ESI/ITMS system we have successfully injected both positive and negative ions into the trap; MS/MS and MS^n experiments have been carried out on the injected ions. Most significantly, biomolecules with molecular weights well beyond the normal mass range of the ITMS, which is 650 daltons, have been successfully analyzed. This is possible because these large biomolecules can be multiply charged in the electrospray, making their m/z values within the range accessible to the ion trap. For example, horse heart cytochrome c, a hemoprotein with a molecular weight of 12360 amu, was successfully injected and then detected as the $(M+17)^{17+}$, $(M+16)^{16+}$, $(M+15)^{15+}$, $(M+14)^{14+}$, $(M+13)^{13+}$ species, which have m/z values compatible with ion trap analysis. Bovine albumin (mw = 66,000) is the largest molecule that has thus far been detected (and the largest attempted). Sample quantities necessary for such analyses on our system appear to be similar to or less than those reported for other ESI systems. In the case of peptide bradykinin (MW =1060 amu), 16 fmol of sample was required for detection. For most other samples studied to date, similar quantities were sufficient to detect the material.

(G. J. Van Berkel, S. A. McLuckey, G. L. Glish)

Explosives Detection

The development of an explosives vapor detector has continued to be a major focus of the applied research. Advances have been made in this area on both the quadrupole/time-of-flight (QT) instrument and the quadrupole ion trap (ITMS). On the QT, a new mode of operation has been developed, referred to as the targeted daughter ion mode. This method of operation is possible with some, but not all, types of instruments capable of MS/MS. It involves operating the first stage mass analyzer as a high pass filter and using a second stage of mass analysis to identify daughter ions from a targeted compound class. Instruments which have a quadrupole as a first mass analyzer are capable of operation in this manner. This mode of operation can be employed in those cases where a parent ion scan is useful. The targeted daughter ion mode, with some sacrifice in specificity, provides a roughly ten-fold improvement in detection limits relative to conventional daughter ion analysis. These findings have been demonstrated with anions derived from 2,4-dinitrotoluene and RDX, a heterocyclic nitramine. The targeted daughter ion mode of operation has been incorporated as an option in the automated detection scheme as the first stage of screening. If an explosive is indicated by this, the most sensitive mode of operation, a more specific mode, such as the conventional daughter ion scan, is used for confirmation.

In the area of explosives detection with an ITMS, we have combined our experience with forming anions from explosives in the ASGDI source with our recent work in ion injection into an ITMS to evaluate the present ASGDI source/ITMS combination as an explosives detector. Under optimum ion injection conditions, we obtain detection limits at least as low as, and sometimes lower than, those obtained with the quadrupole/time-of-flight instrument using a single stage of mass spectrometry. In MS/MS, the ITMS-based device is superior to the QT due, in general, to the much greater MS/MS efficiencies observed with the ion trap. The specificity of the ASGDI source/ITMS combination is superior to the quadrupole/time-of-flight instrument in the MS/MS mode of operation due to the factor of 20-30 enhancement in daughter ion mass resolution with the former instrument. However, because dissociation can occur with particularly fragile ions upon injection into the ITMS the utility of the ASGDI source/ITMS as a detector for nitrate esters is compromised. Using the present approach to ion injection, we detect no high mass ions from nitrate esters. Rather, we readily detect the NO_3^- fragment. Our detection limit may be more than a factor of ten lower than with the quadrupole/time-of-flight instrument, but this is accompanied by a loss in specificity. During the course of this work we have noted that we can readily detect black powder which contains no organic explosives but consists primarily of nitrate salts and elemental sulfur. We detect anions derived from sulfur, primarily S_3^-. This is significant in that no other instrumental explosives detector claims to be able to detect black powder. Indeed, those that rely on the presence of an N-O bond, such as chemiluminescence and metastable atom induced fluorescence, cannot detect sulfur.

A potential application of the explosives detector was investigated for the U.S. Army Toxic and Hazardous Materials Agency. They are testing a technique which employs hot gas to remove explosives from equipment and materials. An integral part of the test is to determine the extent of contamination before and after the materials have been exposed to the hot gas. Both vapor and surface wipe samples were collected on site at the Hawthorne Army Ammunition Plant decontamination facility. R. F. Weston, contractor for the facility, collected similar samples, which will be analyzed by conventional HPLC methods. A comparison of the results from the explosives detector and the HPLC method will be made when the results from Weston are available. Preliminary results indicate that the surface wipe samples are more dependable when sampling in uncontrolled and highly variable temperature and wind conditions.

(S. A. McLuckey, B. C. Grant, G. L. Glish, K. G. Asano, H. S. McKown)

Atmospheric Sampling

We have been examining the utility of our ASGDI source to detect compound classes other than explosives. One such class is organophosphonate compounds. Two alkyl methylphosphonates, diisopropyl methylphosphonate (DIMP) and dimethyl methylphosphonate (DMMP), were studied on the ASGDI source-quadrupole/time-of-flight system and the injection ion trap (ASGDI source/ITMS). The most interesting results were observed during the negative ion analysis. In the negative ion mode, both phosphonates have a base peak corresponding to the loss of an alkyl group. MS/MS spectra showed poorer fragmentation efficiencies in the negative ion mode on the QT than on the injection trap system. However, the daughter ions formed suggest that this compound class would be a very good candidate for screening by the targeted daughter ion mode of operation. Preliminary MS/MS detection limits determined using the conventional daughter ion mode of analysis are in the low parts-per-billion range.

Another class of compounds which has been investigated using the ASGDI with the QT is halocarbons. The ASGDI source provides positive ion mass spectra that are much more informative than those obtained with conventional electron ionization (EI). While the EI mass spectra are dominated by low-mass, structurally uninformative ions, the ASGDI source generates, in most cases, a molecular ion and also high-mass, more structurally informative fragments. In the negative ion mode the ASGDI source generated predominantly molecular species with a few high-mass fragments. Single ion monitoring detection limits were determined to be typically a few parts-per-billion for positive ions and in the parts-per-trillion for negative ions.

(K. G. Asano, D. E. Goeringer, G. L. Glish, S. A. McLuckey)

ASGDI/ITMS

In a somewhat different application of the ASGDI/ITMS, we have performed some studies that are a continuation of our selected reagent ion chemical ionization work. Negative ions are not readily formed in the ion trap because the low-energy-electrons necessary for the formation of negative ions are not trapped in the ITMS. In addition, those negative ions that are formed are often lost via ion/ion recombination due to the large excess of positive ions formed when using the conventional electron ionization of the ITMS. We used our ability to generate negative ions in the ASGDI and injected these ions into the ITMS to overcome this problem. Several different gas mixtures were investigated to generate different reagent ions. We showed, with trinitrotoluene as the analyte, that different reagent ions interact in different ways. Some ionize TNT via electron transfer while others ionize it by proton abstraction. We have also applied this approach, along with the MS/MS and kinetic measurement capabilities of the ITMS, to characterize the ions and reactive neutrals that issue from the ASGDI source.

During the course of characterizing the ions that issue from the ASGDI, we obtained some unexpected results for the anions of m/z 62. We interpreted these results based on the hypothesis that at least two structures of NO_3^- are formed in the ASGDI source and support this contention with both theoretical calculations and novel experiments. The MS/MS spectrum of the m/z 62 anion from normal background (air) of the ASGDI source shows daughter ions at m/z 32 (presumably $O_2^{-\cdot}$) and sometimes at m/z 46 (NO_2^-). The NO_2^- fragment is to be expected from NO_3^- with the D_{3h} structure (i.e., the conventional nitrate anion) However, an O_2^- fragment is unexpected. The MS/MS spectrum of m/z 62 when nitroglycerine was admitted into the ion source showed that the intensity of the m/z 32 ion was unchanged from background while that of NO_2^- went off scale. Others have previously hypothesized the existence of two stable structures of NO_3^- from kinetic data acquired in flowing afterglow studies.

(S. A. McLuckey, B. A. Eckenrode, R. A. Flurer**, G. L. Glish)*

---

*ORAU Post-Doctoral Research Associate
**ORAU Laboratory Cooperative Postgraduate Research Program

Ion Structure Studies

We have performed a series of calculations to elucidate other bound structures for the nitrate anion in addition to the common D_{3h} structure. In addition to the D_{3h} structure, we have located two linear structures with similar energies on the NO_3^- potential energy surface. In each linear geometry the $ON\text{-}O_2^-$ or $NO\text{-}O_2^-$ bond is long and weak, especially for the $NO\text{-}O_2^-$ species. Either linear form can account for the formation of O_2^- upon CID of NO_3^- formed by sampling ambient air. We can assume that the $ON\text{-}O_2^-$ structure is more likely to be stored in the ion trap upon injection from the ASGDI source when sampling ambient air, since the $NO\text{-}O_2^-$ structure, due to its relatively weak O-O bond, is less likely to survive injection into the ion trap.

Due to prohibitively high costs associated with the use of the STC VAXes for calculations such as those in the above study, it has become necessary to curtail the use of these computers and seek other computational facilities. To achieve this end, we moved to the UNIX operating system running on a high-end personal computer, and converted our computational chemistry software to run under UNIX. Having completed our study of the nitrate anion, we have begun to apply our new computational facilities to new problems in organic ion chemistry. One such problem is the structure of the ion formed by loss of NH_3 from the $(M\text{-}H)^+$ of N,N-dimethylaniline.

We have observed that the $(M\text{-}H)^+$ ions from N,N-dimethylaniline lose neutral fragments of 17 and 29 daltons in the MS/MS spectrum. It has been shown by other groups that daughter ion empirical formula information can be obtained by doing MS/MS on naturally occurring isotopic peaks. This method is limited to cases where the natural isotopic peak is not isobaric with another peak in the mass spectrum. For the N,N-dimethylaniline case, however, isobaric interferences were present. We demonstrated a method to overcome this limitation by using multiple stages of mass spectrometry (MS^n) with the ion trap mass spectrometer. An MS^3 experiment was done using the ^{13}C isotope peak of the molecular ion. The results of this experiment were compared to the corresponding MS^3 experiment of the ^{12}C ion to obtain the desired information. It was found that the loss of 17 daltons corresponded to NH_3 and that the loss of 29 daltons was $CH_2{=}NH$. These losses are unexpected since they can only occur via some complex rearrangement. This method for determining daughter ion formulas is very simple and straightforward. Further examples have demonstrated the widespread utility of the technique for structural and reaction mechanism determinations.

(R. A. Flurer*, G. L. Glish, S. A. McLuckey, K. G. Asano)

---

*ORAU Laboratory Cooperative Postgraduate Research Program

Laser Desorption/ITMS

Interest in the N,N-dimethylaniline came about due to observations when doing laser desorption/MS^n experiments. We have continued to explore the utility of laser desorption in an ion trap. While we had been using the 1064 nm wavelength, we have investigated using the fourth harmonic, or 266 nm, output from the Nd:YAG laser. This provides us with a higher power density. We have also found that the variation in laser pulses does not necessarily make it worthwhile to average more than one or two pulses per scan. Using the 266 nm wavelength, we have successfully desorbed porphyrins, such as octaethylporphyrin (OEP) and deuteroporphyrin IX dimethyl ester. These spectra are similar to the EI spectra obtained on other instruments. In addition, sucrose experiments using a probe coated with a KCl solution enabled us to obtain more reproducible spectra that showed a (sucrose+K) adduct ion as well as a molecular ion.

(D. E. Goeringer, R. A. Flurer*, G. L. Glish, S. A. McLuckey)

---

*ORAU Laboratory Cooperative Postgraduate Research Program

Experiments with Hybrid Mass Spectrometers

We have also continued work on instruments other than ion traps. In a continuation of our work with hybrid MS/MS instruments, we have been exploring and comparing the capabilities of the different collision energy regimes for collision-induced dissociation (CID) in our QEB geometry instrument. CID is an integral part of most MS/MS experiments. There are two ion translational energy ranges in which CID is normally performed. Low energy CID is performed with ion translational energies of a few tens of electron volts, while high energy CID uses translational energies of a few kiloelectron volts. Hybrid mass spectrometers, instruments consisting of sectors and quadrupoles, are the only instruments that can readily access both collision energy regimes. One question that has not been satisfactorily addressed in the comparison of the two CID energy regimes is their relative sensitivity. The QEB offers unique capabilities in this area. We have compared indirectly the sensitivity of the two CID regimes by determining the ultimate resolution obtainable on daughter ions formed by low and high energy CID using 3-methyl-2-butanone as the standard compound for comparison. The molecular ion and protonated molecule of this compound both dissociate to give isobaric daughter ions $C_3H_7^+$ and $C_2H_3O^+$. At 9 keV collision energy, the maximum resolution obtainable was approximately 1,000, while at 50 eV collision energy a resolution in excess of 10,000 was obtained. We also demonstrated the capability of performing high resolution parent ion scans with the QEB and the ability to operate it in the targeted daughter ion mode.

We have continued our work in the area of porphyrin analysis. Due to the limitations of our sector instruments, much of this work has been performed on the BEQQ at the University of Tennessee. Having determined the chemistry involved in the reduction of porphyrins to porphyrinogens in the chemical ionization source, and how to control this to our advantage, we have now demonstrated the utility of this for direct analysis of porphyrins. By doing MS/MS on the $(M+7H)^+$ ion we are able to sequence the pyrroles in the porphyrin. Spectra that are much more informative than conventional CI spectra are obtained, allowing totally unsymmetrical porphyrins to be analyzed. We have also demonstrated that even simple mixtures of porphyrins can be analyzed this way. In addition to this work, we have continued our investigation into the analytical utility of doubly-charged porphyrins. We have found that only very low ionization energy targets (i.e. organic molecules and not inert gases) are suitable for electron-capture induced dissociation. These studies are continuing.

(B. C. Grant, G. J. Van Berkel, G. L. Glish, S. A. McLuckey, H. S. McKown, L. K. Bertram, A. A. Tuinman)*

---

*University of Tennessee

Ion Mobility Spectrometry

A new area of interest is ion mobility spectrometry which can be thought of as time-of-flight mass spectrometry at atmospheric pressure. A basic IMS instrument consists of a sample inlet, reaction region, shutter grid, drift region, and detector. It is used to reliably detect chemicals at concentrations in the part-per-billion range. The performance of a conventional IMS system is limited in both resolving power and sensitivity. The shutter-grid pulse-width controls sensitivity and resolution. A long shutter grid pulse is desired to allow more ions into the drift region and therefore provides greater sensitivity, but a short pulse is required for greater resolution. Thus, IMS performance is a compromise between these two parameters. An IMS model has been designed to study the trade-offs of resolution and sensitivity. Several user programs have been written to allow dynamic control of the ring electrode voltages (the current geometry has 10 electrodes) in the ion optical calculation program SIMION. The ions of a particular mobility, K_0, are located at a particular position in the drift region at each instant in time. Their motion can be changed by linear or nonlinear drift field voltage adjustments, and they can be moved to different locations in the drift region at a later time. By reversing the field at specific times, certain K_0's can be isolated. Models of initial spatial spread and initial kinetic energy direction and magnitude in the IMS have been completed. It was found that the initial spatial spread was most severe in limiting resolution. With this result, it was decided to trap the ions into a new starting position and then ramp them to the detector. With this system the time spread of the ions was reduced approximately two orders of magnitude. These theoretical results will be tested when our IMS, which has been ordered, is delivered.

(B. A. Eckenrode, S. A. McLuckey, G. L. Glish)*

---

*ORAU Post-Doctoral Research Associate

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 extreme sensitivity of the SIMS technique. During this reporting period, a purchase order was placed with CAMECA Instruments for the acquisition of a new IMS-4f ion microscope/microprobe. Installation is anticipated for early spring, 1990. This instrument will be used mainly in our inorganic SIMS research program, but will also be used to investigate imaging capability for organic (biological matrices) materials.

Organic SIMS

Our efforts in organic secondary ion mass spectrometry include basic and applied research. We investigate fundamental processes that lead to emission of secondary ions characteristic of organic samples when such samples are impacted by high energy (ca. 5-10 keV) primary ions. These findings are applied toward the use of organic secondary ion mass spectrometry to determine the spatial distribution of fixed organic compounds in various matrices, such as biological tissue samples. Funding for this latter project is provided by a grant from the National Institutes of Health.

In previous work on fundamental processes, we reported evidence that the chemistry governing the abundance of various species of secondary ions appears to occur beneath the monolayer surface. This was determined from the variation in secondary ion emission from glycerol solutions of various alkylamines. It was observed that the relative intensities of amine-characteristic ions varied with the bulk amine concentration rather than the surface concentration. Exactly why this is true is still not clear, but evidence suggests that secondary ion emission from liquids is determined by the kinetics of protonation of the amines in solution.

From our pulsed primary beam experiments, we demonstrated that the solution-phase precursors to glycerol secondary ions were glycerol molecules in solution. We have found more recently that the same is not true of secondary ions characteristic of dissolved amines. The ion intensity of protonated amine rises slower than protonated glycerol ion intensity. This lag, or induction period, indicates that the free base amines in solution must undergo some chemical reaction before they can be emitted as secondary ions. This reaction is most likely amine protonation by protonated glycerol in solution. Other evidence indicates that protonation in solution is the rate-determining step that controls the protonated amine secondary ion intensity. The data include the fact that protonated amine intensity is proportional to free-base amine concentration, which determines the rate of amine protonation in solution. Secondly, secondary protonated amine intensity decreases exponentially with increased primary ion current density. This latter feature arises because, as the primary ion current density is increased, the rate of sample removal is increased. Thus, the time allowed for protonation of any individual amine is reduced, reducing the amount of protonated amine in solution and near the surface.

These findings have practical implications. In particular, design and construction of a practical organic SIMS microprobe depends heavily upon the chemistry and physics of the secondary ions emitted. For example, effects of primary ion induced chemistry must be universal for all points on the sample, or the determined distribution will be flawed. One way to establish a universal primary ion chemistry in a nonhomogeneous sample is to have no effect at all. This can be accomplished by using a very limited dose of primary ions. Of course, using a lower primary ion current results in a lower secondary ion current. Consequently, the mass analyzer used to identify the ions characteristic of the compound of interest must be very sensitive. In terms of mass spectrometers, this means it must have a high transmission efficiency.

In the present design of our prototype organic ion microprobe source, we have employed second order ion optics to effectively collect over 70% of the secondary ions emitted. Unlike most microprobes, this instrument is capable, in theory, of obtaining images from samples up to 2 cm x 2 cm. For such large samples, second order ion optics are necessary to correct for aperture aberrations. The performance of the source is currently being tested using a unique low energy beam imaging device developed for this purpose.

Our expertise in ion optics was employed to design and construct a mass spectrometer for monitoring magnetically confined plasmas. These plasmas -- ionized gases -- will be used in the manufacture of the next generation of solid state electronic compnents. The mass spectrometer we designed will provide information about the mass, population, and kinetic energy of ions and neutral species within the plasma.

Even without primary ion induced chemistry, biological tissue samples are complex mixtures. For any targeted ion, there are likely to be other ions of different structure generated from the sample. To distinguish the targeted ions from other species, tandem mass spectrometry (MS/MS) is employed. That is, for each spot on the sample bombarded by the primary ion beam, the MS/MS spectrum is obtained for ions having the same mass-to-charge ratio as the targeted ions. For an image 100 x 200, consisting of 40,000 picture elements or pixels, almost one megabyte of data is collected. Software and hardware have been developed so that this kind of image can be obtained in about 20 minutes, with the evolving image being displayed in real time.

(*Peter J. Todd, Casey C. Grimm,* R. Timothy Short**)

---

*UT Post-Doctoral Research Associate

Inorganic SIMS

In collaboration with S. A. David and T. Zacharia of the Metals and Ceramics Division, SIMS was used to study properties affecting the weldability of two Al-Li alloys. Al-Li alloys have superior mechanical properties over other Al alloys. However, welding of these alloys significantly degrades these properties in the fusion and heat affect zones.

The alloys studied are:

Alloy 2090: Al (2.2) Li (2.7) Cu (0.12) Zr (wt.%)

Alloy 2091: Al (1.7) Li (1.8) Cu (1.4) Mg (0.09) Zr (wt.%)

Ion images of the above elements in the fusion and heat affected zones showed Cu and Mg to be non uniformly distributed, while Al, Li, and Zr were uniformly distributed. Ion images of the base alloys showed uniform distribution of all the elements. The inhomogeneity of Cu and Mg in the fusion and heat affected zones is the cause of degradation in mechanical properties. The inhomogeneities are irregularly shaped regions of high Cu and/or Mg concentration ranging from 5 to 15 microns in size. The inhomogeneities could be the result of any number of processes, such as a phase change or a precipitate. Abundance measurements for each of the alloy elements were made in and around these regions and in the base alloy. These data are being analyzed and should help identify the process by which the inhomogeneities are formed.

In collaboration with D. B. Geohegan and D. N. Mashburn of the Solid State Division, SIMS was used to study the composition of plumes ablated from a pellet of Y-Ba-Cu high-temperature superconducting material by a pulsed laser. Superconducting thin films are made by the repeated deposition of these plumes onto a $SrTiO_3$ substrate until the desired film thickness is achieved. Understanding the nature of the ablated plume will aid in the development of the deposition process.

The study consisted of allowing the ablated plumes to expand between two oppositely charged silicon plates. The objective was to collect positive ions in the plume on the negative plate. SIMS analysis of both plates showed that Y, Ba, and Cu were collected on both plates in approximately equal amounts. These were not the expected results. Rather than collecting positive ions, it appears that neutrals expanding from the plume were deposited on the plates. Other studies indicate that at least 4% of the plume is composed of positive ions. Further studies of the plume are needed to explain the results of this experiment.

Finally, due to the age of the ARL Ion Microprobe Mass Analyzer, a large amount of time was spent on maintaining its electronics and vacuum system. An unexpected benefit of these efforts was a ten-fold improvement of the vacuum system's pressure. This will increase the life of the ion pumps and will reduce adverse effects, such as hydride and oxide formation, that residual vacuum gases produce during the sputtering process.

(R. E. Valiga, W. H. Christie)

SSMS Analysis of LWR Spent Fuel

Phase One of this program involved the analysis of five small core-drilled fuel specimens (approx. 50 mg each) and a composite of circumferential fragments. A new procedure had to be written to meet NQA-1 standards and to incorporate improvements in the analyses of highly radioactive samples by the high gamma-level SSMS facility in Building 2026. Hot cell methods involving minimal sample handling had to be developed for crushing and powdering the samples, fabricating silver electrodes containing the samples, and mounting them onto graphite support blocks. A solid U_3O_8-matrix standard containing various metals of interest was prepared and characterized. This was the first time solid spent reactor fuel has been analyzed by SSMS without prior dissolution and dilution.

Phase Two of the program, which provides experimental data to validate the ORIGEN source code, was initiated. Well-characterized LWR spent fuel, as collected and archived by the Materials Characterization Center at Battelle Pacific Northwest Laboratories (PNL), is being used for analyses. The computer software programs used in analyzing the SSMS photoplates were documented and validated to rectify the only adverse finding cited in a QA audit that was conducted by PNL's QA department representative.

(D. O. Vick, L. Landau, W. H. Christie)*

---

*Y-12 Plant Laboratory

SPECIAL PROJECTS

H. H. Ross

Determination of Radioiodine

The measurement of ^{125}I and/or ^{129}I activity in environmental samples is often complicated by two factors: 1) the small decay energy of the nuclides, and 2) the low specific activity usually present. Low specific activity usually means that some form of concentration procedure is required in order to make reasonably precise measurements. Such concentration efforts are especially exacting for iodine nuclides; loss by volatilization is a frequent problem.

Photon emissions from both ^{125}I and ^{129}I include a variety of gamma and x-rays, primarily in the energy range of 20-40 keV. ^{129}I also has a beta emission with a maximum energy of 154 keV. Such low energies complicate the assay of these nuclides by photon spectroscopic techniques, especially at environmental levels. Sample self-absorption and counter geometry are critical parameters. Beta measurements of ^{129}I in solid samples prove even more demanding.

We have developed a new technique to make radioiodine measurements using a liquid scintillation counter. Liquid scintillation techniques offer the advantages of no sample self-absorption, 4-pi counting geometry, and high counting efficiencies for beta and low-energy photon radiation. The novel aspect of our method is the use of what we call an "extractive-reactive" scintillator (ERS). In the method, all of the iodine in the sample (organic and inorganic) is converted to the iodide ion. Further treatment converts the iodide to elemental iodine in the presence of the ERS. The generated iodine is extracted into the ERS and simultaneously reacts with the ERS to form a non-colored, non-quenching counting medium. The ERS secures three important objectives in the technique: concentration of iodine, transformation of volatile iodine to a non-volatile form, and generation of scintillation photons in the counter. Another advantage of the ERS method is that radiochemical contamination of the iodine-ERS by other radionuclides is virtually nonexistent.

We have compared the ERS method with photon counting techniques using thyroid samples from deer that contained ^{129}I. Excellent agreement was achieved. Although we have not yet optimized our counting system specifically for ^{129}I counting, even with the standard setup we can detect 0.004 Bq in 5 minutes. Work is continuing on studies of natural and spiked groundwater using both ^{125}I and ^{129}I.

(H. H. Ross and C. Stockton)*

---

*STRIVE participant, ACD, 1989

Radiochemistry Course at the Savannah River Site

In the spring, a nuclear and radiochemistry course was conducted at the Savannah River Site, South Carolina. The presentation was carried out over a seven week period and consisted of 30 hours of lectures, problem sets for homework, and a final exam. Lectures were at the graduate level.

Course content covered a broad spectrum of topics in nuclear and radiochemical technology; special emphasis, however, was placed on nuclide detectors and measurement techniques, nuclear instrumentation, and radio-analytical concerns. Also, specific questions were addressed to meet the needs of the course attendees. Sixteen SRS participants were involved in the class; these were primarily chemists but also included were several engineers of various disciplines.

(H. H. Ross)

Photon Scattering Effects in Heterogeneous Scintillator Systems

Flow-cell scintillation detectors are used extensively for monitoring alpha- and beta-emitting nuclides in flowing aqueous or organic streams. Major applications of such cells include liquid chromatography detectors, in-line process monitors, and a variety of environmental measurement and control devices. For low-energy emitters, two quite different approaches are used: the heterogeneous and the homogeneous flow-cell. Both, however, use a scintillation process.

Heterogeneous detector cells are characterized by contacting the flowing liquid to be measured with a solid phase scintillator, most often in powder form. Such a flow-cell must fulfill certain physical requirements for efficient operation. Obviously, detection geometry must be high in relation to the energy of the nuclide(s) to be measured. Powdered scintillator detector cells exhibit deficiencies that are characteristic of their design. For example, radiation generated by weak emitters degrades significantly in its passage from the sample liquid phase to the solid fluor. If the sample absorption path length is sufficiently large, and the radiation energy sufficiently low, total absorption takes place and the event is lost to the system. Attempts to use even finer particles to improve the geometry have not improved detection efficiency as expected, and this suggests that a factor other than geometry has a critical influence on cell response. We have completed an experimental study with scintillating plastic beads to correlate the detection efficiency of heterogeneous cells with both particle size and photon scattering parameters.

Monte Carlo computer simulations carried out for heterogeneous flow-cell radiation detectors fabricated with spherical scintillator beads show the geometric response functions for alpha and beta emissions to be somewhat different. For alpha radiation, the computed response is flat up to a bead radius of about 40 microns and then drops off significantly. This result implies that particles smaller than 40 microns probably will not materially improve alpha detection efficiency in practical implementations. The experimental data observed with alphas from ^{241}Am support the shape of the observed simulation function and confirm the idea that ultra-small particles are not needed for good alpha response. The overall maximum pulse-height and spectral resolution (but not counting efficiency) exceed those obtained with a typical homogeneous cocktail for aqueous samples.

Conversely, in beta counting the ^{14}C response functions (computed and experimental) show a peak in the detection efficiency-bead radius curve. On one side of the peak, geometry is the controlling factor; on the other side (smaller particle size), photon scatter determines the response. Thus, experimental data demonstrate that significant photon scattering occurs with small particle scintillators and is an extremely important limitation in heterogeneous cells. Under the conditions investigated, these cells may be 3-4 times more sensitive to photon scatter and absorption than to geometry. The conclusion is clear that the development of high-sensitivity heterogeneous flow-cell detectors may ultimately be determined more by the optical rather than physical properties of the scintillator cell. This work was reported at the International Conference on New Trends in Liquid Scintillation Counting and Organic Scintillators and will appear in the proceedings.

(H. H. Ross)

2. RADIOACTIVE MATERIALS ANALYSIS

J. R. Stokely

The Radioactive Materials Analysis Section performs radiochemical and neutron activation analysis, chemical and instrumental analysis of radioactive materials, and special developmental projects for a large number of Laboratory and DOE programs and a few non-DOE governmental agencies and private corporations. The section provides major support to Laboratory environmental monitoring, waste operations, and waste and environmental remediation efforts. Applied R&D and special projects make up about 25% of the section's activities.

The section has continued its heavy involvement in projects to characterize mixed radioactive/hazardous wastes stored in approximately 40 tanks at ORNL. Characterization of the waste is required to establish the regulatory status of the tanks and to aid in the design of processes for disposal or fixation of the waste. A large number (35-40) of chemical analyses and physical properties measurements are made on the waste providing a fairly detailed knowledge of the waste composition and properties. This work has utilized the capabilities, expertise, and personnel of several groups in the division.

Analyses for low-levels of radionuclides in environmental materials is a major involvement for the section. This work consists of both routine analysis to monitor for radionuclides in soil, water, vegetation, fish, and air in the vicinity of the DOE's Oak Ridge facilities and special projects to identify and measure uptake and retention of radionuclides by wild animals on the Oak Ridge reservation. Each fall for the past few years, the section has provided field measurement of radionuclides in deer taken during annual hunts on the Oak Ridge Wildlife Management Area. These measurements are made to prevent release of contaminated deer to hunters. This year, similar assistance was provided to the DOE Paducah Gaseous Diffusion Plant in field and laboratory monitoring of radionuclides in deer taken on managed hunts near the Paducah plant.

Neutron activation analysis (NAA) service and R&D work has been curtailed for the past three years because of the reactor shutdowns. Startup of the High Flux Isotopes Reactor is expected soon, which will allow resumption of our work in this area. A new very high-flux reactor (Advanced Neutron Source) is presently being designed at ORNL with projected startup in the late 1990s. Six irradiation facilities are proposed for the reactor for NAA work including conventional pneumatic irradiation tubes, a neutron beam for prompt gamma analysis, and a beam tube for cold neutron activation analysis. When built, the new reactor will give us an opportunity to develop one of the best NAA facilities in the world providing unique capabilities for some types of analyses.

Upgrading of analytical and radiochemical capabilities is a continuing activity within the section. Over the past year, we have continued to improve our service operations by addition of new instrumentation and procedures. ICP and AA spectrometry instruments located in highly radioactive containment hoods are in full operation now.

A total organic carbon analyzer has been set up for radioactive samples. A modern liquid scintillation counting system is being placed in service along with two additional high purity germanium detectors for gamma-ray spectrometry. The section is actively involved in upgrading laboratory, operating, and QA procedures and in improving training of personnel to meet current standards.

LOW-LEVEL RADIOCHEMICAL ANALYSIS

J. W. Wade

The Low Level Radiochemical Analysis Group provides analytical support and services for several divisions and programs at ORNL. During the past year, we analyzed over 6,800 samples and provided over 22,000 analytical measurements. With the completion of work on the Idaho site for the DOE Environmental Survey, our involvement with that program came to an end. The survey demanded a great deal of our time over the past year, and we will continue to feel its impact for years to come. Many SOP's, procedures, and other documentation that were required by the survey are applicable to other work that we do.

We analyzed over 400 samples of grass, soil, fish, air filters, and water in support of environmental monitoring programs here at ORNL. Over 2,000 analyses were performed on these samples including isotopic uranium, thorium, and plutonium; total radioactive strontium; gross alpha and beta; total radium; and several gamma emitting radionuclides. There was a 20 percent increase this year in the number of grass and soil samples and a 10-fold increase in the number of air filter samples. We provided similar analytical support to Paducah for their Environmental Monitoring Group's annual report. Samples analyzed included vegetation, fruits and vegetables, small animals, deer, fish, and water. Radionuclides that were determined in these materials included isotopic uranium and plutonium, ^{237}Np and ^{99}Tc.

The Department of Environmental Compliance at ORNL continued with routine sampling of monitoring wells during the past year. The high level of quality assurance required is complicated by low detection limits. Some of the monitoring wells are located near the perimeter of ORNL burial grounds, and the data we provide monitor possible movement of radionuclides from the burial grounds to the groundwater system. Most wells have been relatively free of radionuclide contamination, but we have seen a few with elevated levels of tritium and ^{90}Sr. All wells will be sampled quarterly for one year; thereafter, they will be sampled annually unless radioactivity above background is detected. We expect the sample load to increase approximately two fold during the next year as new wells are installed.

We completed a software package that interacts between IBM PC's and Mettler AE163 analytical balances. The program is menu driven and allows either planchettes or petri dishes to be weighed. The program saves valuable time and eliminates calculational errors.

Most of our instrumentation has functioned very well during the past year. One of our older germanium detectors failed; a replacement was ordered for delivery in late 1989. We are in the process of upgrading our muffle furnaces with new microprocessor controlled units. Our current furnaces are approximately 10 years old and nearing the end of their useful life. The new furnaces are smaller, and will fit in a regular hood without modification to either the furnace or the hood.

(L. D. Bible, C. R. Cooper, J. S. Delashmitt, P. S. Gouge, C. R. Granger, C. M. Johnson, R. D. Johnson, S. H. Prestwood, L. C. Tabor, N. A. Teasley, J. W. Wade)

Status Report on AnaLIS

Backlog and report batch jobs were modified to use a different method of gathering and sorting data. The change made a dramatic decrease in CPU time charges for the operation of the 8300 VAX. A total time reduction of 83% has been achieved.

All results for EPA semivolatile and volatile analyses may now be electronically transferred into AnaLIS using programs which read an ASCII file of the EPA CLP-type form that is created by the HP computers in the Organic Analysis Laboratory. These programs have greatly reduced the time required for reporting data for volatile and semivolatile constituents and eliminated the possibility of transcription errors. Reporting time has been reduced by approximately 96%.

The PURCHASE-REQUISITION Database is now being fully utilized and is available for use by anyone in the division. A previous purchase requisition may easily be called up for viewing by any of a number of key fields. All purchase requisitions are now entered into AnaLIS as they are created. AnaLIS prints the purchase requisition onto forms which are then submitted to Purchasing.

The number of ACD customers wanting electronic transfer of their completed data continues to increase. Programs are run approximately 20 times each night, electronically transferring customers' data.

(N. A. Teasley, J. W. Wade)

TRANSURANIUM ANALYTICAL LABORATORY

J. M. Keller

The Transuranium Analytical Laboratory (TAL) 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 the Waste Operations Department (WO) of the Environmental and Health Protection Division (EHPD). In addition, the group has provided analytical support to the Remedial Action Program (RAP) within EHPD and the Waste Tank Characterization Program within CTD. More than 11,000 samples have been received by the TAL group with approximately 34,000 analytical determinations completed during 1989. About 94% of this work was in support of EHPD programs.

The TAL QA program has been completed and accepted by the ORNL Quality Department as a QA Plan. The program is based on the requirements of ANSI/ASME Nuclear Quality Assurance Standard (NQA-1). When fully implemented, the program will provide for quality assurance within TAL that complies with NQA-1. Not all of the 18 elements listed as requirements in NQA-1 apply to TAL. The TAL program is based on nine of the requirements which represent a combination of most of the 18 elements listed. These elements are: (1) organization; (2) training;

(3) design control; (4) instructions, procedures, and drawings; (5) document control; (6) control of nonconforming items; (10) QA and laboratory records; (11) computer software; and (12) other operations (e.g., housekeeping). Of the twenty SOP's required by the QA Program, sixteen have been completed.

The TAL group is now engaged in a formal, documented training program for all laboratory personnel. Shift personnel who work in the TAL group are required by the group QA program to successfully complete three phases of training; this includes facility, generic, and occupational on-the-job-training. The facility training is provided by CTD and includes written examinations on specific subjects relating to Building 7920 such as building layout, safety equipment, HP instrumentation, and radiation safety. The generic training is provided by Industrial Hygiene and Environmental Safety personnel and also includes written examinations on safety and waste related subjects. The occupational training is provided by ACD personnel and includes discussion of written procedures, SOP's and SAM's, demonstration of techniques used in all phases of the laboratory operation, demonstration of specific procedures and methods, and documentation of trainee proficiency using written examinations.

Due to new requirements, the TAL must restructure the current Training Program to satisfy DOE Order 5480.18, *Accreditation of Performance-Based Training for Nuclear Facilities*, (11-01-89). In an ORNL review REDC and HFIR were identified as the two ORNL facilities required to have an accredited training program (ATP) which follows DOE specifications. Since the TAL group operates within the REDC facility we must structure our training to meet the DOE requirements. Based upon a review of REDC/TAL training program, done in November, we expect the current TAL training program to satisfy some of the new requirements.

The DOE ATP requirements include a highly structured and formalized training plan with extensive documentation that covers job descriptions, job entry requirements, lesson objectives, lesson plans, and testing. In addition, the training instructors must be DOE certified. Based upon current information, we will have about three years to implement the new training program.

Radiochemical analytical support for the RAP was continued on the inactive liquid waste tanks. Also, similar work has continued during this year for the Waste Characterization Task within CTD on the active waste tanks. It is anticipated that both projects will continue into the next calendar year. We will provide analyses that include gross alpha and beta determinations, actinide identification by alpha spectrometry, gamma-ray spectrometry for the fission products and other gamma emitters, ^{90}Sr determination, pH, and the alkalinity determination for hydroxide, carbonate, and bicarbonate content.

(J. L. Botts, J. M. Peele, K. O. Jeter, D. L. Dihel, C. Cook, R. A. Jones, R. T. Pack, R. F. Peacher, L. C. Tabor, D. A. Caquelin, B. K. Larkins, J. E. Sutherland, C. S. White)

Instrumentation Upgrades

The TAL is upgrading computer software and counting instrumentation to reflect technology advances and group needs. Quality control (QC) software from Nuclear Data was implemented this year to monitor all counting room measurements and provide QC plots each week. An old 8% efficient Ge(Li) detector was replaced with a new Tennelec 25% efficient high purity germanium (HPGe) detector in September. This now gives the

TAL two 25% efficient HPGe detectors, which are mostly used for tank farm samples received from ORNL waste operations. In addition, the electronic components (e.g., amplifiers, ADC's, etc.) for these detectors and all other counting systems are being evaluated and upgraded as well.

The TAL is also upgrading its gas proportional counters. Our high-level alpha counting systems, which consist of Nuclear Measurements Corporation (NMC) shielded gas proportional counters, were upgraded with new decade scalers and windowless detector assemblies. We also plan to upgrade our low-level counting system to a Tennelec low-background LB-4000 gas proportional counter when funding becomes available. The LB-4000 is a computer controlled, multi-detector system which will fill a critical need for the TAL by providing the capacity to handle the increasing sample load from waste operations.

Tests with a surface barrier detector were conducted to determine if dependable qualitative and quantitative analyses of alpha emitters could be obtained for REDC process samples. The Tennelec TC-256 Alpha Spectrometer, with a 1000 mm^2 surface barrier detector, was capable of giving accurate and consistent alpha counting results with standard alpha plates. Further tests on samples that more closely represent those analyzed during a TRU campaign will be completed on a new alpha spectrometry system we are currently placing in operation. The new system will consist of several TC-256 alpha spectrometers interfaced to the ND-9900 multichannel analyzer system. A new alpha spectrometry software package from Nuclear Data will be used for spectral analysis. In addition, an Alcatel high speed vacuum pump was installed during August to speed-up the alpha counting process and to provide consistent low pressures suitable for alpha spectrometer operation.

(J. M. Keller, J. M. Peele, K. O. Jeter)

Special Studies

Analytical support for the Mark-42 Assembly Process flowsheet development is currently in progress. The development of a flow sheet to ultimately obtain pure ^{243}Am from the Mark-42 assemblies from the Savannah River Site is a major project for REDC. TAL will provide most of the analytical support for this project. Several other groups within ACD will also be involved. Currently TAL has analyzed approximately 70 samples for ^{241}Am and ^{244}Cm from a series of ion exchange column separations that were made in the hot cells at REDC. In addition, TAL personnel were involved with the initial development work for the hot cell column separation; this work has now been taken over by REDC personnel. In addition to the Am-Cm separation studies, the TAL group has also provided analytical support for plutonium extraction studies, which is a different aspect of Mark-42 flow sheet development project. TAL sample load should increase dramatically with the continued flow sheet development followed by actual processing of the Mark-42 assemblies. 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.

Analytical support was also provided for several REDC special projects. Test specimens from

REDC were irradiated in the FFTF reactor at Hanford, Washington to determine the feasibility of actinide production from this reactor. In support of these tests, TAL has prepared numerous samples for mass spectrometry analysis. Each sample was for a specific actinide and contained not more than 5 nanograms of material per sample. A special effort was made to obtain maximum adsorption on the resin beads and to avoid cross contamination. Another special project supported by the TAL group involved the determination of ^{198}Au. The ^{198}Au content, as a measure of the neutron flux, was determined by gamma spectroscopy on a series of ^{252}Cf irradiated gold foil samples. These tests are part of a study of ^{252}Cf as a treatment for malignant brain tumors.

The TAL group has also provided analytical support for the testing of coating materials. The objective here was to determine the decontamination efficiency of various coating materials, usually paint, to be employed at nuclear reactor facilities. Prepared specimens, either steel panels or concrete blocks, were received from prospective vendors of these coating materials. These specimens were contaminated with a tracer solution of near equal amounts of ^{137}Cs and ^{60}Co. The initial contamination was measured by gamma spectroscopy. The relative gamma activity was then measured after each of three decontamination steps. The decontamination steps consisted of 10 minute immersions with stirring; first in water, then in an acid solution of oxalic acid, sodium fluoride, and hydrogen peroxide, and finally in the same acid solution at 90°C. If 90% or more of the gamma activity were removed from the test specimens the decontamination characteristics of the coating material was considered to be excellent. During the past year, 60 coated specimens were tested by the TAL facility.

(J. L. Botts, J. M. Peele, K. O. Jeter, D. L. Dihel, C. Cook, R. A. Jones, R. T. Pack, R. F. Peacher, L. C. Tabor, D. A. Caquelin, B. K. Larkins, J. E. Sutherland, C. S. White)

INORGANIC AND PHYSICAL ANALYSIS

J. L. Botts

The Inorganic and Physical Analysis Group (IPA) provides analysis of intermediate and high-level radioactive materials that must utilize glovebox or hot cell procedures in the High Radiation Level Analytical Laboratory (HRLAL). During this period, the group processed approximately 2,000 samples and performed some 5,000 analyses, which is about the same level of productivity as for the 1988 report period.

Radioactive Waste Characterization

Several projects are underway to characterize mixed radioactive/hazardous chemical waste at ORNL. These characterizations include chemical, physical, and radiochemical measurements necessary to classify the waste and to evaluate methods for treatment and disposal. The goal here is to provide data necessary to meet both regulatory and engineering waste treatability requirements.

A project to characterize waste in approximately 25 inactive tanks at ORNL was essentially completed this year, and a report was published describing this work$^{(1)}$. These inactive tanks contained low-level waste that was collected from the late 1940's to the early 1970's and varied in composition from contaminated rainwater to complex mixtures containing aqueous, organic, and sludge phases. Where they applied, EPA and Contract Laboratory Program (CLP) methods were used. The characterization of material in active tanks began this year for waste collected since the early 1970's. This waste is typically 3-5 M in nitrate with a pH of 10-13, with the major radionuclides being ^{90}Sr and ^{137}Cs. The sludge phase is high in alpha activity from the uranium, plutonium, americium, and curium which has precipitated. Analytical support for stored waste characterization has been in progress throughout the year and has involved numerous groups within the division. The main portion of the work, organization, sample preparation, distribution, etc., has been done by the IPA group. The analytical characterization has included radiochemical and physical measurements, spark source mass spectrometry, anion analysis, metal analysis by ICP/AA and organic analysis.

(J. L. Botts, C. J. Baggett, R. N. Ceo, C. Cook, Jr., M. T. Davis, D. L. Dihel, H. J. Hall, L. R. Hall, M. G. McClung)

Decontamination of Hot-Cell Facilities

HRLAL personnel are involved in the decontamination of the Building 3019B hot cell facility in preparation for final decommissioning of the facility. This work is supported by the Remedial Action Program as part of the plan to decommission all surplus ORNL facilities. The operating area and the cell access area (behind the cells) have been cleaned and cleared of all equipment. Solid waste removal from the cells has been initiated to reach the point where a commercial contractor can implement the final decontamination prior to decommissioning the facility.

In addition to clean up activities in Building 3019B, a procedure has been written and approved to remove the accumulated radioactive waste from the HRLAL storage cell. No high-level radioactive waste has been removed from the facility in a number of years due to changes in waste disposal methods at the Laboratory.

(C. Cook, H. J. Hall, J. L. Botts)

Upgrade of Capabilities

The group has continued to maintain and develop analytical capabilities to meet the needs of the various waste-related programs. The Perkin-Elmer Model 6500 Inductively Coupled Plasma Spectrometer and the Perkin-Elmer Model 5100 atomic absorption spectrometer continued to be used for elemental determinations on radioactive samples. These systems primarily support the characterization of the mixed radioactive waste samples and other samples requiring cation analysis. These systems were also used in determining the failure mechanism for a leaking capsule containing ^{137}CsCl retrieved from the storage pool at the Radiation Services, Inc. facility in Decatur, Georgia. The analysis of intermetallic alloys containing neptunium and curium was made to verify their mole ratios. Alloys of ^{248}Cm and barium were also analyzed for barium.

---

(1) *Autrey, J. W.; Costanzo, D. A.; Griest, W. H.; Kaiser, L. L.; Keller, J. M.; Nix, C. E.; Tomkins, B. A.; Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL, ORNL/RAP-53, 1989.*

A number of routine IPA group operations have been improved to provide a more efficient and state-of-the-art operation. All weighing operations have been modified and improved by using a Mettler AT250 balance interfaced to a PC. A microwave digestion and dissolution system has been installed to be used primarily to dissolve sludge samples from the various waste tanks. The fluorimetric uranium method has been improved by replacing the old conventional flame fusion equipment with a programmable muffle furnace. A new Dohrmann high temperature total carbon analyzer was purchased and has been put into operation.

An Ethernet II communications network is being installed in the HRLAL complex. A central PC is being set up to receive raw data from all the PC-based instruments within the building. At this central point, the data are reviewed before transmitting the final results to AnaLIS.

All QA/QC related work within the HRLAL complex is being upgraded. Facility group QA plans are now in draft form and into the review process. Qualification cards and lesson plans for a comprehensive group training program have been developed. The program is now being put into operation. SOPs are being written for normal routine operations and all procedures and methods are being reviewed and revised.

The radiochemical capability at HRLAL has been improved by the acquisition of new instrumentation and improved documentation and QA procedures. A new software package has been acquired from Nuclear Data Corp. for alpha spectrometry which includes peak search, calibration, and nuclide identification. A new Packard liquid scintillation spectrometer containing a multichannel analyzer, enhanced data manipulation, and PC control has been acquired. The new instrument will be interfaced into the new Ethernet system for data transfer.

(C. J. Baggett, R. N. Ceo, J. L. Botts, D. L. Dihel)

Support to Consolidated Fuel Recycle Program

A special analytical chemistry laboratory located in Building 7602 continues to provide services for process and engineering R&D studies at the 7600 Fuel Recycle facility. This effort is associated with the Consolidated Fuel Recycle Program (CFRP). The laboratory provides support for continuous processing campaigns to develop technology for reprocessing breeder fuel. Chemical analysis and physical measurements are performed as well as study and testing of prototype equipment developed for this processing of the uranium/TBP/nitric acid system. Throughout the year over 1000 analyses were performed on some 400 samples from this program. The laboratory is now undergoing a cleanup and modernization campaign.

(M. T. Davis, J. L. Botts)

RADIOCHEMICAL AND ACTIVATION ANALYSIS

J. F. Emery

The Radiochemical and Activation Analysis Group (RAA) provides general neutron activation analysis (NAA) services, radioisotopic assays, gamma-ray spectrometry services, oxygen analysis by 14-MeV NAA, and general technical assistance for projects for a number of Laboratory and WFO organizations. Because of the continued shutdown of the HFIR, no reactor NAA service work could be performed this year. In addition, special requests for radionuclide analysis by gamma-ray spectrometry services have diminished to a low level. Demand for oxygen analysis by 14-MeV NAA has continued at about the same level as in the past. A number of developmental projects have been performed by the group to support ORNL and WFO programs. We have provided radon emanation measurements on concrete and concrete components for the U. S. Navy, have continued a project to determine cobalt and ^{60}Co in steel from Hiroshima, Japan, have been involved in several projects investigating radionuclides in wildlife on DOE reservations in Oak Ridge and at Paducah, Kentucky, and have been involved in planning for analytical chemistry facilities at the Advanced Neutron Source (ANS).

Radiological Survey of Canada Geese

The population of resident Canada Geese on the Oak Ridge Reservation (ORR) has increased over a period of several years. In order to plan for hunting season and locations, the Environmental Sciences Division in cooperation with the Tennessee Wildlife Resources Agency conducted extensive tagging of the geese at six locations during mid-June to determine the movement of the geese. After capture, the geese were tagged with standard leg bands and loose-fitting throat collars that are visible with binoculars at some distance. Several hundred geese were tagged and collared during this study.

A similar round-up in 1988 was conducted, but throat collars were not used. Twenty-six selected geese from the 1988 round-up were assayed in a whole-body counter containing a 15- x 15-cm NaI detector housed in a massive lead shield. The detection limit for ^{137}Cs in this counter was determined to be approximately 0.04 Bq/g. A similar program of radiological measurements was performed on 8-10 birds from each capture location duirng the 1989 round-ups. Thus, 52 geese from ORGDP, Clark Center Park, CARL, Solway Park, and the ORNL Swan Pond were assayed. The gamma-ray spectrum from each whole-body count was examined for the presence of gamma-emitting radionuclides. A special search was concentrated on the photopeak region where ^{137}Cs would be found. None of the 52 geese from the 1989 round-up or the 26 from the 1988 collection yielded ^{137}Cs whole-body concentrations exceeding the detection limit of 0.04 Bq/g. These measurements indicate that the off-site transport of contamination from ORNL is of low probability.

An entire flock of thirteen geese from the ORNL Swan Pond were collared and assayed in mid-June. The birds were released at the capture location following the measurements. A week or two following the mid-June round-up, the collared geese (Swan Pond) along with an equal number of un-tagged birds were observed inside the main ORNL enclosure. Plans were initiated to capture the entire flock for subsequent measurements. Three weeks after the initial capture at the Swan Pond, twenty-one geese including eleven that were collared earlier were captured near the aeration pond of the Sewage Treatment Facility. All of the birds showed measurable uptake of ^{137}Cs, but the concentrations in the un-tagged geese were only 1/3 to 1/2 those of the eleven collared ones that had shown no ^{137}Cs three weeks earlier. This indicates that the "new" birds joined the Swan Pond flock some time after the Swan Pond birds entered the Laboratory. Several of the geese containing higher levels of ^{137}Cs were sacrificed for subsequent laboratory measurements by Environmental Sciences Division personnel. This latter collection shows that there is a potential for off-site transport of radionuclides by Canada Geese if such birds are allowed to reside within the ORNL enclosure for any appreciable time span.

(J. S. Eldridge)

Radiological and Chemical Baseline Surveys of Deer from West Kentucky State Wildlife Management Area (PGDP)

Deer hunts near the Paducah Gaseous Diffusion Plant (PGDP) have been restricted to property included in the West Kentucky State Wildlife Management Area. For several reasons including the need to lessen deer-vehicle collisions, land adjacent to the PGDP will be opened to hunters during the 1989 season. Because of the potential for off-site transport of radiological and chemical contaminants by the resident deer, a survey of animals collected from the new hunting area is being conducted. We were asked to provide assistance in sample collection and analysis for this program because of the four-year experience at ORNL in conducting radiological surveys for the local deer hunts.

Deer were collected as part of an abomasum parasite study in the PGDP herd. The sampling locations were chosen so as to provide maximum probability of detecting any adverse contamination conditions. We provided on-site assistance with the organ collection at the time of sacrifice when the stomachs were removed for the parasite study. Twelve deer were sampled in a single evening and night in mid-August. Following the field sampling expedition, samples of liver, muscle, fat, hair, thyroid, and bone from each animal were brought to ORNL for radiological and chemical characterization. In addition to typical fallout radionuclides, the PGDP herd may contain several specialty nuclides that are found in the vicinity of gaseous diffusion plants (^{99}Tc, ^{237}Np, as well as uranium isotopes). Analyses for these radiological contaminants as well as PCB's and priority metals are being performed in several laboratories within the Analytical Chemistry Division. Subsequent samples from two deer sacrificed at a distance of 40-45 miles from PGDP were obtained so as to provide control information for the Paducah study. Preliminary information showed higher concentrations of fallout nuclides in one of the controls than in the PGDP animals.

(J. S. Eldridge)

An Expert System Training Tool for Gamma-Ray Spectroscopy

In many radiochemical laboratories, aside from the expert analyst, only a few individuals are trained to interpret gamma-ray spectra. The expert most often is responsible for training which is usually informal and places a great deal of emphasis on instruments and their operation. Much of the expert's time can be consumed by the analysis of both routine and complicated spectra. In order to reduce the expert's involvement and to generate a more accessible training process, an expert system is being developed for gamma-ray spectroscopy. This knowledge base is designed to supplement existing computer programs by emphasizing the importance of spectral features such as peak area, peak width, background, and counting statistics. It also attempts to make the user aware of the possible presence of interferences from artifacts such as escape peaks, sum peaks and backscatter. This activity is a prelude to the development of an expert system which will assist in the actual identification of radionuclides in gamma-ray spectra.

(Larry Robinson)

Proposed Analytical Facilities for the Advanced Neutron Source

The Advanced Neutron Source (ANS), presently in its conceptual design stage, is a proposed reactor with a nominal 350 MW power to be cooled with heavy water and to have a small replaceable pressure vessel surrounded by a large heavy water neutron reflector. ORNL is the lead contractor in the ANS design. Although construction on the reactor is not scheduled to begin until 1994, efforts are presently underway to describe in some detail the experimental systems needed by the scientist involved. Currently the reactor is projected to go critical in 1998.

The Analytical Chemistry Division has proposed six experimental facilities in the ANS including a cold neutron beam in the guide hall for capture gamma ray measurements, a cold neutron beam (slant beam tube) for neutron depth profiling studies, three pneumatic tubes for neutron activation analysis, and one gamma irradiation facility for materials studies. The capture gamma ray facility would make use of a curved guide that would transmit neutrons with wavelengths about 0.4 nanometer and have a neutron flux of about 10^{10} neutrons $cm^{-2}s^{-1}$. Each of the pneumatic tubes would be located near the outside of the reflector where the neutron flux is about 5×10^{14} neutrons $cm^{-2}s^{-1}$. One of the pneumatic tubes would have a large diameter and would accept a rabbit with a capacity of about 0.2 liter, thus making it possible to irradiate many samples at one time in the highly uniform flux of the reflector. Laboratory facilities to accommodate 20 persons have also been proposed. These include four radiochemistry laboratories, four counting rooms, an irradiation room that would house sample storage areas and pneumatic tube loading stations in the appropriate shielded cells, a class 100 clean room, a sample preparation room, offices, an equipment storage room, and a resources room with special computer equipment.

A presentation about these facilities was made at our Gatlinburg Conference held October 10-12, 1989, and a special roundtable discussion session was held at the American Nuclear Society Winter Meeting in San Francisco, November 26-30, 1989. The purpose of the roundtable discussion was to hear the ideas of additional scientists from the U. S. and around the world about the plans that we have made for the use of the ANS.

(F. F. Dyer, Larry Robinson, J. F. Emery)

Status of the Californium Cold Neutron Source

A Seed Money Proposal to perform a feasibility study of the Californium Cold Neutron Source (CCNS) has concluded that although the device would most likely yield a cold neutron flux useful to analytical chemists, the overall cost to maintain the CCNS at ORNL would be prohibitive. For example, modifications to TURF and installation of the CCNS there were estimated to cost nearly two million dollars. The grand total for the project was estimated as 6.5 million dollars. These findings as well as other technical information about the proposed experimental system were included in a final report [2].

(L. Robinson, F. F. Dyer)

---

[2] *Alsmiller, R. G.; Henderson, D. L.; Montgomery, G. H., "Final Report on Seed Money Project 3210-036: Feasibility Study for Californium Cold Neutron Source," ORNL/TM-11027, October, 1988.*

Measurement of ^{60}Co in Hiroshima Steel

Analysis of the data, discussed in last year's annual report[3], obtained in measurements of the ^{60}Co in steel specimen from Hiroshima, Japan was completed, and a report describing the findings is being published. This study was prompted by the fact that previously measured ^{60}Co specific activities (dpm/gram) in Hiroshima steel taken from areas of about the same distance from the blast as were these samples, namely 1300 meters, were about 4-5 times larger than activities calculated using neutron transport codes. Close agreement was found between calculated and measured specific activities for the steel specimen from the building at 700 m. It was found, however, that the measured values for the bridge sample at 1300 m were approximately twice the calculated value. It has been concluded that a systematic error exists in the transport calculations for neutrons from the Hiroshima bomb.

Since the work above was completed, another effort was begun to measure ^{60}Co in a reinforcing rod taken from the building at 700 m. This measurement is nearly complete and is being carried out by dissolving the steel sample, which weighed about 290 grams, separating the cobalt and measuring the ^{60}Co as was done on the steel plate from the railing of that building. Previously, Co^{+2} was separated from Fe^{+3} by loading them in 9 N HCl on Dowex-1 anion exchange resin pretreated with 9 N HCl, and eluting the Co^{+2} from the column with 4 N HCl. The Fe^{+3} was then eluted with 0.5 N HCl to clean up the column, and the column was treated again with 9 N HCl to begin another separation. Due to the fact that the resin capacity was rapidly taken up with Fe^{+3}, only about 18 grams of Fe^{+3} could be processed with columns containing 500 grams of resin. This procedure for separating traces of cobalt from large amounts of iron was very laborous and time consuming. In the current work, a process was found to avoid this problem entirely and make it possible to separate the cobalt from 100 to 200 grams of iron in one operation. A paper describing this process is being prepared for publication.

(F. F. Dyer)

---

[3] *Shults, W. D., Analytical Chemistry Division Annual Progress Report for Period Ending December 31, 1988, ORNL-6547, pp. 29-30, 1989.*

3. INORGANIC CHEMISTRY

W. R. Laing

The Inorganic Chemistry Section provides analytical support in areas of classical and instrumental analyses and physical measurements to a variety of ORNL, DOE, NRC, DOD and outside contractor programs. Environmental support was the largest segment of work performed during the year. Every member of the section was involved in the analysis and monitoring of surface and well waters, soils, sediments and environmental materials for toxic metals, cyanides, sulfides, asbestos and other potentially hazardous materials. Effluent monitoring programs which ensure compliance with DOE, EPA and state discharge regulations were the largest single segment of support for the section.

Other important programs to which the section contributed included remedial action studies, toxic metals in groundwater and PCBs in fish, decommissioning of former uranium mines and mills, US Air Force surveys, the Strategic Petroleum Reserve, nuclear coatings and superconductors.

New equipment and facilities included a Zeeman atomic absorption instrument, a sample preparation laboratory for asbestos samples and a renovated laboratory with a self contained heating and ventilating system for an ICP/MS instrument.

Quality assurance emphasis continued with new documentation in the form of QA plans, standard operating procedures and standard analytical methods. External QC programs included EPA performance evaluation and water pollution samples, NPDES studies and proficiency environmental testing samples. Internal QC programs included QC samples related to programs, blind controls and spiked samples.

CHEMICAL AND PHYSICAL ANALYSIS

N. M. Ferguson

The Chemical and Physical Analysis (CAPA) group provides technical support to a multitude of ORNL programs, and to a variety of external organizations including the US Army and Air Force, the Nuclear Regulatory Commission, the Strategic Petroleum Reserve, and the DOE Environmental Survey Program. 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. During this year the CAPA group reported 68,000 analyses.

The Environmental and Health Protection Division continued to generate the largest number of samples.

The ICP lab continued to experience instrument problems with the JY48 polychromator. The spectrometer failed catastrophically on January 20, 1989. The instrument was inoperative from this date until March 10. A service engineer replaced all 45 photomultiplier tubes in the main spectrometer and several phototube socket assemblies. Instability problems continued through March. The polychromator became unstable again in June. After numerous consultations and a service call, the problems were again corrected. During the inoperative period we met all required analysis for state discharge permits by utilizing a commercial laboratory and K-25 ICP facilities.

Support of the DOE Environmental Survey Program continued. The ICP analyses of the Idaho samples were completed and Contract Laboratory Program forms were generated. CAPA sample data were reviewed for the Argonne, Brookhaven, Idaho, and Lawrence Livermore/Sandia sites. Case files and quality control summary reports were prepared for anion and "exotic" (hexavalent chromium, PCB, recoverable oil and grease, total cyanide, total dissolved solids, total uranium) data. Data quality evaluations were made. Also EPA data packages were prepared for these sites. Files for the Rocky Flats site were removed and sent to Idaho Nuclear Engineering Laboratory.

This year we did a complete reevaluation of our asbestos program. More rigorous requirements for asbestos analysis [brought about by the Asbestos Hazard Emergency Response Act (AHERA)] led to improvements in the polarized light microscopy (PLM) and transmission electron microscopy (TEM) laboratories. AHERA was signed into law on October 22, 1986. Accordingly, the EPA promulgated the final rules for asbestos in school buildings by October 17, 1987. These rules are now the only definitive legal guidelines for controlling asbestos-containing materials in buildings. Under the new AHERA rules, analysis of bulk samples is to be done by PLM by laboratories accredited by the National Institute of Standards and Technology (NIST). Phase contrast microscopy (PCM) will be allowed for clearance of small projects and for clearance of some larger projects during phase-in of the TEM requirements. The TEM requirements began on October 7, 1989 and will be phased in for a period of one year. Personnel have been trained in the PLM technique for determining asbestos in bulk materials such as tiles, insulations, and soils. We have installed a small Class I High Efficiency Particulate Air Filter (HEPA) hood for the handling of bulk samples. The standard operating procedure for the "Determination of Asbestos in Bulk Materials by Polarized Light Microscopy" has been written. A new refractometer has been placed in operation for verification of the refractive indices (RI) of standard RI liquids. This will meet the requirements of the National Voluntary Laboratory Accreditation Program (NVLAP).

The major thrust of our improvements has been focused on our TEM sample preparation area. Modifications to Room E-7 (4500N) were made so that TEM sample preparations could be made according to the EPA-NVLAP guidelines. New lab benches and tops have been installed, a sink has been built, water lines have been connected and an ultra pure water supply (Milli-Q) has been connected. Two class 100 HEPA hoods have been installed and two fume hoods are in place. A new plasma-asher has been installed. Personnel have also been trained in TEM asbestos analysis. A second standard operating procedure, the "Determination of Asbestos in Water", has been written.

During this period we refurbished the mercury purification laboratory. It was upgraded to ensure improved environmental and safety conditions. The glass extraction columns were rebuilt using thicker wall glass tubes, and a design change was made in the joint connection. The electrical system was updated so the equipment could be run from one position. The existing pumps were refurbished and all lines were replaced, along with two pumps. One spare pump was purchased. The entire area was cleaned and all trash and waste material were removed. Use of shoe covers and gloves for operator protection is now standard procedure. Shelves were fabricated and installed to get all equipment off the floor, which greatly eased cleanup and organization of the work area. The control system for the tube furnaces was improved with microprocessor control.

A laser fluorometer was evaluated for the measurement of uranium in aqueous samples with good results. The instrument was calibrated from 0.006 to 600 ng/ml. Precision and spike recovery of "clean" water samples were satisfactory with an analysis time of approximately five minutes.

Over 500 samples of fish tissue were analyzed for PCB's and lipids. About mid-year, PCB contamination was found in our procedural blanks. After examination of the method, three problem areas were found. Modifications of the procedure eliminated the source of the contamination. CAPA participated in two PCB round robin tests with TVA and the Tennessee State Environmental Laboratory and measured 1254 and 1260 PCB isomers and lipids for both programs. There was excellent agreement between TVA and CAPA results, but the Tennessee State Environmental Laboratory results were extremely low.

The Extraction Procedure (EP) Toxicity Test Method is designed to simulate the leaching which a waste will undergo if disposed of in a sanitary landfill. The waste (liquid, solid, and multi-phase samples) is extracted for 24-28 hours with distilled water maintained at a pH of 5 using acetic acid. The extract obtained from the EP leach is analyzed by ICP to determine whether any of the thresholds established for As, Ba, Cd, Cr, Pb, Se, or Ag have been exceeded. CAPA assumed responsibility for these extractions during this period.

(D. J. Batiste, S. J. Bobrowski, P. V. Ditavong, J. H. Hackney, R. L. Holmes, C. S. MacDougall, N. E. Owens, B. Philpot, J. C. Price, W. F. Rogers, S. E. Schow, S. I. Simms, J. K. Thompson, K. I. Webb, K. S. Whaley, C. Yandell)

ENVIRONMENTAL ANALYTICAL LABORATORY

T. B. Shope

The Environmental Analytical Laboratory (EAL) provided analytical support for the Environmental Sciences Division (ESD) primarily, but also had a significant amount of work from other ORNL divisions. Approximately 45,000 analytical results were reported during this period.

Compliance samples continued to generate a substantial portion of our workload. Weekly, bi-weekly, and monthly effluent samples were analyzed to demonstrate compliance with National Pollution and Discharge Elimination System (NPDES) permits. Groundwater samples were analyzed quarterly to meet Resource Conservation and Recovery Act (RCRA) requirements. Special project samples, such as those analyzed for the United States Army Toxic and Hazardous Materials Agency (USATHAMA), met project-specific compliance needs. In addition, blood, urine, and air filter samples were analyzed for Industrial Hygiene groups. Technical support for the DOE environmental survey was completed during this report period; however, we continued to analyze quarterly performance evaluation samples from EPA to maintain active Contract Laboratory Program (CLP) qualification. Instrument detection limits were determined for As, Ag, Hg, K, Na, Pb, Se and Tl on a quarterly basis. The laboratory also analyzed several samples as part of the Water Supply Laboratory Performance Evaluation Study 25 (WSO25). EAL used a cold vapor atomic absorption method to determine mercury, flame atomic absorption methods to determine sodium and potassium, and graphite furnace methods to determine other metals.

In the ACD annual report for 1987 (ORNL 6474), EAL reported the purchase of a Lachat flow injection auto analyzer. During this year, final revisions were made on software programs which enabled direct data transfer from the Lachat instrument to the ACD data management system, AnaLIS. (Hardcopy reports were retained for record storage.) The auto analyzer was used for the routine measurement of NH_3-N, NO_3-N, PO_4-P, Si, total phosphorus and total kjeldahl nitrogen. EAL is in the process of preparing direct data transfer capabilities for other instruments in the laboratory. This capability will be functional during the next report period.

The laboratory purchased a Perkin Elmer 5100 atomic absorption system this year. This instrument is controlled by a laboratory computer and is capable of running for long time periods with little or no analyst supervision. The system was installed in May 1989 and has been in routine use since. Software is being written to provide this instrument with direct data transfer capabilities to the ACD data management system.

EAL has begun the investigation of the use of ion chromatography for the analysis of metal cations. The immediate goal is to be able to determine Na^+, K^+, Ca^{2+} and Mg^{2+} in water samples. Li^+ and NH_4^+, in addition to the four metals listed, can also be determined in a single scan. Long-term interests include the ability to determine transition metals by ion chromatography. Of particular interest is the ability to determine metal ions of different oxidation states. A good example is the determination of Fe^{2+} and Fe^{3+} in a single scan. In addition, EAL has investigated and placed into operation a procedure for regenerating anion columns which doubles column lifetime.

(T. L. Baxter, L. S. Barringer, L. A. Greenman, S. A. MacIntyre, M. L. Moore, S. J. Morton, J. Summers, C. L. Watson)

SPECIAL PROJECTS GROUP

J. H. Stewart, Jr.

The Special Projects Group was established in April 1989 to coordinate interactions between ORNL programs and the ACD. Non-routine unusual analytical requests are now routed through this group, and the appropriate ACD staff is notified. One request was to assist in developing the practice for an on-line continuous CO_2 monitoring and control system for an Environmental Sciences Division study of the greenhouse effects on forestation. This involved analyzing and controlling large volumes of air in 305 x 508 mm environmental chambers containing growing trees. This project was successfully coordinated between ACD, AIRCO (Chattanooga), ESD, and the I&C Division of ORNL.

The new non-radiation waste water treatment plant is being prepared for initial test operation. Assistance was requested to verify the removal of water from sulfuric acid lines prior to their being filled with acid. Special Projects located a humidity meter and a portable heated air line system for purging the water from the lines. The operation was successful and the lines are ready for routine use.

A major effort was expended in writing procurement specifications for the new ACD inductively coupled plasma-mass spectrometer (ICP-MS) analyzer system. The analyzer was acceptance tested for performance prior to shipment to ORNL and was installed in December 1989. An important concern was the quality of the laboratory environment in which the analyzer would be installed. Expert advice was sought, the resulting clean facility information was evaluated and used to upgrade an existing laboratory. The renovated facility will meet all room environmental requirements, be clean, well lighted, and convenient to use.

Interfacing of Analytical Instruments

The ACD continues to be concerned with possible corruption of data resulting from calculation and transcription errors. Wherever possible, therefore, we are implementing ways to eliminate hand calculations and manual data entry into the ACD data management system, AnaLIS. In a previous ACD annual report (ORNL-6547) we reported the development of a program, FIS_PARSE, to assemble and review data from a Lachat, Inc., flow injection spectrometer (FIS) and to store it in AnaLIS.

In its present state of development, FIS_PARSE includes features to process data from its four channels; i.e., from four analyses that may be performed simultaneously. Analyses are presently performed for ammonia, nitrate, phosphate, total N and P, and silicon. To facilitate review and storage, data from several trays of up to 40 vials each from the auto-loader are concatenated to form one file for processing. A search routine was incorporated so that data for a specific customer, data set, sample, element or any other identifier could be located and processed.

The program was designed to uncover faulty sample identification, results that are true outliers, and missing and/or improperly formatted data. The Lachat instrument reports all data on an elemental basis. Some customers prefer their data to reflect a species other than the element or to report only results above some minimum value. Any calculations or data manipulations are performed by the software and needed reference values are taken from tables in the program.

The FIS_PARSE program was written in VMS FORTRAN 77 for the VAX. A version of this program was also written in Quick BASIC (Microsoft, Inc.) to run on IBM PC's or compatible clones under MS-DOS, version 3.3 (Microsoft, Inc.). One implementation of the BASIC program, MERCURY, prepared data from reports for incorporation in AnaLIS from data generated by an acquisition program used with the Milton-Roy, cold-vapor, mercury analyzer described previously (ORNL-6547).

An expanded version of the BASIC program was written for use with a Perkin-Elmer Model 5100 atomic absorption spectrometer (5100 AA) which was installed in mid-year. The spectrometer is operated by an NCR Model 916 (16MHz) via a IEEE 488 buss. Data processing is accomplished by a program which, although following the general pattern of the FIS_PARSE and MERCURY programs, is considerably more complex. The 5100AA instrument is equipped with both flame and graphite furnace sources with Zeeman background correction attachments and can be operated in fully automatic, semi-automatic, or manual modes. Further, different types of elemental line sources are available, and nearly all of the elements can be detected and/or determined. A single sample report may contain data for up to 15 different elements contained in 1000 to 1500 lines of data generated by the instrument.

In order to evaluate the data generated, the reviewer needs perhaps 20 to 30 of the operating parameters displayed for evaluation of their impact on the results. Color coding of the monitor display was used to highlight the more important of these and of those data that change from sample to sample.

For all of the above programs, only an image of the original data is employed in the preparation of the file to be reported to AnaLIS. Backup copies of the original files are made on floppy discs, and hard copy reproductions are also stored. A copy of the original data is sent to the ACD VAX so that supervisory review may be accomplished at any time.

We anticipate that modifications will continue to be made to the present program as new analysis protocols and changes in the ACD data base are implemented. The BASIC program is currently being modified to acquire and process data from a gas chromatograph (Perkin-Elmer, Model Sigma 300) and three Dionix, Inc., ion chromatrographs.

Our work with these interfacing applications leads to the conclusion that a set of data format standards is needed. The customer, not the instrument manufacturer, needs to specify the format compatible with the customer needs. If a set of standard formats were available, the customer could specify at the time of purchase the exact format for his data base requirements and avoid such nearly meaningless specifications as "ASCII output" and the costly process of recovering and re-formatting the data.

(T. R. Mueller)

Electrochemical Investigation Leading to Speciation of Chromium At Trace Levels

The purpose of this work was to identify the conditions under which a representative analysis for the ratio of Cr(VI) to Cr(III) in Cr-containing samples could be obtained. Since the total amounts of both species is expected to be quite low, the method must be sensitive as well as specific. A method using ammonium acetate as a supporting electrolyte was developed for Cr(VI) standards that yielded a method good to 5% relative error at the 50ng/L level (Crosmun and Mueller, Analytica Chimica Acta 75, 199-205, 1975). Present work indicates that the detection limit for Cr(VI) by differential pulse polarography (DPP) may be more than two orders of magnitude lower when optimum conditions for analysis are determined. Also, DPP provides enough resolution between reduction waves for $Cr_2O_7^{-2}$ and CrO_4^{-2} to estimate the ratio of these species as a function of pH.

The electrochemistry of Cr(III) is also quite complicated. Because of the large number of species that appear when complexing agents are present and because ligand exchange is slow, interpretation of polarograms is difficult. In the eight weeks available for this study, we concentrated our efforts on identifying supporting electrolytes that could be used for analysis. The following materials were evaluated for the purpose: NH_4^+/0.2M $(NH_4)_2SO_4$, pH 9.2; NH_4^+/0.05M $(NH_4)_2SO_4$, pH 8.0; Tris[1]/0.01M $(NH_4)_2SO_4$, pH 8.0; HCl; KCl; 0.01M $Na_2B_4O_7$; 0.01M Na acetate. Additional work will be required to select the best medium.

(W. Hussein, T. R. Mueller)*

Analytical Assistance to the DOE Strategic Petroleum Reserve

The ACD has been investigating interlaboratory variability of analytical results from DOE Strategic Petroleum Reserve (SPR) analytical facilities at the request of the SPR Washington DOE office. The major cause was found to be gross inhomogeneity of the "blended" material that had been submitted to the SPR laboratories for analysis. The ACD developed a technique for blending small crude oil samples (100 ml) and demonstrated an analytical standard deviation of 8%. The DOE then requested a technique for blending liter-sized crude oil specimens from five separate SPR sources. Viscosity of these varied from very light to exceedingly thick crudes. The technique used for the small specimens was ineffectual for the liter-sized crudes. A variety of techniques were evaluated, ranging from simple to exotic. The latter included a dual chambered, heated, stirred apparatus which was connected by tubing to a peristaltic pump for continuous mixing. The resulting homogeneities from the several tests were not acceptable. Evaluation of a simpler technique using 70°C heated crude oil in a Waring blender resulted in a homogeneous product that was analyzed with a standard deviation which met the desired 8% goal. The five liter-sized SPR materials have been blended, subsampled, and analyzed for completion of the initial stage of the project. The subsets have been distributed to the National Institute for Petroleum and Energy Research (NIPER), and Sandia National Laboratory for additional testing. Further experimentation to reduce the SPR variabilities is underway.

(C. Feldman and J. H. Stewart, Jr.)

Superconductor Materials Analysis

The discovery of liquid-nitrogen-temperature superconductor materials, such as the $Y_1Ba_2Cu_3$ oxides, has generated much research at ORNL. The ACD has provided highly accurate analyses to assist in determining stoichiometry of the compounds being fabricated and tested by the Metals and Ceramics Division staff. The copper was electrodeposited and measured gravimetrically, the yttrium was double-precipitated and gravimetrically measured as the fluoride, and the barium was determined gravimetrically as the sulfate. The specimen analyses were performed on

---

*Professor of Chemistry, Jackson State University

[1] Tris (hydroxymethyl) aminomethane

10 mg crystals, with precisions of ± 2.1% for Y, ± 0.08% for Ba, and ± 0.08% for Cu.

The ICP scanning monochromator was evaluated as an alternate technique for rapid, low cost analysis of starting materials. The initial results were encouraging; the three elements have been determined at the 1 ppm concentration level with 1% relative standard deviation. Further improvements and modifications of the method are being evaluated. New superconductor materials are now being received, including the bismuth-calcium-copper oxides, and methods for stoichiometric analyses are being tested.

(C. Feldman)

Determination of Fluoride in Aluminum Nitrate Raffinate

Aluminum nitrate is used in liquid-liquid uranium extraction processes to ensure transfer of the uranium from the aqueous phase into the organic extractant. Taking into account the initial cost of the aluminum nitrate and the cost of waste disposal of used salt, there would be a significant economic advantage in recycling and reusing the salt if fluoride from the process did not accumulate in the salt. The ACD method for vapor transport of fluoride from acidified aqueous media as a hexamethyldisiloxane (HMDS) fluoride complex was found to be successful for the process test solutions. These solutions contained percentage quantities of Al and potential complexing agent impurities of Fe, Zr, and Hf. The process solutions were spiked with 100 micrograms of fluoride and the HMDS vapor transport experiment was performed. The fluoride recovery was 96%. A series of process solutions were analyzed using the HMDS technique and showed that the fluoride did not concentrate in the aluminum nitrate salt; thus recycling and reuse of the salt is feasible.

(C. Feldman)

Nuclear Coatings Testing Program

Coatings used within the primary containment of a nuclear power generating plant must be able to withstand exposure to high humidity and cumulative radiation dosage at elevated temperatures. These coatings must also be easily decontaminable and must be of sufficient durability to withstand projected conditions of certain Design Basis Accidents. A coating system must pass three tests in order to qualify: radiation stability, decontaminability, and Design Basis Accident (DBA). ORNL is the only independent facility with capabilities of conducting all three tests. (Irradiations of the specimens are accomplished elsewhere using ^{60}Co sources during the HFIR shutdown.)

An upgrade of our DBA testing apparatus is complete. Automatic monitoring and control of all process parameters is now possible through the use of a Bristol Controller, pneumatically controlled valves, temperature and pressure transmitters, and controller software. The new system includes an IBM/AT computer and a multichannel programmable chart recorder.

At this time, there are about ten utilities and manufacturers under contract for continuing testing at ORNL. We completed extensive testing projects for five companies in 1989.

(D. O. Vick)

4. 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 natural 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 with fluorescence detection, displacement chromatography, and supercritical fluid chromatography are the principle separations methods under development. Research continues to emphasize environmental media and is expanding to include physiological media. Field sampling and direct-sampling mass spectrometry methods have been developed for the rapid determination of organic pollutants in water, soil, wastes, and air. Thermal desorption ion trap mass spectrometry has been shown to be very promising for determining constituents of urine. Progress has also been made in applying our unique analytical capabilities to physical and material sciences problems. Examples include the use of laser ablation Fourier transform mass spectrometry for the generation and analysis of aluminum cluster ions and the use of reverse chromatography to characterize the surface properties of ceramic powders. New or expanded activities are under way in the areas of military propellants, explosives chemicals, environmental tobacco smoke monitoring, and radioactive mixed waste characterization. Our analytical services operation has expanded and is now the largest activity in the section. 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 infra-red 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 primary focus of this group is the development of spectroscopic techniques for the unambiguous identification and quantitation of trace organics in biological and environmental matrices. Trapped ion techniques, including Fourier transform mass spectrometry (FTMS) and ion trap mass spectrometry (ITMS), are the principle tools used for these investigations. Conventional gas chromatography/mass spectrometry (GC/MS), nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy are also employed. The development of new analytical approaches for the unambiguous identification of DNA adducts continues to be a major area of research, including the identification of alkyl and larger adducts, as well as UV-induced photodimers. New approaches for sample introduction and for detection of picomoles of adducted nucleotides and higher molecular weight oligomers are being investigated. This includes direct analysis of these and other biological compounds from chromatographic plates using laser desorption FTMS. Investigations into fundamental processes of laser desorption have led to demonstration of the ability to generate negatively charged clusters containing 3 to 50 aluminum atoms. Examination of the stability and reactivity of the various clusters gave experimental results which supported previously published theoretical calculations. This work demonstrated the ease of forming aluminum metal clusters without an elaborate experimental setup (e.g., molecular beams and cooling bath gases).

New approaches for the prompt analysis of environmental and physiological samples by mass spectrometry have also been developed. A direct thermal desorption ITMS instrument, which was designed and constructed here, was demonstrated to detect less than 50 pg of chemical agent simulants in a total analysis time of less than two minutes. This instrument was shipped to Tooele, Utah and successfully field-tested using actual chemical agents. Trace detection of volatile and semivolatile organics from a wide variety of matrices, including water, soil, air, and physiological media, has been demonstrated using direct sampling ITMS and glow discharge quadrupole mass spectrometry. Numerous special spectroscopic studies using FTMS, GC/MS, NMR and IR were conducted in support of programs in the Organic Chemistry Section, as well as other groups within the Laboratory.

Structural Examination of DNA Adducts Using Fourier Transform Mass Spectrometry

Previous research here has shown that Fourier transform mass spectrometry (FTMS) is applicable to the structural characterization of methyl nucleoside adducts at the picomole level. For example, five isomers of methyl guanosine can be differentiated based on differences observed in the fragmentation of negative ions from these compounds. We have now applied FTMS to the analysis of a variety of other DNA adducts, including ethyl nucleosides, alkyl phosphotriesters as well as polycyclic aromatic hydrocarbon (PAH) adducts. New instrumental methods, such as direct laser desorption of thin layer chromatography (TLC) plates and construction of an external ionization source for the FTMS, have also been addressed.

Laser desorption of ethyl thymidine adducts was found to generate pseudomolecular ions $(M+Na)^+$ and $(M+K)^+$, which could be used to verify the molecular weights of the adducts. In the negative ion spectra, an abundant ion corresponding to elimination of the sugar ring was observed. Collisional dissociation of either positive or negative ions from isomers of ethyl thymidine indicated only one fragment product: elimination of ethylene. Because the adduct was lost in all cases, these isomers could not be differentiated based on fragmentation information alone. Alternate means of differentiating these isomers, such as selective ion-molecule reactions, are currently under investigation.

Alkylation of the phosphate linkage of an oligonucleotide forms a phosphotriester which is another common alkyl DNA adduct, and must be differentiatied from nucleotides containing alkylation of the sugar ring or the nucleic base. Laser desorption of methyl- and ethyl-thymidine phosphotriester dinucleotides generated characteristic negative ions corresponding to cleavage of either the nucleic base (thymine) or the phosphate ester linkage. The collisional dissociation of these negative ions provided detailed structural information, including alkyl phosphate ions, which could be used to verify the site of alkyl attachment. Accurate mass and high resolution measurements were needed in order to separate isobaric ions in several cases, especially for the ethyl phosphotriester.

Detailed structural information for amino-PAH adducts of guanine can also be obtained with this experimental technique. Standards of several C8 amino-PAH guanine adducts synthesized by C.-h. Ho of the Separations and Synthesis Group were examined by FTMS. Laser desorption of these compounds generates negative ions at $(M-H)^-$, which can be further examined by collisional dissociation experiments. The $(M-H)^-$ ions for these compounds fragment to give $(M-NH_3)^-$, $(adduct+CN)^-$, and $(adduct-H)^-$. These fragment ions were sufficient not only to identify the adduct but also to verify the position of attachment, which was C8 for all compounds. This technique was used to characterize the guanine adducts of ortho-toluidine, 8-aminopyrene, beta-aminonaphthalene, para-aminobiphenyl, and 2-aminofluorene. We have extended these studies to include PAH adducts of nucleotides, such as 5-methylchrysene-deoxyguanosine-3'-phosphate and benzo(a)pyrene-deoxyguanosine-3'-phosphate. These two nucleotides adsorb strongly to the stainless steel target used for the laser desorption experiments and require higher laser energies for desorption/-ionization. Since these higher laser energies cause extensive fragmentation, alternate sample surfaces are being examined.

Laser desorption FTMS has been demonstrated to be well suited for the direct detection and identification of compounds on TLC plates. The laser provides high spatial resolution and can be used to ionize compounds directly from TLC plates with virtually no sample preparation. Research has been directed at examining the application of this technique for several different biological compounds and different types of TLC plates. The chromatographic media examined included silica gel and modified (C18, C8) silica gels. Laser desorption of compounds on C18 silica plates gave the best ion signals, whereas compounds were difficult to desorb and ionize from conventional silica plates. These results suggest that the adsorption of the compounds onto the silica stationary phase controls the desorption and ionization process. Detection limits for the C18 plates were found to be in the low nanogram region. The effects of laser power and wavelength may also influence the application of this technique and are under investigation.

An external ionization region is under construction for the FTMS. This externally-pumped vacuum region will allow investigation of alternative ionization techniques, such as fast atom bombardment and ion spray, as well as providing a means to couple chromatography with the FTMS. The vacuum system has been constructed and an electrospray ionization source has been built. The design of the ion optics needed to transport the ions into the FTMS cell is currently being examined.

(R. L. Hettich, M. V. Buchanan, J. C. Dunphy, and E. L. Kerley**)*

Generation and Examination of Aluminum Cluster Anions

There is considerable interest in ionic metal clusters because they may serve as models for studying catalysis and related processes. We have recently demonstrated the generation of aluminum cluster ions (Al_n^- where n=3-50) by laser ablation of a flat aluminum metal target (Figure 4-1). The ions were then trapped and examined in a Fourier transform mass spectrometer (FTMS). The ease of cluster ion formation in this case was quite surprising since no bath gas was present to cool the clusters during formation. The addition of a static pressure of argon did not change the cluster ion distribution, implying that these clusters did not contain substantial internal energy after formation. Cluster ions were observed ranging continuously from Al_3^- (m/z 81) to Al_{50}^- (m/z 1349), with Al_{13}^- (m/z 351) as the most intense ion, as seen in Figure 4-1. The odd-numbered clusters were more abundant than the even-numbered, implying an increased stability (or reduced reactivity) for these odd-numbered species. The intensities of the ions containing more than 13 atoms decreased almost uniformly, except for the ions of Al_{14}^- and Al_{24}^-, which were observed in very low abundance.

The electron affinities of these clusters were obtained by examining charge exchange reactions of the cluster ions. Specifically, each aluminum cluster ion was isolated and allowed to react with either nitrogen dioxide (E.A. = 2.30 eV) or p-benzoquinone (E.A. = 1.89 eV). All clusters for Al_n where n = 4-23 had electron affinities between nitrogen dioxide and p-benzoquinone. Al_3^- will charge exchange with p-benzoquinone and nitrogen dioxide, implying an electron affinity for Al_3 below 1.89 eV. These values were in good agreement with previously published theoretical and experimental results.

The cluster ions Al_n^- for n = 3-13 were collisionally dissociated in order to probe the structures and fragmentation mechanisms of these species. These cluster ions fragmented either by aluminum atom elimination or electron detachment, depending on which process was lower in energy. Cluster anions for n = 4,5,8-13 fragmented by loss of one or more aluminum atoms, whereas clusters of n = 3,6,7 fragmented primarily by electron detachment.

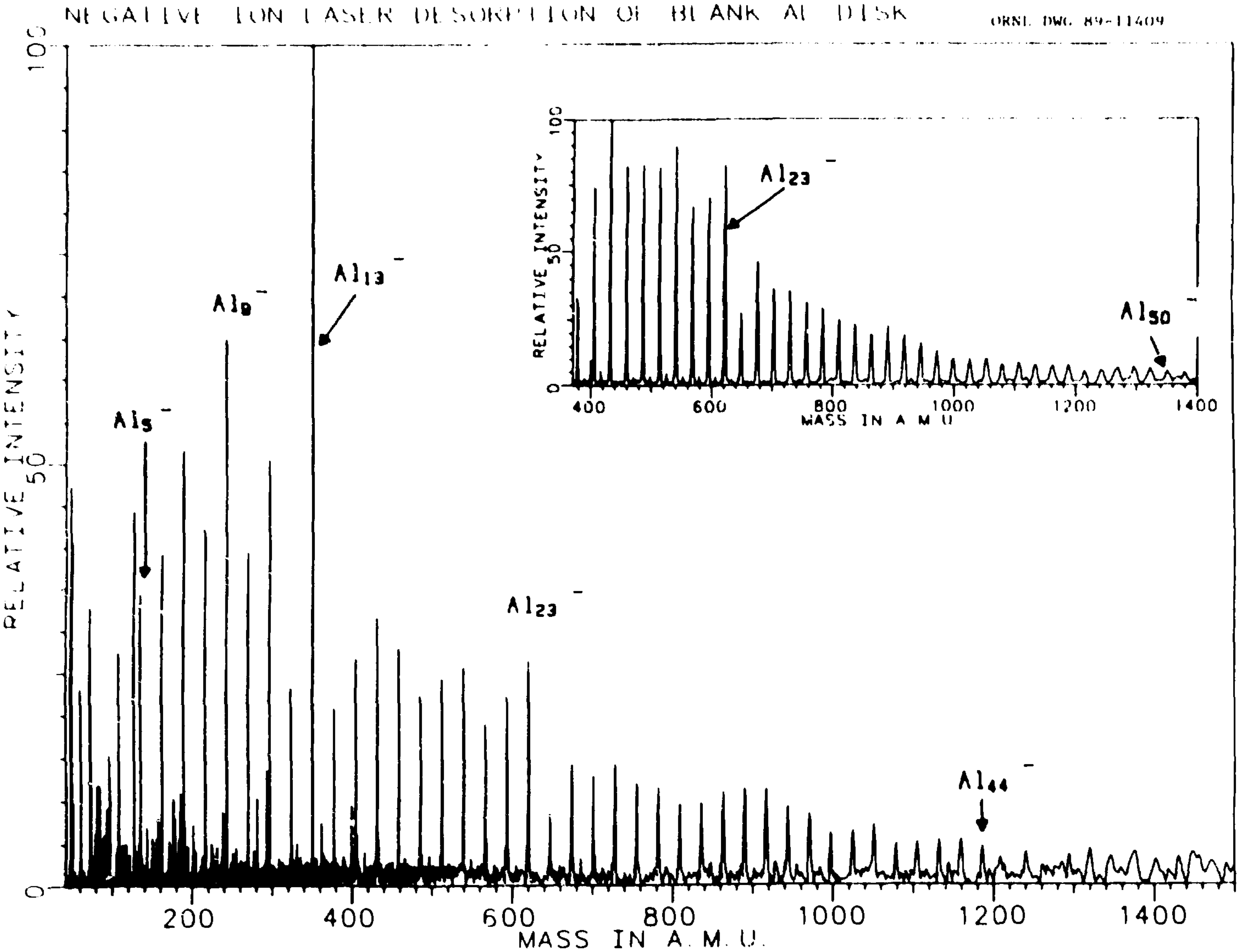
Apart from charge exchange reactions, these cluster ions were unreactive with most small molecules, such as N_2O and CH_4. However, these cluster ions react readily with O_2. Clusters of Al_n^- for n = 3-8 react rapidly with O_2 to generate both AlO^- and AlO_2^-. Clusters containing more than eight aluminum atoms react with O_2 in a size-specific manner. The even-numbered clusters react

---

*ORAU Lab Grad Research Participant - University of Indiana

**ORAU Postdoctoral Research Associate

Figure 4-1


NEGATIVE ION LASER DESORPTION OF BLANK AL DISK
ORNL DWG 89-11409
RELATIVE INTENSITY
100
50
0
MASS IN A. M. U.
200
400
600
800
1000
1200
1400
Al_5^-
Al_9^-
Al_{13}^-
Al_{23}^-
Al_{44}^-
Al_{23}^-
Al_{50}^-

rapidly with O_2 to form the two ionic products mentioned above, whereas the odd-numbered clusters are virtually unreactive with O_2. This size-dependent reactivity may be related to the stability of the neutral aluminum clusters which are formed.

Laser ablation FTMS has proven to be very useful for the structural characterization of aluminum cluster anions. The selective ion trapping and manipulation of FTMS can be used to examine the nature of the cluster ions, thus providing a method of measuring both the reactivities and structures of these species.

(R. L. Hettich)

Thermal Desorption MS/MS of Military Chemical Agents

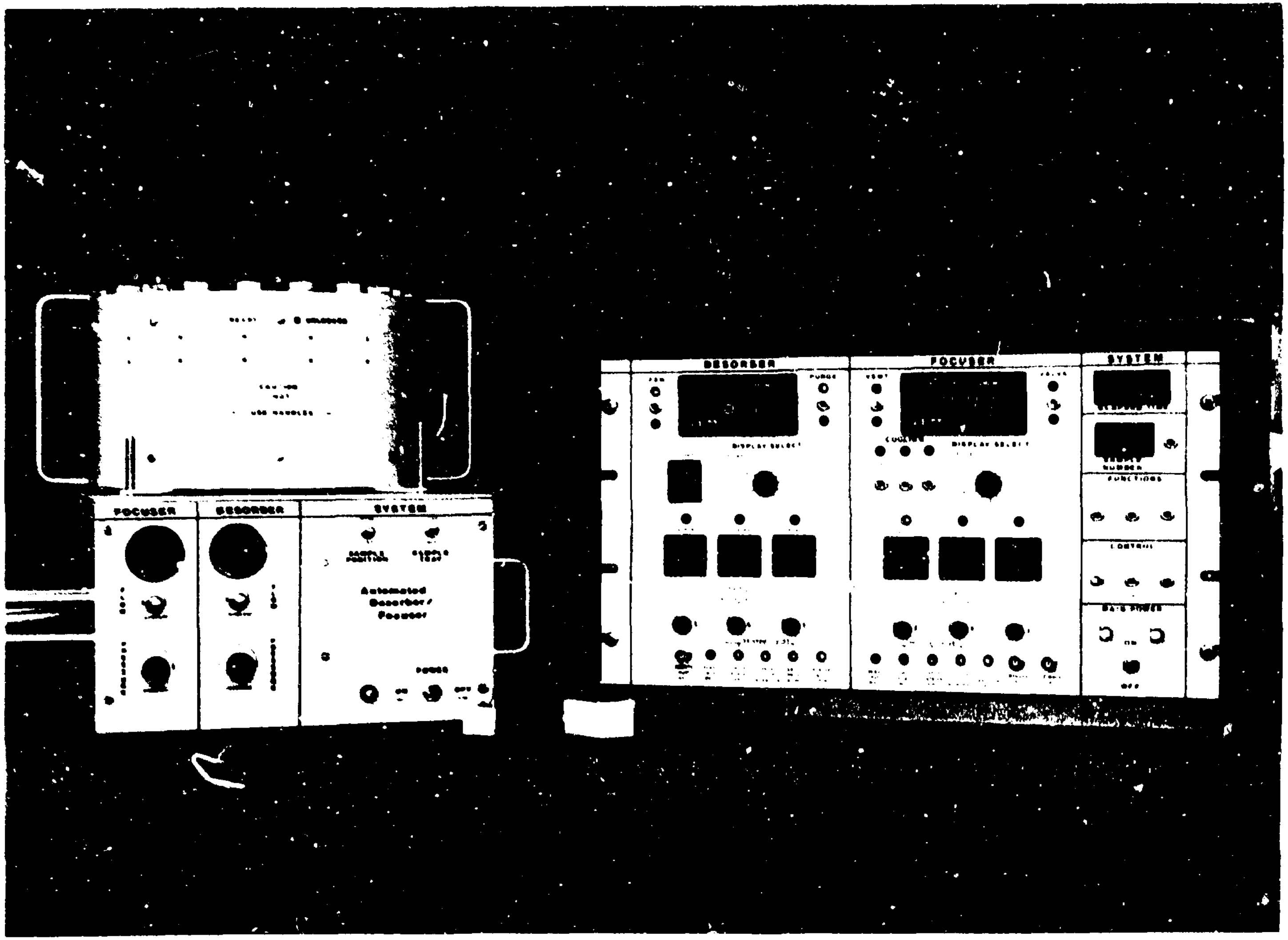
Construction of an automated thermal desorption unit was completed and interfaced to an Ion Trap Mass Spectrometer (ITMS). A photograph of the thermal desorption device is shown in Figure 4-2. Methods were developed for the rapid (< 2 minutes) determination of chemical warfare agent simulants, including dimethylmethyl phosphonate (for agent GB), diisopropylmethylphosphonate (for agent VX) and dibutylsulfide (for agent HD). A series of tests were then performed for each simulant to determine the detection limits, precision, and accuracy of the analytical methods. The results of these tests were statistically analyzed by the U.S. Army sponsors and found to fall well within the requirements for linearity, detection limits, and precision. Army personnel and technical staff from the Chemical Agent Munitions Demilitarization Site (CAMDS) laboratory at Tooele Army Depot were trained here in late June in the operation and maintenance of the automated thermal desoprtion ITMS. The instrument was then packed and shipped to Tooele, Utah for final testing with actual chemical warfare agents. ORNL personnel set up the instrument at Tooele and tested it to verify its performance. Later, tests with all three chemical agents demonstrated the ability of the system to desorb and determine the compounds in less than two minutes. Precision and accuracy tests, as well as a reliability and maintainability tests, were completed by the end of the year.

In addition to operating the automated thermal desorber with the ITMS, the Army made an additional request to interface this device with a gas chromatograph for analysis of Depot Area Air Monitoring System (DAAMS) tubes. This would allow current analytical procedures used at Tooele to be automated. Additional transfer lines were constructed and electronic modifications were made so that the desorber could be used with a Hewlett Packard 5890 gas chromatograph. At present, final reports for this project, including an operating manual, a technical data package, and a final project report are being compiled.

In addition to this primary project, some work was also performed for the Army in support of a related project being conducted by another laboratory. This project involved the real time detection of chemical agents in stack emissions using MS/MS. This particular project was hampered by the presence of low levels of compounds in the stack matrix which interfered with the determination of the targetted chemical agents. That is, these interfering compounds were isobars of the chemical agents and yielded the same daughter ions. Our work involved an evaluation of data obtained in this project, as well identification of chemical interferences present in the stack matrix using ITMS

Figure 4-2

Automated Thermal Desorption Instrument



and FTMS. Using GC/ITMS, sixteen compounds were observed which yielded daughter ion spectra containing the three ions being monitored for agent GB, for example. The most useful information was obtained from GC/FTMS, which yielded the elemental composition of the interfering daughter ions and demonstrated that eight of the interferants were isomers of decene and that the other eight contained oxygen. Suggestions were made to modify the other laboratory's procedures by using ammonia chemical ionization to selectively detect the more basic chemical agents in the presence of the less basic interferences.

(M. B. Wise, R. H. Ilgner, and M. V. Buchanan)

New Approaches for the Prompt Detection of Organics by Mass Spectrometry in Environmental and Physiological Media

Work continued on the evaluation of direct sampling mass spectrometry using ion trap mass spectrometry (ITMS) and glow discharge mass spectrometry (GDMS) for the rapid determination of organics in environmental samples. A number of compounds in water were tested to establish the detection limits and linearity of response using direct sampling into an ITMS. Some of the compounds studied included benzene, toluene, methylene chloride, trichloroethylene, tetrachloroethylene, and several hydrocarbon fuels. Water containing part-per-billion levels of these materials was purged with helium at a rate of about 100 mL/min. The purged material was split at a ratio of about 100:1 through a split-open-split interface and allowed to enter the ITMS through a heated transfer line. Purge times of two minutes were typically required for sample analysis. Chemical ionization using either water or isobutane was employed and full scan mass spectra were generated for single component samples and mixtures. Tandem mass spectrometry was investigated for more specific compound identification. Detection limits for volatile compounds in water were typically 1 ppb or less. Because of the 100:1 split at the split-open-split interface, most of the sample is being diverted from the mass spectrometer. By placing a sorbant trap on the split vent, purged material may be trapped for later analysis. This feature could be very important when the instrument is operated in a screening mode in a field situation. In this case, if a sample tested positive, a split from the same sample could be sent back to the laboratory for confirmatory analysis without having to worry about accurately reproducing field sampling.

Volatiles in soils have also been investigated using direct introduction into the ITMS. An aqueous slurry was made of soils contaminated with jet fuels by mixing 5 grams of soil with 15 mL of water. These slurries were purged in the same manner as with the volatiles in water. Using water chemical ionization to selectively protonate aromatic compounds, alkyl aromatics in the fuels were easily identified. Detection limits with the direct purge ITMS method were found to be at least as good as that of the standard method (about 10 ppm), which includes ultrasonic extraction into an organic solvent, concentration, and analysis by gas chromatography. An important feature, however, is that the ITMS method required less than 5 minutes per sample, including sample preparation, as opposed to four hours for sample preparation and analysis using the standard GC method.

Pilot studies were also conducted to assess whether the ITMS could be used for direct air monitoring without the need for major modifications to the instrument and the conventional ionization source. An air sampling pump was placed on the vent of the standard open-split interface and a source of helium was mixed with ambient air as it was drawn into the interface line. Using this arrangement, benzene and toluene vapors were easily detected in air.

A new ITMS has been purchased by the Army Toxic and Hazardous Materials Agency to enable extensive testing and methods development for the rapid detection of organics in environmental samples. In addition, a new set of quadrupole rods and a spectrometer controller were purchased to repair and upgrade the glow discharge mass spectrometer, which is also being evaluated for direct analysis of environmental samples. This system has been assembled and tested with an axial electron impact ionization source. Using a purge device similar to that used with the ITMS, a number of volatile organics in water were purged into the mass spectrometer and easily detected. For example, a calibration curve for benzene showed a detection limit below 1 ppb with excellent linearity. A new version of the glow discharge ion source is in the design stage and a prototype will be constructed soon which will be considerably more versatile than the present source.

(M. B. Wise, M. V. Buchanan, C. V. Thompson, and M. R. Guerin)

Rapid Detection of Nicotine in Environmental Tobacco Smoke and Urine

Direct sampling ITMS was evaluated for the rapid detection of nicotine in ambient air and in urine as part of our National Cancer Institute program. For both experiments, direct thermal desorption into the ITMS was used with no chromatography. For the measurement of nicotine in ambient air, cigarettes were smoked in a test laboratory in order to produce a controlled concentration of environmental tobacco smoke (ETS). Samples of laboratory air were collected on Tenax traps (7.5 cm long and 0.6 cm in diameter) by pulling a few hundred mL of air through the traps. Simultaneous samples were collected on treated fiberglass filters for analysis by a conventional gas chromatographic method for comparison. No internal standards were added to the Tenax traps prior to analysis. The traps were desorbed by heating them for 10 seconds at 200°C while purging them with helium at a flow of 25 mL per minute. The sample was split through the open-split interface of the ITMS and introduced directly into the instrument. Isobutane chemical ionization was used to generate protonated nicotine at m/z 163. All ions were ejected except for the m/z 163 ion, and collision induced dissociation was used to produce characteristic fragment ions at m/z 84, 106, 120 and 139. The extracted ion currents for these ions were integrated over the width of the thermal desorption peaks (typically 15 seconds) for quantitative measurements. Detection limits were found to be equivalent to or better than the standard GC method for the determination of ambient nicotine. Additionally, the time required for analysis and quantification by thermal desorption ITMS was less than 10 minutes per sample.

Experiments for the detection of nicotine in urine were performed in an identical manner except that the Tenax traps were replaced with glass tubes containing glass wool packing. A 1 μL aliquot of urine was injected through a septum on the thermal desorber body and onto the glass wool. The samples were flash heated for 10 seconds at 200°C and purged with helium at a flow rate of 25 mL per minute. ITMS conditions were identical to those described previously for the detection of nicotine in ambient air. Experiments demonstrated that nicotine could readily be observed in the urine of a smoker (with only 1 µL of this solution injected) or in samples of urine spiked with nicotine at levels of 1 µg/mL. Analysis time was less than five minutes per sample.

(M. B. Wise, C. E. Higgins, and M. R. Guerin)

Special Spectroscopic Studies

A variety of specialized studies were performed for researchers within the Organic Chemistry Section, as well as in other ORNL divisions. Gas chromatography/mass spectrometry was the primary tool employed, although Fourier transform mass spectrometry (FTMS), nuclear magnetic resonance (NMR), and Fourier transform infrared spectroscopy (FTIR) were also used.

As part of a project conducted in the Special Projects Group, compounds in rocket propellant exhaust generated from M-7 and M-36 test motors were characterized using GC/MS. The samples were collected on triple sorbant traps and thermally desorbed into the GC/MS for analysis. Results indicated that although the background level of volatile components was relatively high, a number of compounds related to the rocket exhaust could be identified. In addition, a number of specific polycyclic aromatic hydrocarbons (PAH) and nitro-PAH were quantitatively determined using single ion monitoring and isotope dilution techniques.

Positive and negative ion chemical ionization have been used to characterize a number of compounds for projects conducted in the Separation and Synthesis Group, including compounds collected from HPLC analyses of DNA-related materials and synthesized trinitrotoluene metabolites. In addition, FTMS was used to establish the elemental composition of some of these compounds, while ^1H and ^{13}C NMR were used to confirm molecular structures in some instances.

Special support was also given to the Organic Services Group to better characterize samples which gave ambiguous spectra when analyzed with the conventional mass spectrometric methods employed by them. Using positive ion chemical ionization allowed the molecular weights of compounds which extensively fragment under electron impact conditions to be determined. Negative ion spectra were obtained on samples suspected of containing trace levels of polychlorinated biphenyls and/or pesticides, which respond only weakly under electron impact conditions.

GC/MS and direct-probe MS have been used to characterize a number of metabolites and synthesized compounds for researchers in the Health and Safety Research Division, Chemistry Division, and Chemical Technology Division. FTMS has been used to establish molecular weights for some of these materials, as well. In addition, laser desorption FTMS has been employed in the analysis of compounds with low volatility.

A series of studies have been conducted with R. N. Compton of the Health and Safety Research Division involving the generation of atomic clusters and negatively charged ions using FTMS. This work spawned ideas that have been approved for a ORNL Seed Money project, which will begin in early 1990.

Combined GC/FTIR has been used to complement GC/MS data for the analysis of complex mixtures in a number of studies. For example, GC/FTIR was used to confirm the presence of carbonyl-containing compounds in environmental tobacco smoke. Diffuse reflectance FTIR (DRIFT) was employed to characterize impurities in polymer samples for the Metals and Ceramics Division. In addition, NMR was employed for projects in the Biology, Chemistry, and Chemical Technology Divisions.

(C. Y. Ma, R. L. Hettich, and M. V. Buchanan)

SEPARATIONS AND SYNTHESIS

W. H. Griest

The focus of this group is the development and application of organic chemical separations and synthesis to environmental and health issues. This year, energetics-related activities were increased while analytical services to other Laboratory divisions were limited to organic analysis of radioactive mixed wastes. Some shifts in staff and equipment to other groups in the Organic Chemistry Section resulted from this narrowing of services responsibilities. Group funding is mainly from the U.S. DOE Office of Health and Environmental Research, the U.S. Army Biomedical Research and Development Laboratory, and the U.S. Army Armament, Munitions, and Chemical Command.

Chromatographic Isolation and Detection of DNA Adducts

Chromatographic separation and detection schemes necessary to identify and quantitate primary structural alterations in DNA resulting from either chemical or physical insults are being developed to facilitate studies in molecular dosimetry and repair processes. Isolation and enrichment of trace amounts of modified DNA structures or adducts from excess normal constituents have been approached using preparative liquid chromatography under column overload conditions. When the column capacity is exceeded, the band profiles become broad and unsymmetrical, the retention times are shifted toward lower values, and the resolution between closely eluting compounds is decreased. Peak shapes may also be distorted due to competition for adsorption sites on the stationary phase. If the elution behavior can be accurately predicted then the optimum collection times for a given recovery may be specified. In a collaborative study with G. Guiochon's group, the band migration of the thymine-thymine dimer has been investigated as a function of thymine concentration. The separation factor for dilute solutions of these compounds is 1.11 but at elevated levels of the monomer the peaks are not separated. The semi-ideal model of nonlinear chromatography was used to predict elution behavior and to determine the contribution of each component to the observed, combined profiles in binary mixtures of varying composition. Given a 1 to 24,000 mixture of dimer to monomer, it was shown that collected fractions could be recycled twice to yield a final solution where the ratio of the dimer to the monomer is close to unity and the recovery is 95%. The agreement between the experimental and theoretical data was excellent. The approach provides a method of generating samples at a purity level required for analysis by other techniques. Related work using displacement rather than overloaded elution is also being explored as a means of sample enrichment.

Fluorescence has been used to improve the detectability of photoproducts and other selected adducts. A method for the determination of the pyrimidine dimers has been developed based upon derivatization with coumarin. The products are separated by HPLC and can be detected by conventional fluorescence at 5 picomoles/mL or 40 femtomoles in the detector. The advantages of the method are that analyses are performed entirely by high performance liquid chromatography (HPLC), products are obtained that can be detected by any number of highly sensitive fluorescence techniques, and the fluorophore may be immobilized on solid supports to enable reactions in the solid phase, thereby improving selectivity and reducing background. The method is being used in UV exposure studies for animal cells to determine repair rates for uracil dimers and in plant studies to examine concentration/dose relationships.

Several carcinogenic aromatic amine guanine adducts have also been synthesized (o-toluidine, b-naphthylamine, 2-aminofluorene, p-aminobiphenyl, and 1-aminopyrene) for spectroscopic and chromatographic investigations. The approach was a nucleophilic substitution of the aromatic amines at the C8 position of guanine-3-N-oxide in dimethylsulfoxide/dimethylformamide. After azeotropic solvent removal, the adducts were purified using HPLC. Fluorophore tagging at the amine functionalities using a variety of reagents has been examined for sensitivity, yield, and reaction rate.

(R. S. Ramsey, C.-h. Ho, and G. A. Guiochon)

Analysis of Energetic Compounds

Major initiatives this year have involved the development and application of analytical methods for energetic compounds in biological tissues, compost, and ordnance materials. A joint project with the Environmental Sciences Division (ESD) will measure the concentrations of 2,4,6-trinitrotoluene (TNT) and several TNT metabolites in tissue samples from animals harvested in explosives-contaminated areas of an Army ammunition plant. This is part of an Army investigation to determine if the animals are suitable for human consumption and if the area can be opened to hunting. A related issue requiring similar analyses is whether or not composting will decontaminate wastes from explosives processing to safe, nontoxic products which can be disposed by surface application.

Both of the these projects have required the purchase or synthesis and purification of eight TNT metabolites including two monoamino-dinitro isomers, two diamino-mononitro isomers, a hydroxyamino-dinitro metabolite, trinitrobenzyl alcohol, trinitrobenzoic acid, and an azoxy dimer. For the first time, an HPLC separation has been developed for TNT, the eight TNT metabolites, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), tetryl (N-methyl-N,2,4,6-tetranitroaniline), di- plus trinitrobenzenes, and 2,4- plus 2,6-dinitrotoluenes. Two HPLC methods have been developed. The first is a reverse phase separation on a 150 mm x 4.6 mm ID Zorbax octyldecylsilane column with a complex acetonitrile/water gradient ranging from 25% to 75% acetonitrile. This method utilizes a 250 μL injection and UV absorbance detection at 230 nm, and required 80 min. per sample. It can detect TNT metabolites to ca. 0.02 µg/mL injected concentration. Unfortunately, the trinitrobenzoic acid is difficult to separate from the solvent peak because of its high polarity, and the injection solvent must contain no more than 25% acetonitrile because of the very large injection volume. For these reasons, an improved separation method based upon a mixed mode combination of anion exchange and reverse phase has just been perfected. The column contains both reverse phase (octadecylsilane) and anion exchange (tertiary amine) functionalities, and utilizes a complex ternary elution gradient involving 0.015 M phosphate buffer at pH 5 in water:methanol (9:1, vol:vol), methanol, and acetonitrile. The run time is halved, and the sensitivity is increased because of the improved peak sharpness. Most importantly, both ionic (e.g., trinitrobenzoic acid) and neutral compounds are retained and well-separated in a single HPLC run.

The latter HPLC method is being applied to TNT and metabolite tissue extraction recovery samples prepared by investigators in the ESD to complete the analytical method development. Both HPLC methods have been applied to regulatory leachates of composted explosives wastes, and have demonstrated the presence of mg/L to µg/L concentrations of HMX, RDX, TNT and two monoamino-dinitrotoluenes. Toxicity testing of the leachates, explosives, and metabolites standards by collaborators in the ESD and Health and Safety Research Division (HSRD) shows only very low toxicity. The bacterial mutagenicity appears attributable mainly to the TNT residue. The HPLC methods also have demonstrated the biotransformation of TNT in cell cultures prepared by collaborators in the HSRD. Solid phase extractions were used to concentrate and fractionate the samples.

Military ordnance issues are the subject of a recently-initiated project aimed at understanding and developing a predictive model for the weakening of a glue joint and the case wall in the M829 120 mm kinetic energy antitank round. The unique feature of this round is a nitrocellulose-based cartridge case which is consumed in firing. The case wall and glue joint strength are being determined in both full-up rounds and case wall coupons exposed to different combinations of temperature and humidity or pollutants. Because nitroglycerin and diethyleneglycoldinitrate migrating from the propellant appear to weaken the wall and glue joint, a method for their determination in the nitrocellulose case wall material is being developed. Initial experiments show that 0.01% of nitroester in the case wall can be detected in a methanol extract using packed column supercritical fluid chromatography (SFC) on a Deltabond cyanopropyl phase column with carbon dioxide mobile phase and UV absorbance detection at 210 nm. Spike recovery studies and a comparison with HPLC will be performed. It is also likely that supercritical fluid extraction can be directly coupled with the SFC for an efficient, direct analysis.

(C.-h. Ho, J. E. Caton, R. L. Schenley, B. A. Tomkins, W. M. Caldwell, and W. H. Griest)

Analytical Services:
Organics in Radioactive Mixed Wastes

The analytical services of the group were focused this year on the organic analysis of radioactive mixed wastes. The characterization of ca. thirty inactive and five active nuclear waste storage tanks was completed. U.S. Environmental Protection Agency SW-846 and Contract Laboratory Program (CLP) methods and QC procedures were adapted for radioactive sample use. The services conducted by this group included the remote purge and trap of volatile organics in a glove box, the determination of major organic solvents by direct aqueous injection gas chromatography (GC) in a radioactive contamination-zoned laboratory, and the preparation and GC screen of semivolatile organics extracts in a contamination-zoned laboratory. The volatile organics traps and semivolatile organics extracts from aqueous liquids or sludges and PCBs in diluted organic liquids were low enough in radioactivity for analysis by GC-MS or GC (PCBs only) in conventional laboratories by the Organic Analysis Group. The modified EPA methods generally performed very well and the recoveries of surrogate standards and matrix spikes were comparable to the QC Acceptance Limits required for soil or water under SW-846 or the CLP. Method blanks were clean. Future work will improve the sensitivity for semivolatile organic compounds and recoveries of acid compounds.

The observation that the regulatory organics determinations usually accounted for less than 20% of the organic matter suggested to be present in the waste tank liquids by total organic carbon (TOC) analyses prompted an investigation to account for unidentified organic matter. It was found that more information could be gained from the regulatory semivolatile organics extract if it was chemically derivatized prior to GC-MS. Although additional compounds such as dibutyl phosphate, di-(2-ethylhexyl)phosphate, and fatty acids were found in the extracts, they still failed to account for the TOC. Previous work at the Pacific Northwest Laboratory showed the presence of chelators, extractants, decontamination agents, and their degradation products in nuclear wastes. We developed a method for the determination of compounds in the aqueous liquids, based upon pH adjustment, evaporation, trimethylsilyl derivatization of the residue, and GC. Although the TOC accounting was increased (ranging from 25% to nearly quantitative in one sample), the bulk of the TOC was not identifiable. Laser desorption Fourier transform mass spectroscopy and reverse phase HPLC suggest that the TOC consists of highly polar compounds with molecular weights ranging up to the low 700s, with most less than ca. 300. Additional work is needed on isolation and separation methodology for these compounds.

(R. L. Schenley and W. H. Griest)

Facility Management

The facilities at the Hazardous Materials Analytical Laboratory in Building 2026B are being upgraded with the installation of additional benches and cabinets, a more efficient rearrangement of the office and laboratory space, and the start of the construction of a change room/bathroom. The radioactive contamination-zoned laboratory for preparation and analysis of nuclear mixed wastes and other radioactive samples has been operated for over one year without significant contamination and the background radiation level remains very low.

The DOE Synthetic Fuels Repository collection remains in inactive archival status because of the very high cost of disposal through current Laboratory disposal contractors and a continuing low level of sample requests. A much lower disposal cost through a fuels recycle program has been located, and the suitability of this company will be investigated through Laboratory channels.

(W. H. Griest and R. L. Schenley)

SPECIAL PROJECTS

R. A. Jenkins

The generation, sampling, instrumental monitoring, and chemical characterization of controlled and/or specialty atmospheres continues to be a major focus of this group. Field and environmental analytical chemistry is becoming an increasingly important component of its efforts. In general, funding for the group continues to be issue-oriented, originating predominantly with the Department of Defense and the National Institutes of Health.

Tobacco Smoke Studies

This year, we performed an independent characterization of the components of the smoke aerosol of a cigarette recently introduced to the commercial market which heats, but does not burn tobacco. The cigarette uses a burning charcoal element to produce hot air. The hot air warms a cartridge containing a glycerol/propylene glycol solution of nicotine and other flavor components. The resulting warm vapors condense as they leave the cigarette, and a smoke aerosol is produced. Because the composition of the aerosol is so different from conventional cigarette smoke, a new gas chromatographic method was put in place which simultaneously determines the major particulate phase compounds in the aerosol (glycerol, propylene glycol, and nicotine). Results from the analyses indicated that the smoke component deliveries were 20 - 50% greater than those reported by the manufacturer. This was subsequently determined to be due to significant batch-to-batch differences in the cigarettes themselves.

An important issue related to sampling, analysis, and human risk assessment associated with exposure to indoor air pollution is whether a sample acquired in the general area where an individual is exposed is likely to provide an estimate of exposure identical to that from a sample acquired in the breathing zone. There is an increasing body of evidence to indicate for those exposures where the activity of the exposed individual is likely to be the source of the exposure (e.g., cooking), the breathing zone sample is likely to provide a much greater exposure estimate. The situation is not so clear when the exposed individual does not generate the exposure. Such is usually the case for a nonsmoker exposed to environmental tobacco smoke (ETS). We are currently investigating the extent to which area samples describe the exposure of a nonsmoker to ETS, as determined by a breathing zone measurement of vapor phase nicotine. The study has both a laboratory and field component to it. First, in our ETS room, a converted office with modified ventilation and a number of on-line monitoring instruments, a wide range of concentrations of ETS were generated using a new aspirator apparatus linked to a sidestream smoke generator. The system can produce a continuously variable and highly reproducible concentration of ETS in a fixed volume environment. These atmospheres were sampled simultaneously, using both the area sampler (a pump/XAD-4 resin cartridge combination) and the personal sampler (a smaller pump/Tenax resin cartridge combination).

The data from multiple samplings over a range of nicotine concentrations of 1 - 150 $\mu g/m^3$, followed by GC analysis using nitrogen specific detection, indicated the two systems produce virtually identical concentration values. The next phase of the study will be to place both area samplers, and individuals wearing the personal samplers in the field in public places, such as bowling alleys, restaurants, and gaming establishments. The individuals will move through the areas in a manner similar to that of a nonsmoking individual, while the area sampler will remain stationary. A comparison of the two suites of samples will provide an estimate of the extent to which an area sample of vapor phase nicotine can estimate an individual's exposure to environmental tobacco smoke.

(C. E. Higgins, J. H. Moneyhun, R. L. Moody, and R. A. Jenkins)

Military and Specialty Atmosphere Studies

Our aerosol technology program includes projects related to the generation and characterization of test atmospheres for military and other purposes. During the past year, our work has been predominantly experimental. Last year, we completed development and characterization of a laboratory scale generator for a military biphasic obscurant aerosol. One phase is generated from a petroleum based liquid (PBL) using evaporation/condensation technology previously developed in our laboratory. The other phase is generated from finely divided solid material which is deagglomerated and dispersed using a small jet mill. The two aerosol clouds are mixed at ambient temperature and delivered to a chamber for characterization or inhalation exposure. We initiated construction on five generator systems. This year, we completed construction on those systems, and installed and tested them at the Illinois Institute of Technology Research Institute in Chicago, where they are now being used to study the inhalation toxicity of the combination aerosol.

Characterization of exhaust from test scale rocket motors from hand-held anti-tank weapons systems has continued. The purpose of the effort is to provide both a data base for health risk assessment and input into improved computer model projections of exhaust products. For this study, the concentrations of both major and minor vapor and particle phase constituents are being determined. Since many of the potential species are reactive, real-time monitoring systems to determine levels of particulates, ammonia, oxides of nitrogen, hydrogen cyanide, carbon monoxide and dioxide, and hydrogen chloride are used. Analytical methods validation experiments are being performed using free burns of small quantities of the candidate propellants in a small chamber at Building 5507. Samples for the actual characterization studies are collected from firings of scaled down test motors in a 19.6 m^3 chamber at the Army's Signature Characterization Facility (ASCF) at Redstone Arsenal in Huntsville, Alabama. One sampling trip was made to the ASCF in late January. Another took place in early December of 1989. The January tests of a 25 gram 1/4 scale motor, containing a large fraction of ammonium perchlorate in the fuel formulation, produced exhausts that were relatively high in both CO and HCl (330 and 115 ppm, respectively) when diluted with the clean atmosphere of the chamber. Particulate concentrations were about 40 mg/m^3, of which aluminum, copper, and lead represented a significant fraction (3.5, 4.5 and 2 mg/m^3, respectively). Vapor and particle phase organics are still to be analyzed. This is a joint project with the Computing and Telecommunications Division, whose staff are examining existing computer models to determine the extent to which such models can predict the concentrations of major and minor toxic constituents produced. Interestingly, in the initial comparisons of the first propellant characterized, the agreement between the observed and predicted concentrations of HCl, CO, and CO_2 have been outstanding.

We have also been involved with a small, but interesting new project involving the control of pest species of birds. Currently, the avicide 2-chloro-p-toluidine (CPT) must be sprayed at very high concentrations from airplanes over blackbird or starling roosts so that a sufficient quantity of the spray will contact the feathers and be absorbed through the skin. Because the concentration and concomitant environmental burden is so high, there is some question as to whether CPT can receive approval for routine use. Consequently, the Department of Agriculture's Denver Wildlife Research Center (DWRC) wanted to investigate the inhalation toxicology of an aerosol of CPT, to determine if a more effective route of administration could be found. ORNL was requested to develop a laboratory scale generator for an aerosol of CPT to support animal studies, and chemically characterize the resulting material. Because of chemical thermodynamic considerations, the development of a controlled atmosphere of a relatively volatile compound with a significant fraction of the target compound in the liquid is not straightforward. A number of approaches were investigated. A small nebulizer intended for human use proved most efficacious. In one approach, a water-propylene glycol solution was nebulized at a sufficiently high rate so as to saturate the atmosphere in the exposure chamber and impede evaporation sufficiently to retain a significant fraction of the CPT in the liquid phase. In another approach, the CPT, a primary amine, was titrated in the formulation with HCl. The resulting hydrochloride salt (CPTH) is very nonvolatile. In fact, an aerosol with virtually all of the CPTH in a solid phase can be generated easily. Initial determinations of aerosol concentrations and particle size distributions were performed by collecting filter or impactor stage samples, eluting the deposited solution, and determining the CPT or CPTH with UV absorption at 245 nm. A series of scoping experiments were performed at the DWRC with the aid of ORNL staff in October. The results suggested that CPT delivered in an inhalable size (3 - 5 micron diameter) aerosol is substantially more toxic to target species than even CPT administered intravenously. If the remainder of the scoping studies prove equally promising, we are expected to have a major role in the development of a more sophisticated laboratory and field aerosol generation system.

(R. A. Jenkins, J. H. Moneyhun, C. V. Thompson, R. L. Moody, C. E. Higgins, and T. M. Gayle)*

---

*Instrumentation and Controls Division

Environmental Studies

The other major component of the group's activities is environmental analytical chemistry. The major focus of the work is field analysis, with the goal being to facilitate, reduce reliance on, and/or replace laboratory analysis. In collaboration with staff from the Radioactive Materials Analysis Section, we performed a detailed evaluation of a portable X-ray fluorescence (XRF) system for the field analysis of copper, arsenic, mercury, and lead in contaminated soil and water. This work was sponsored by the Army's Toxic and Hazardous Materials Agency (USATHAMA) in support of ongoing programs at Rocky Mountain Arsenal (RMA). In initial evaluation experiments, temperature was shown to have no effect on the system performance. The ruggedness test for pressure determined a 2.2% difference in response for standards run at the elevation of RMA (ca. 1600 m) and those run at the elevation of ORNL. Also, variation of the iron content of the soil was shown to have an effect on apparent copper concentration. However, this effect was shown to be small, compared with other factors. Certification of the analytical methods was performed in the laboratory and under field conditions according to USATHAMA guidelines. Repeated field analyses of actual environmental samples were conducted with one sump water and four large surface soil samples collected at RMA. For soil, certified reporting limits (CRL) were determined to be 112, 187, and 192 ppm for arsenic, mercury, and lead in RMA soil, respectively. CRL's for copper, mercury, and lead in water were 38, 39, and 176 ppm, respectively. For samples acquired in the field and returned to the laboratory for analysis, the XRF system was shown not to be equivalent to the lab analysis, in terms of precision and/or accuracy in those cases where the contaminant level was above that of the CRL. However, in nearly all of the element/sample comparisons, the XRF system was able to accurately determine whether the contamination level was above or below the CRL, and the approximate level of contamination. Thus, it appears that the XRF system can be used for screening soils and waters contaminated above the 100 - 300 ppm range.

As part of the overall goals of remedial action at DOE facilities, there has been increasing research emphasis on performing field-based screening and/or quantitative analysis of environmental samples. As a result of a detailed technology assessment conducted for the US Army's Toxic and Hazardous Materials Agency (USATHAMA), a number of promising strategies for the rapid field processing, screening, and/or analysis of volatile and semivolatile organic contaminants were identified. These included, among others, the use of industrial hygiene type, colorimetric indicator tubes for field screening of volatiles, and the use of triple sorbent resin traps for the concentration or stabilization of volatiles prior to field screening or return to the laboratory for detailed analysis. We have initiated laboratory evaluation of these two approaches. Colorimetric indicator tubes for benzene, toluene, carbon tetrachloride, tetrachloroethylene, and acetone were interfaced to a small, field portable purge device. Following studies designed to minimize the impact of water aerosols on the tubes, analytical detection limits were established. The detection limits observed were 50 µg/L for benzene, carbon tetrachloride, tetrachloroethene, toluene, and trichloroethene, and 1000 µg/L for acetone. Because of the criteria chosen for determining the detection limits, a conservative estimate for the dynamic range for these colorimetric indicator tubes is two orders of magnitude. The rationale behind using a triple sorbent trap is that the use of a second stage and a third stage sorbent significantly increases the number of constituents visualized and reduces breakthrough. Most of the compounds in the evaluation study were chosen to bracket a large range of volatilities for compounds found on EPA's target compound list (TCL), and because they have been identified as contaminants at a number of DOE sites. The trisorb traps were shown in laboratory evaluation to effectively trap VOCs purged from spiked water samples, with 100% retention except for 1,1 dichloroethene and benzene at high purge flow rates, where percent breakthroughs were <30%. The purge efficiency and component recovery from the traps was 53% and greater, with the efficiency and recovery increasing with contaminant level. Both of these approaches will be field tested in the coming year.

Our studies of determination of pre-analytical holding times for environmental samples were transferred to the Special Projects Group at mid-year. These studies have been directed toward determination of the extent to which environmental samples can be held prior to analysis without "significant" degradation of the target analytes. These studies have been accomplished by spiking selected soil and water matrices, storing the samples under a variety of conditions, and analyzing them at preselected intervals. The effects of various preservation strategies have been investigated. During this past year, experimental efforts have been directed toward the emplacement of analytical methods for the determination of suites of semivolatile compounds in soil and water. Currently, we have in place analytical procedures for organochlorine pesticides by GC/ECD, phenols and phthalates by HPLC, and PAH's by HPLC, using programmable wavelength fluorescence detection. Our data evaluation studies have been directed toward a detailed statistical determination of maximum pre-analytical holding times (MHT's) for volatile organics in water. For most of the species, in both unpreserved samples, and samples preserved with ascorbic acid or sodium bisulfate, MHT's could be determined using zero- or first-order approximating models of the diminution of concentration of the target species with time. However, in some cases, a cubic spline fit of the data was required. In general, for those species which had minimal stability in unpreserved samples, preservation with acid significantly increased holding times. However, addition of acid did not necessarily reduce the variability of the concentration measurement, and neither of the acids tested uniformly achieved longer MHT's for the volatiles. During the coming year, we expect to continue our data evaluation of experimental results obtained earlier for explosives in soil and water, and begin the experimental phase of our studies of holding times of semivolatile species.

(R. L. Moody, C. V. Thompson, C. E. Higgins, F. F. Dyer, C. K. Bayne,** B. A. Tomkins, and R. A. Jenkins)*

---

*Radioactive Materials Analysis Section
**Computing and Telecommunications Division

ORGANIC ANALYSIS

M. P. Maskarinec

The Organic Analysis Group performs qualitative and quantitative determinations of organic compounds in a wide variety of sample matrices. Virtually all of these matrices are environmental in origin, and work can be roughly divided into routine environmental analyses and compliance analyses. Most methods used are multicomponent in nature and capable of achieving low part-per-billion sensitivities. The group supports Laboratory programs as well as similar external and work-for-others programs. The group currently consists of fourteen full-time staff members.

The primary function of the group is supported by four interdependent efforts: 1) administration, consisting of sample receipt, tracking, reporting, and quality control; 2) sample preparation; 3) gas chromatographic analysis; and 4) gas chromatography/mass spectrometric analysis. In each of these areas, both staff and equipment capabilities have been expanded and/or upgraded.

Administration

Sample tracking and chain-of-custody procedures are now in place and have been approved in various audits. Consequently, it is possible to precisely locate any sample in the system with minimal effort. All standard operating procedures have been updated, and several new procedures have been written. There are still procedures which must be implemented, and this will undoubtedly be a continuing process.

Several other steps have been taken in order to improve the quality of data generated by the group. A group Quality Assurance Plan has been written and is currently under review. In-house quality control samples are now being run on an ongoing basis. These will probably assume a major role in quality control as external performance evaluation materials become less available. We have implemented a data base style system for customer tracking and charging, and have developed a formal system for sample receipt. We have continued our participation in the USEPA Quarterly Performance Evaluation system, and our scores over the last three quarters have been acceptable.

There are several steps still to be taken to improve the administration of the group: one additional staff member is needed for the receiving/reporting area, space is required for a formal sample receiving area, and sample preparation information ought to be electronically entered. The latter should be accomplished soon.

(M. P. Maskarinec, L. J. Wachter, and R. L. Williams)

Sample Preparation

The sample preparation area is currently staffed by five technicians. Their primary function is preparation of samples to a point where instrumental analysis is possible. Several significant changes have been made to the preparation laboratory this year. First, the effort has been divided according to sample matrix and final analysis required. One full laboratory has been devoted to the preparation of soil, waste, and tissue samples. This laboratory has the capability to perform all of the required Resource Conservation and Recovery Act (RCRA) methods, including Soxhlet extraction (six extractors), ultrasonic extraction (four sonicators), the newly approved Soxtec extraction (12 units), Kuderna-Danish concentration, Florisil and gel permeation chromatography cleanup, and all associated procedures (pH, % lipids, etc.). A second full laboratory has been devoted to the analysis of water samples. This laboratory also has the capability to perform all approved RCRA methods, including separatory funnel liquid/liquid extraction, continuous liquid/liquid extraction, extract concentration, and alumina cleanup. One small laboratory remains dedicated to the cleanup and final concentration of pesticide extracts.

There have been several benefits to this division of effort. First, the staff member assigned to the preparation of a group of samples is now responsible for the entire preparation, rather than only one step in the process. This reduces the chain-of-custody problems and helps assure that no errors in communication are made between the sample preparation technicians. Second, the equipment (glassware) used in each area is now kept separate. Since the water samples are generally clean and contain the analytes at low concentrations, it is critical that the glassware remain uncontaminated. However, waste samples, soil, and tissue samples are often very high in contamination. This made it difficult to maintain clean glassware for the low level analyses. Third, new technicians added to the group are generally assigned to the sample preparation area first. The division of methods makes training a simpler task, since each method can be taught from start to finish, and proficiency can be tested to assure competency.

There have been several additions to the sample preparation laboratories in terms of equipment. As mentioned earlier, the Soxtec extractor is now set up and available. This device, which is approved for the extraction of polychlorinated biphenyls (PCBs) in soil, is much more rapid than Soxhlet extraction and has higher throughput than ultrasonic extraction. Unfortunately contamination and carryover have been problems which have limited the utility of the device. Because of the contamination problem in general, a large oven which is capable of providing high temperature bake-out of glassware was acquired and installed. This oven has been operated up to 380°C, and we are hopeful that its use will eliminate many of the contamination problems.

We have also acquired three automated evaporation units. These units, manufactured by Zymark, are capable of replacing the time and labor intensive Kuderna-Danish evaporators. Each unit can evaporate six samples at once. The evaporation is carried out using a nitrogen stream aimed at the sample in such a way as to create a helical motion in the concentration tube. This motion provides a relatively high evaporation rate without aerosol formation and the resulting analyte loss. The concentrator tube is a simple design with a nippled bottom; very easy to clean. The units are equipped with a thermostatically controlled water bath and optical sensors for endpoint detection. The units can be set to evaporate to dryness or to 0.5 mL. In operation for approximately three months, these units have been quite useful in the concentration of pesticide/PCB extracts, since they can also be set to perform a solvent switch (methylene chloride to hexane) as required by the USEPA methodology. The time involved in the concentration has been reduced approximately 50%, glassware cleaning is now trivial, and operator attention is no longer necessary. We are currently optimizing the unit for the concentration of semivolatile extracts.

The primary methodology addition has been the establishment of a dilution system for the analysis of waste samples. Each waste sample is diluted with methanol for the analysis of volatile organics and "F-list" solvents. A second aliquot of the sample is diluted with methylene chloride for the analysis of semivolatile organic compounds. Finally, a third aliquot of the sample is diluted with hexane and cleaned up using Florisil for the determination of PCB's. With the addition of GC screening analysis (described below), we have been able to cope reasonably well with the large number of waste samples received over the last twelve months.

(M. P. Maskarinec, G. M. Henderson, D. A. Jenkins, D. D. Pair, P. L. Pierson, and C. D. Varnadore)

Gas Chromatography

The gas chromatography laboratory is presently staffed by four chemists. There are nine gas chromatographs available, six of which have automated sample injectors. Six instruments are equipped with electron capture detectors, three with nitrogen/phosphorus detectors and all with flame ionization detectors. All have capillary capability, either narrow bore or megabore. However, only two of the instruments were purchased in the last five years, and four are 12 years old. The limited reliability of these instruments causes considerable down time. The laboratory also contains a Nelson Analytical PC-based data system. We are hoping to add a VAX-based data management system in the near future.

Methodology used in the gas chromatography laboratory includes any of the RCRA 8000 series GC methods, although method 8080 (pesticides/PCBs) is used for the majority of the samples analyzed. However, due to the large number of waste samples characterized during the past year, a capability was established for gas chromatographic screening of the diluted samples. This screening process allows us to more accurately predict the appropriate dilution if gas chromatography/mass spectrometry (GC/MS) analysis is necessary, and in addition allows us to eliminate the GC/MS analysis for those samples not containing chromatographable components. Initially, the screening was done manually by direct injection for both the volatiles and the semivolatiles. However, the capability became more and more necessary as the year progressed, and both systems are now automated, with the volatiles being analyzed by purge and trap injection.

(M. P. Maskarinec, R. M. Edwards, S. M. Smith, and R. Merriweather)

Gas Chromatography/Mass Spectrometry

The GC/MS laboratory performs routine analysis primarily on environmental samples. The laboratory has been staffed by as many as four chemists/-technicians. Currently, three staff members are assigned to the laboratory, with an anticipated addition of one technician in the near future. Four instruments are available, two each for volatile analysis and semivolatile analysis. All instruments are maintained on vendor service contracts, which has allowed the instruments to be operated with minimal down time.

Hardware improvements in GC/MS have again been significant during this year. A second central computer system has been added and dedicated to the instruments performing volatile organic analysis. This greatly improves the data processing and reporting capabilities of the two systems. Improved interfacing capability has also been added, although this caused considerable difficulties during startup. The full capabilities of the system have not yet been tested.

One of the volatile organic systems has now been equipped with a heated, automated purge and trap device. This capability is required by EPA methodology. However, several difficulties were encountered in the initial validation, which resulted in modification of the device. Needle spargers with valves were added to the individual purge units, so that internal standards and surrogates could be added to a closed system, as is done with water samples. This eliminated the problem of poor internal standard response and surrogate recovery. The connectors were modified to accept a VOA vial, so that soil samples could be analyzed without weighing and/or transfer. Other work in the section had indicated that this was necessary for precise measurement of volatiles in soil. We now have confidence in the analysis of volatiles in soil, although there is still some question about the techniques used for sampling.

Also during the past year, EPA has approved the use of wide bore capillary columns for the analysis of volatile organics. We have installed such a column in one of the instruments and anticipate converting the other instrument as well. The new method offers the usual advantages over the previous packed column: faster analysis, better chromatographic resolution, and higher sensitivity. At the present time, we are working to develop the required software to take full advantage of the new technology. We anticipate that capacity will be doubled by the use of the new methodology.

During this year, EPA created a working group for the improvement of identification of tentatively identified compounds (TICs). One member of the OAL staff (MPM) was invited to join this group. As a result of this interaction, we have begun the formidable task of creating a new library of mass spectra which includes only those TICs with a high probability of occurrence in environmental samples. There are two sources of possible compounds: 1) alternate lists of analytes used by EPA programs other than the CLP such as the RCRA Appendix IX list and the Drinking Water list of volatiles, and 2) a database generated by the CLP Sample Management Office on those TICs reported to EPA by the entire CLP community during the last eighteen months. We have begun to construct this library using the alternate lists, both because of compound availability and because of the possible need to perform analyses on these compounds for regulatory purposes. We are currently including three pieces of information in the database: 1) the mass spectrum, 2) the gas chromatographic retention index with reference to the internal standards, and 3) the relative response factor of the compound versus the internal standards.

We have also added the capability of performing analysis of sorbent traps for the presence of volatile organics. The need for this type of determination arises from two sources: 1) industrial hygiene investigations, and 2) the purging of radioactive samples in controlled areas onto traps, which are subsequently returned to OAL for analysis. The methodology is still somewhat cumbersome, and we anticipate improving this capability during the next year.

(M. P. Maskarinec, S. H. Harmon, G. S. Fleming, and S. D. Glover)

ORNL/UTK RESEARCH PROGRAM

G. A. Guiochon

The recent years have seen a rapidly growing interest devoted to the theory of nonlinear chromatography and to its various applications. Considerable scientific activity is taking place in this area and great progress has been achieved in the understanding of the behavior of large concentration zones in chromatographic columns, and in the development of the first serious attempts at optimizing the experimental conditions under which a separation is run, in order to maximize the production at a stated degree of purity, as well as in various other applications.

The research work conducted by the group deals with the relationships between the chromatographic signals obtained at high concentrations and the thermodynamics and kinetics of the interactions between the chromatographic system (mobile and stationary phases) and the components of the mixture studied.

Theory of Chromatography

Important advances in the theory of chromatography now permit the understanding of the migration of large concentration bands along chromatographic columns. The theory of chromatography is based on the solution of a system of equations which accounts for:

- the mass balance of each chemical species involved in an infinitely thin slice of the column.
- the kinetics of mass transfer of these chemical species across the column and between phases.

All the components of the sample must be considered, since the presence of one compound influences the kinetics of sorption and desorption of all the other components. Similarly, we ought to consider as well all the components of the mobile phase, except that we may assume, by a proper choice of the adsorption convention, that the weak solvent is not sorbed. But certainly the presence of the strong solvent (the organic modifier) changes the sorption kinetics of the sample components: the purpose of using these additives is to adjust the retention, i.e., the rate of adsorption, of the mixture components.

Two kinds of models of chromatography have been developed: equilibrium models (ideal and semi-ideal models) and kinetic models. The models of the first kind predict correctly the elution and the displacement of large concentration bands, the gradient elution of such bands, and system peaks in most chromatographic systems used in the high performance implementations of the method (normal and reversed phase HPLC, ion exchange, size exclusion and hydrophobic interaction chromatography). They are relatively simple to use since they require only the competitive equilibrium isotherms of the compounds involved. They are incorrect, however, when the kinetics of the retention mechanism become slow, such as in affinity chromatography or in the determination of breakthrough curves in adsorption processes. Then kinetic models must be used. These require information regarding the kinetics of mass transfer and of phase equilibria which is often difficult to obtain.

In both cases, it is not possible to derive an exact analytical solution of the system of partial differential equations to which the selected model leads, except in some specific cases. The ideal model and the kinetic model can be solved in the case of the Langmuir model of adsorption. Otherwise, numerical solutions may be obtained. They are in excellent agreement with experimental results, provided the proper equilibrium or kinetic equation be used.

The main roadblock seems to have become the lack of proper model for these equations, in fact, the very limited theoretical background on the kinetics and thermodynamics of adsorption for complex systems. We are collecting adsorption data for various compounds and for several binary mixtures (alcohols, phenols, optical isomers of amino-acids, peptides and proteins). These data are fitted against those corresponding to the known models. Considerable difficulties come from the lack of suitable isotherm equations, especially for the competitive adsorption of several compounds combined with the extreme sensitivity of the chromatographic band profiles to minor changes in the isotherm. Supplying the isotherm data to the chromatographic program as a table requires an accurate procedure of interpolation.

Comparison between the individual elution profiles of the components of binary mixtures and the profiles predicted by our simulation program gives excellent results when the correct isotherms are available.

(G. A. Guiochon, M. Z. El Fallah, A. M. Katti,** and J. V. H. Schudel**)*

---

*Postdoctoral research associate
**Predoctoral student, University of Tennessee

Optimization of Experimental Conditions

The development of a reliable and useful theory of optimization of the experimental parameters of a preparative chromatographic separation requires essentially a rapid, convenient and accurate method of determination of mixed, competitive isotherms. This, in turn, requires some significant advances in our understanding of adsorption mechanisms.

Various procedures have been suggested for the optimization of experimental parameters. The main ones have been described by Hupe, by Snyder, and by us. The first two are empirical. As such they are valid only within the range of experimental conditions where they have been determined. The same is true for the conclusions derived from computer simulations, which require exact numerical values. In both cases, general conclusions may be based only on the results of a large number of results, obtained for a broad range of values of the parameters involved. The combination of an exact simulation algorithm and a Simplex optimization procedure has given excellent results.

More general conclusions can be derived from the analytical solutions of the ideal model which we have recently obtained. The difficulty, once again, is in the proper introduction in the theoretical model of the exact isotherm equation. Any optimization procedure which does not take into account the interaction between the compounds to be separated and their competition for the available sites in the stationary phase is doomed to fail to predict correctly the elution profiles of each compound. Any prediction procedure which takes these phenomena into account is very complex and requires the preliminary acquisition of large amounts of data.

It has been possible to demonstrate that the production yield for each of two compounds to be separated and isolated with a certain degree of purity increases, at constant sample size, with increasing column efficiency. However, the production increases with the flow velocity, since the injection frequency increases. Since the column efficiency decreases with increasing flow velocity, there should be some optimum flow rate, for which the production of a component at a stated degree of purity is maximum. There is no reason, however, that this optimum flow rate to be the same for the different components of a complex sample. It has not been possible yet to determine exactly what this flow rate is or how an experimentalist can find it out rapidly.

(G. A. Guiochon and A. M. Katti)*

---

*Predoctoral student, University of Tennessee

Surface Properties of Ceramic Powders.

This work is an application of our previous results in the theory of non-linear chromatography. Pure compounds are used as probes to investigate the physico-chemical properties of the surface of ceramic powders. Plugs of pure compounds are injected on open tubular gas chromatographic columns whose walls are covered with a layer of these powders. The elution profiles are recorded and analyzed. They contain the information necessary to derive the surface energy distribution of the particles.

Specialty ceramic products have achieved great importance, notably in the production of high temperature materials for aeronautic engines and of materials with unusual dielectric, magnetic or electric properties for electronic devices. In most cases, considerable difficulties are met when molding and firing these ceramic parts. The raw material used is a very fine powder (size distribution between 0.2 and 1 μm) of the desired oxide, nitride or carbide. After mixing with other powders (flux), a binding agent (usually polymeric), a dispersant (surface active agent), and an appropriate solvent, the powder is agglomerated and molded, then fired. During the thermal process, the parts, which are originally porous, unconsolidated agglomerates, shrink, while their porosity decreases from ca 40% to almost none. This change in volume is often accompanied by the appearance of internal stress resulting in the rupture of the part or the formation of cracks. Ceramic materials having the same origin and apparently the same properties behave very differently, some giving satisfactory products, others not.

Growing evidence has been accumulated that this phenomenon is due to differences in the surface chemistry of the particles, differences which are not shown by tests conventional in the ceramic industry, such as the titration curves, the zeta potential, the pH of a suspension of the powder, etc. Other methods of studying the chemical properties of the surface appear to be necessary.

Our aim is the development of a series of tests based on the determination of the adsorption isotherms for a series of appropriate probes, followed by the derivation of the energy distribution function and of the energy of formation of a monolayer for all these compounds. The probes are chosen after consideration of the nature of the binding agent, the surfactant and the solvent used in the ceramic processing, since the relationship between the surface energy of the powder and the properties of these chemicals is of great importance. The adsorption isotherms are determined from the elution profiles of high concentration plugs of each probe compound, using dedicated computer programs we have developed. The surface energy distribution is derived from these isotherms, using a model which assumes that the surface is an irregular quilt made of uniform surface energy patches, on which the adsorption isotherm is given by the Langmuir isotherm. The coefficients of these Langmuir isotherms are related to the patch surface energy.

The characteristics of the energy distribution functions and of the monolayer formation energies of the probe compounds for a certain surface will be related to the performance of samples of the corresponding material in actual production. If it proves possible to distinguish the products which perform well from those which behave poorly, the method will permit the development of a quality control program for the high technology ceramic industry.

(G. A. Guiochon, E. V. Dose, and J. L. Roles**)*

---

*Postdoctoral research associate
**Predoctoral student, University of Tennessee

5. ORNL ENVIRONMENTAL PROGRAMS

W. R. Laing

Environmental analyses are an important part of the work done by this division. Samples from the Environmental and Health Protection and the Environmental Sciences Divisions and the DOE Environmental Survey totaled 216,000 measurements; this accounted for 70% of the ACD analytical support work. The number of groundwater samples from monitoring wells increased as did the number from remedial action activities related to waste area groups and inactive storage tanks. Details of these activities are found in individual section reports.

DOE ENVIRONMENTAL SURVEY

This year saw the winding down of the DOE Environmental Survey. The remaining samples from Idaho National Engineering Laboratory (INEL) were completed by the end of December. A data quality and useability review of the organic results using EPA guidelines was completed in January. This review showed that the results from the Pantex, Lawrence Livermore/Sandia and Argonne sites were 51% quality level 1 and 2 and 49% quality level 3. Quality level 3 results were further evaluated for useability and 90% were found to be useful data. Overall, 95% of the results were of sufficient quality to be of value to the Survey.

In July a team from EPA Las Vegas visited ORNL to review the data quality evaluation and to perform two audits. Their report found that the evaluation had been done properly. There were no major findings in the audit reports.

All of the site reports have been issued and accepted by DOE. The remaining sample materials have been sent to waste and a purge of our files and records is in progress. The file purge will be indexed and sent to INEL for storage.

Quarterly performance evaluation samples from EPA were analyzed for inorganic and organic constituents. The average score was 85 for inorganics and 78 for organics. Our inductively coupled plasma spectrometer was out of service for most of the year and only two of the inorganic PE samples were reported. EPA had problems with the third quarter organic samples and no grade was issued. The radiochemical lab analyzed a variety of sample types from the Environmental Measurements Laboratory with a score of 91.4 and soil samples from EPA with a score of 94.3.

A third party audit of the Pantex site data had no major findings.

REMEDIAL ACTION PROGRAMS

Work on the characterization of waste area grouping (WAG) 6 began this year. Samples from a suite of wells drilled around the perimeter of the WAG were tested for organics, inorganics and radioactivity. Over 28,000 results were reported for this program.

The inactive tank sampling program expanded to include a total of 29 tanks. Some of the samples required hot cell separations and extractions prior to analysis. An initial report was issued in August for part of the work so that planning could begin on the fate of the tank contents. The program will continue with sampling of active tanks. This work is discussed in detail in the reports from the Organic Chemistry and Radioactive Materials sections.

Other remedial action work slowed because of funding, regulations, and a reorganization of the Operations Division during the year.

6. QUALITY ASSURANCE, SAFETY AND TRAINING

QUALITY ASSURANCE/ QUALITY CONTROL

P. L. Howell*

The Analytical Chemistry Division (ACD) continued an effort of upgrading its QA Program to the requirements of DOE Order 5700.6A, i.e., the use of Quality Assurance Program Requirements for Nuclear Facilities (NQA-1). The development of an 18-element NQA-1 QA Program began in FY88. To develop the program, small group meetings were held to discuss the requirements of each NQA-1 element followed by discussion of how the requirements were applicable within ACD. Procedures were then drafted and sent out for review and comment. The manual is in reproduction and document clearance stages and will be distributed to ACD staff in early CY90. Two ACD groups have issued QA Plans to supplement the manual; four other plans are in draft stages.

The use of Quality Circles to identify and resolve problems was reinstated during CY88. The quality circle concept, coupled with performance improvement projects (PIP), originally operated as the ACD Quality Council. The name has recently been changed to Analytical Improvement Council (AIC). A charter was approved by division management in April, 1988, and a number of areas identified for follow-up by PIPs. The charter stated that the function of the newly formed ACD Quality Council (now the AIC) is the "study of any issue concerning quality of work, efficiency of work, or methods of improvement." Team members were chosen so that each section and facility in the division would be represented.

PIP projects considered during 1989 were a Central Personal Computer Resource Facility, Standardization of Secretarial PC's, and Investigation of Provisions for Greater Flexibility in Changing Jobs. Some positive results from the projects included 1) installation of a central PC resource room which allows division staff members access to printers, plotters, a LaserJet printer, various PC software packages, and a facsimile machine, 2) standardization of use of some commercially software packages on secretarial PC's, and 3) better communication between the division director and non-supervisory staff members through periodic "Brown Bag Lunch" meetings without the presence of supervisory staff. One team considered the possibility of cross-training people and decided that it should be determined on a case-by-case basis.

The low-level radiochemical analysis laboratory made two improvements in process operations that resulted in considerable time savings and generally more efficient operations. The time required to perform analytical balance operations was reduced by 85% by computer interfacing and the time required to maintain liquid nitrogen Dewars was reduced by 80% by connecting a series of pipes and boxes to a self-pressurized liquid nitrogen holding tank.

A cost savings was realized through the actions of two ACD chemists aided by ACD quality assurance personnel. The chemists wrote specifications for an inductively coupled plasma/mass spectrometry (ICP/MS) instrument which was going to be leased. The specifications were reviewed by the QA specialist and a QA checklist prepared. Purchase specifications were written to include provisions for a vendor surveillance and a technical performance demonstration. Upon visiting the manufacturing plant, the chemists presented a QA checklist to the vendor, who provided appropriate documentation, including documentation of nonconformances during construction and corrective actions. However, the instrument did not meet technical performance expectations. This failure resulted in the chemists' declining to accept the instrument until all problems were corrected and acceptable performance demonstrated and documented.

ACD groups are continuing to identify needs for standard operating procedures (SOPs). An enhanced system for division document control has been initiated which promotes a more systematic and disciplined approach to distribution and control. Previously developed SOPs and standard analytical methods (SAMs) are being refined and written to conform to NQA-1-type format. Many SOPs are being combined for a division-wide application as opposed to a group approach which resulted in too much duplication.

A Quality Assurance/Quality Control bulletin board has been erected in R-corridor of Building 4500 South to inform ACD staff of upcoming activities, availability of reports, results of performance evaluations, and other quality-related events.

Quality Assurance and Quality Control staff members participated in twelve training courses and also served as instructors themselves in several training sessions. The QA Coordinator presented an invited seminar on QA to a group at Argonne National Laboratory on the subject of developing an NQA-1 QA Program. The Quality Control Officer and a chemist did a data quality and usability review on 1500 samples from the Department of Energy (DOE) Environmental Survey Program.

Database tracking systems were installed for tracking standard operating procedures, inventory of quality control and reference materials, and external reviews and evaluations of ACD work (both technical support and research and development).

A total of 20 quality assurance audits, surveillances, and reviews took place in ACD laboratories and facilities. Of the 20, three were customer-sponsored audits or reviews, two were ORNL audits, two were internal audits, and two were radioactive operations reviews. There were 11 surveillances; nine internal and two associated with ORNL Isotope Generation and Depletion (ORIGEN) Code Verification Program activities.

Quarterly and monthly quality control (QC) solutions continued to be provided to ACD inorganic, organic and radiochemical analysis laboratories. Monthly inorganic control solutions were purchased from Analytical Products Group (APG), Belpre, Ohio and submitted as blinds. Results were reported to APG and statistically evaluated with 30-plus laboratories throughout the country. All DOE analytical chemistry laboratories operated by Martin Marietta Energy Systems, Inc. participate in this monthly program. Of the 539 results reported January through November, 1989, 98% have been acceptable. During the last quarter of CY89, the ACD organic group also participated in this program on a trial basis in order to accumulate a database on organic analysis. APG plans to offer organic controls for purchase in 1990.

Laboratories performing environmental compliance analyses continued to participate in Environmental Protection Agency (EPA) administered performance evaluation (PE) programs in addition to the internally-administered ones. The average score for two inorganic PE sets was 85.2% (out of a possible 100%). The average score for three organic PE sets for the same period was 78.3%. The low-level radiochemical laboratory scored an average of 91.4% for 31 parameters in four matrices and 94.3% on round robin soil samples from the Environmental Measurements Laboratory. Additional "water pollution" QC samples were submitted quarterly and annually to the laboratories to monitor other inorganic measurements not covered by the PE sets. A score of "Acceptable" was received for all such sets.

A cooperative program was established between ACD Quality Control and two customers in the Environmental and Health Protection Division in which quality control samples were prepared by the QC Officer, given to the customer and the customer submitted the "double blind" samples with routine environmental samples. The "double blind" samples were coded such that the QC Officer was able to access and evaluate the data. A total of 303 double blind samples were analyzed, 87% had recoveries of 80% or greater.

Quality Control summaries for the ACD QC program were not available because of the changeover to the Analytical Laboratory Information System (AnaLIS) data management system. Software to summarize and generate reports is under development.

(W. R. Laing, S. K. Holladay, C. E. Higgins)

---

*ORNL Quality Department

SAFETY PROGRAM

S. D. Wright

A Safety Action Plan was implemented as a guide toward better safety in the Analytical Chemistry Division during 1989. The Division experienced five (5) first aid cases against seven (7) 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 reporting period:

1. Safety Meetings held: 44; total attendance: 814.
2. Training Guide updates for our facilities at building 2026 and 7920 continue.
3. Spring Clean-up week activities in May included fire training at building 2026 and 4500N.
4. Special Seminars relating to Technical Safety Appraisals were given.
5. Monthly safety meetings at Building 2026 were implemented.
6. Nineteen operational safety summaries for ACD laboratory operations were documented.

As a result of DOE's Technical Safety Appraisal and 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.

This division continues to maintain a high level of safety awareness and accident prevention among our personnel as evidenced by a superior performance rating this year.

TRAINING

M. P. May

Our training function, goals, and responsibilities have continued to expand during 1989. Training, in some capacity, has become a part of everything we do. Many changes have occurred on the corporate, plant, and division levels.

Martin Marietta Energy Systems training methodology is based upon performance-based training (PBT), providing employees with the knowledge, skills, and ability necessary to perform their assigned tasks. This corporate methodology is being adopted throughout the Energy Systems sites and will become our model approach to training.

Energy Systems held the first "Martin Marietta Energy Systems Training Conference" in September, 1989. It brought together, on a large scale and for the first time, people from all levels of training at DOE, Martin Marietta, MM Energy Systems, and field offices. The conference included invited talks (one by the ACD training coordinator), workshops, and breakout sessions covering the technical, management, philosophy, and regulatory aspects of training. Due to its success the conference will be held on an annual basis.

Energy Systems has created several new positions: Martin Marietta Training Director (Charles Emery), MMES Technical Training Manager (Duane Hymer), and ORNL Technical Training (Al Officer). This will provide more structure and support for training efforts. To respond on a plant site to the DOE Training Accreditation Order, MMES created a Training Accreditation Steering Committee comprised of divisional representatives for the affected facilities (W. D. Shults is the ACD representative).

The MMES Technical Training Committee, whose function is to share training resources among the 5 sites, created several subcommittees during 1989 to focus on specific training concerns (industrial safety, radiation safety, mobile equipment, etc.) The Analytical Laboratory Subcommittee deals with sharing training resources between the analytical laboratories at each site; Melanie May is the ORNL representative. The subcommittee has already shared many lesson plans, training program plans, on-the-job training checklists, etc. One of the major action items of the subcommittee for FY90 is to develop a laboratory analyst general certification program.

Within ACD, training at our non-reactor nuclear facilities has undergone significant change and growth. At HRLAL, J. L. Botts took over as facility manager in June. He assigned the laboratory group responsibilities to D. E. Dihel. Together they are reworking the HRLAL training program to more closely meet the needs of those working there. The Facility Orientation Training Course, covering facility operating rules, safety guidelines, and emergency preparedness, is now offered in several different formats to accommodate laboratory personnel, facility nuclear operators, maintenance and craft personnel, visitors, and temporary personnel. They have completed a facility/group QA plan which is now in the review stages. The training program for both the facility and the group has been reviewed and rewritten. They are currently writing and updating both analytical methods and standard operating procedures.

The Transuranium Analytical Laboratory (TAL) at the Radiochemical Engineering Development Center acquired J. M. Keller as the new group leader in June. He has continued to implement and update the formal, documented training program for all laboratory personnel begun by the previous staff. (See ACD Annual Report for 1989, ORNL-6606, Chapter 2, "Transuranium Analytical Laboratory", for a more detailed description of training efforts at TAL).

DOE Training Accreditation Order 5480.18 spells out new and more stringent requirements for training at selected DOE facilities. The ACD has employees working at both of the selected ORNL facilities: REDC and HFIR. (See ORNL-6606, Chapter 2, for Training Accreditation Program requirements). With the signing of the order in November 1989 by Secretary Watkins, the affected facilities will now have 3 years to develop and put in place a fully accreditable training program based upon the TAP requirements and PBT. A training process review was completed in November for HFIR and REDC, and revealed our deficiencies against accreditation standards. For FY90, ACD will have to set forth a Training Program Accreditation Plan (TPAP) and complete job/task analyses. To assist and manage the TPAP development process, these facilities were assigned TPAP Program Element Coordinators, with W. D. Shults (Mike Guerin- substitute) having that responsibility for ACD. Melanie May attended both the DOE Training Accreditation Workshop in May and the PBT- Design Phase Course held in June so that we will better understand the TPAP requirements, how they apply to ACD, and to learn the PBT methodology needed to respond. These training programs rely heavily on a solid QA/QC program base, so during FY90 we will be conducting an internal QA Audit of our non-reactor nuclear training programs. At the current time, HRLAL Facility is not on the DOE current list of selected facilities to be accredited, but that could change in the future.

ACD has completed the 3 planned sessions of the "Illegal Substance Abuse Awareness Program" to be given to all employees before Dec. 31,1989. The program was deemed highly effective and successful both by division employees and plant-wide personnel.

ACD also purchased a computer authoring system called "Course Builder", which has the capability to allow programmed instruction with voice overlay. Future plans include developing a course of instruction using this computer based training technique. Together with instructional design experts from ORAU, a proposal was presented to the Office of Operational Safety on "Developing/Implementing an Interactive Video Computer Based Training System on Emergency Preparedness, Alarms and Evacuation for Workers at 2026 (Hot Cell Facility)".

(M. P. May, J. M. Keller, J. L. Botts)

7. SUPPLEMENTARY ACTIVITIES

The division maintains liaison with the academic community through its Advisory Committee, consultants, and various ORNL and ORAU programs. We also make facilities available for student and faculty research and training programs.

ADVISORY COMMITTEE

The 1989 Advisory Committee was composed of:

D. D. Bly, Central Research Department, DuPont Experimental Station, Wilmington, DE.
R. G. Cooks, Chemistry Department, Purdue University, West Lafayette, IN.
J. C. Giddings, Department of Chemistry, University of Utah, Salt Lake City, UT.
E. D. Pellizzari, Research Triangle Institute, Research Triangle Park, NC.

CONSULTANTS

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

R. R. Meglen, University of Colorado, Denver, CO.
S. Arnold, Polytechnic University, Brooklyn, NY.
A. C. Schaffhauser, Metals & Ceramics Division, ORNL, Oak Ridge, TN.
M. Poslusny, North Texas State University., Denton, TX.
R. D. MacFarlane, Texas A&M University, College Station, TX.
D. M. Schrader, Marquette University, Milwaukee, WI.
R. M. Barnes, University of Massachusetts, Amherst, MA.
J. S. Morris, University of Missouri, Columbia, MO.
A. J. Boyer, University of Nevada, Las Vegas, Las Vegas, NV.
D. F. Hunt, University of Virginia, Charlottesville, VA.
Y. R. Shen, University of California, Berkeley, Berkeley, CA.
A. P. Toste, Southwest Missouri State University, Springfield, MO.
J. C. Wright, University of Wisconsin, Madison, WI.
C. B. Boss, North Carolina State University, Raleigh, NC.
J. A. Leary, University of California, Berkeley, Berkeley, CA.
R. K. Marcus, Clemson University, Clemson, SC.

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

G. Mamantov, University of Tennessee, Knoxville.

A. G. Marshall, Ohio State University, Columbus, OH.

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

L. B. Rogers, University of Georgia, Athens, GA.

F. H. Field, Camille & Henry Dreyfus Professor, Oak Ridge, TN.

EDUCATION PROGRAMS

John Dale and Debra Bostick served as University Relations Coordinators for student guests and faculty during 1989.

OAK RIDGE ASSOCIATED UNIVERSITIES PROGRAMS

Postgraduate Research Programs. Perry R. Blazewicz (Yale University) completed his research in laser and microwave spectroscopy with Mike Ramsey and Bill Whitten in the Analytical Spectroscopy Section.

Brian T. Buckley (North Carolina State University) began working with Mike Ramsey to develop a plasma source for multiphotoionization spectroscopy.

Brian A. Eckenrode (Michigan State) is pursuing research development projects in mass spectrometry/mass spectrometry with Gary Glish and Scott McLuckey.

Eric Kerley (Texas A&M) has begun research in the development of an external ionization source for FTMS to enable investigation of high molecular weight biomolecules with Michelle Buchanan.

ORAU Graduate Student Research Program. Rick A. Flurer (Indiana University) is working with Gary Glish and Scott McLuckey in the area of organic mass spectrometry.

ORAU Laboratory Graduate Participation Program. Jocelyn Dunphy (Indiana University) is working with Michelle Buchanan in the investigation of laser desorption Fourier transform mass spectroscopy for detection and characterization of trace levels of biological molecules isolated on chromatographic plates.

ORAU Faculty Research Program. Subrahmanyam Pendyala (SUNY, Fredonia) returned for the summer to continue his work with Dave Smith and Lester Hulett on positron spectroscopy.

Elizabeth A. Stemmler (Bowdoin College) began collaborative research in gas-phase ion chemistry and isomeric differentiation using mass spectrometry.

John A. Howell (Earlham College) returned to continue laser spectroscopy research with Mike Ramsey.

ORAU Faculty Research Program for Historically Black Colleges and Universities. Wedad Hussein, an associate professor at Jackson State University, worked with Ted Mueller in the Chemical and Physical Analysis Group on R&D projects in the field of electroanalytical chemistry.

SUMMER INTERN PROGRAM

Summer Intern Program. The division hosted several participants in the summer intern program.

Steve Lyle, Southern Arkansas University, with C.-h. Ho studied labeling techniques for HPLC determination of DNA-aromatic amine adducts.

C. Wayne Lyle, Southern Arkansas University, participated in chromatographic research on DNA adducts with Michelle Buchanan.

Joseph G. Louderback, Davidson College, studied atomic spectroscopy using semiconductor diode lasers with Bob Shaw.

David P. Moore, Gustavus Adolphus College, worked with W. B. Whitten in the study of resonance-enhanced laser ionization of atoms and molecules.

Robert J. Shine, Harvard University, participated in the study of HPLC separation and enrichment of trace constituents in DNA with Rose Ramsey.

CO-OP PROGRAM

Co-Op Program. Jamie McKinney continued her co-op assignment with Jeff Wade in the low-level radiochemical analysis group.

UNIVERSITY OF TENNESSEE PROGRAM

Distinguished Scientist Program. Dr. Georges Guiochon is continuing his work through the University of Tennessee/ORNL Distinguished Scientist Program. Post-docs Mark L. Aubel, University of Georgia, Eric Dose, Rice University, and Martin Czok, University of Tennessee, and predoctoral students, Jennifer Schudel, Anita Katti, and Jeffry Knoles are continuing their work at ORNL. An additional post-doc, Mohammed El Fallah, University of Tennessee, has been added to Dr. Guiochon's staff.

Postgraduate Research Program. Gary J. VanBerkel (Washington State University) completed his assignment in the Analytical Spectroscopy Section.

Casey Grimm (Florida State University) is continuing his research of organic secondary ion emission with Peter Todd.

R. T. Short (University of Tennessee) began his participation in NIH-funded research with Peter Todd.

Predoctoral Program. Michael R. Troutman (Indiana University, University of Tennessee) is working with Gary Glish on QEB instrument development and application.

SCIENCE TEACHERS RESEARCH INVOLVEMENT FOR VITAL EDUCATION (STRIVE)

Charlotte M. Stockton, Dyersburg High School, worked with Harley Ross on the development a new technique for the detection of ^{129}I in the environment.

TEACHER RESEARCH ASSOCIATES PROGRAM

Judy L. Wayman, Knox County Schools, investigated novel mass spectrometric techniques for analysis of trace organics with Michelle Buchanan.

PATENTS

Marcus B. Wise and Michelle V. Buchanan were granted two patents in 1989, "Multiplexed Electronically Programmable Multimode Ionization Detector for Chromatography" and "Variable Pressure Ionization Detector for Gas Chromatography."

INTERNATIONAL CONFERENCE ON NEW TRENDS IN LIQUID SCINTILLATION COUNTING AND ORGANIC SCINTILLATORS

This conference was co-sponsored by the Analytical Chemistry Division of ORNL and the Center for Applied Isotope Studies of the University of Georgia. Held in Gatlinburg, Tennessee, October 2-5, 1989, the organizing committee was composed of Harley Ross of ACD, and John Noakes and Jim Spaulding of the University of Georgia. Attendance was over 200 with 13 foreign countries represented. Papers were presented in seven sessions. Proceedings of the conference will be published in 1990.

ORNL/DOE CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

The 31st Annual Conference was held in Gatlinburg at the Riverside Motor Lodge, October 10-12, 1989. The theme of the conference was "Technology for Today's Challenges". Attendance was 256, with representatives from foreign countries, academia, industrial institutions, DOE contractors, and other government agencies. There were 19 exhibits (38 vendor representatives). Major topics included new ideas in mass spectrometry, mathematical solutions to analytical problems, applications of plasma mass spectroscopy, recent development in field monitoring, novel methods for trace analysis, and interactive analytical seminars.

A. L. Harrod and S. D. Wright were Arrangements Chairmen, W. R. Laing was Technical Program Chairman, and R. K. Bain was Treasurer. S. D. Cates and R. L. Williams were Conference secretaries. Other conference committee members were J. S. Jessup (INEL), R. W. Morrow (ORGDP), W. H. Christie, J. S. Eldridge, R. L. Hettich, W. D. Shults, and D. H. Smith.

SEMINAR PROGRAM

Speaker	Title	Date
R. R. Meglen Ctr. for Env. Science, Univ. of Colorado, Denver, CO.	"Chemometrics in the Analytical Laboratory"	Jan. 13, 1989
S. Arnold Dept. of Physics Polytechnic Univ., Brooklyn, NY	"Fluorescence Spectroscopy and Energy Transfer in Microparticles"	Jan. 17, 1989
A. C. Schaffhauser Metals & Ceramics Div., ORNL Oak Ridge, TN	"High Temperature Superconductivity Pilot Center Program"	Jan. 23, 1989
M. Poslusny North Texas State Univ., Denton, TX	"Analysis of PAH and PCB Emissions from the Combustion of Densified Refuse Derived Fuels"	March 29, 1989
R. D. MacFarlane Chemistry Dept., Texas A&M Univ., College Station, TX	"The Use of Nuclear Fission as a Probe in Analytical Chemistry"	April 26, 1989
D. M. Schrader Marquette Univ., Milwaukee, WI	"Theory of Positron Chemistry"	May 1, 1989
R. M. Barnes Chemistry Dept., Univ. of Massachusetts, Amherst, MA	"Inductively-Coupled Plasma Mass Spectrometry--Basics and Applications"	June 23, 1989
J. S. Morris Res. Reactor Facility Univ. of Missouri, Columbus, MO	"Application of Neutron Activation Analysis to Epidemiological Studies"	Aug. 18, 1989
A. J. Boyer Univ. of Nevada, Las Vegas, NV	"Applications of Mass Spectrometry to Environmental Problems"	Aug. 21, 1989
D. F. Hunt Chemistry Dept., Univ. of Virginia, Charlottesville, VA	"Protein Sequence Analysis by Mass Spectrometry: New Techniques and Instrumentation"	Oct. 9, 1989
A. P. Toste Southwest Missouri State Univ., Springfield, MO	"Environmental Behavior of Organoradionuclides"	Oct. 13, 1989

J. A. Leary College of Chemistry, Univ. of California, Berkeley, CA	"MS/MS of Lithium Cationized Peptides: Mechanism of Ion Formation and Sequencing Strategies"	Nov. 2, 1989
J. C. Wright Chemistry Dept., Univ. of Wisconsin, Madison, WI	"New Chemical Measurement Capabilities with Non-Linear Laser Spectroscopy"	Nov. 10, 1989
C. B. Boss Chemistry Dept., North Carolina State Univ., Raleigh, NC	"Use of the Electrical Characteristics of a Microwave Plasma as a Gas Chromatography Detector"	Dec. 1, 1989
R. K. Marcus Clemson University Clemson, SC	"Glow Discharge Mass Spectrometry: New Sources, Analyzers, and Applications"	Dec. 6, 1989
Y. R. Shen Physics Dept., Univ. of California Berkeley, CA	"Some Recent Experiments of Surface Studies by Nonlinear Optics"	Dec 18, 1989

AWARDS AND HONORS

Michelle Buchanan received the Martin Marietta Technical Achievement Award. She also was named to the Editorial Board of Organic Mass Spectrometry.

Bob Hettich was elected treasurer of the East Tennessee Section of the American Chemical Society.

Pat Trentham, Gail Vineyard, and Debbie Blazier received the President's Award for Performance Improvement for the Standardization of Secretarial Computers in the Analytical Chemistry Division.

ADDITIONAL PROFESSIONAL ACTIVITIES

Asano, K. G.

ACD Representative: Carcinogen Control Program at Y-12

Baxter, T. L.

Member: ACD Quality Circle

Bostick, D. A.

ACD Representative: University Relations Coordinator

Buchanan, M. V.
Editorial Board: *Biomedical and Environmental Mass Spectrometry*
Organic Mass Spectrometry
Treasurer: American Society for Mass Spectrometry
Advisory Board: National Science Foundation, Biological Centers Program
Chairman: East Tennessee Mass Spectrometry Discussion Group
Member: Martin Marietta Energy Systems Advisory Committee for Values
ORNL Values Committee

Carter, J. A.
Advisory Panel Member: DOE/ISA Laboratory Advisory Group for Effluent Research (LAGER)
Laboratory Coordinator: ISPO Programs

Ceo, R. N.
Chairman: Brown Bag Committee
Member: ACD Seminar Committee

Christie, W. H.
Member: Technical Program Committee, 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology

Dale, J. M.
ACD Representative: University Relations Coordinator

Eldridge, J. S.
Chairman: Membership Committee, Environmental Radiation Section of the Health Physics Society
ACD Quality Circle
Member: Oak Ridge Reservation–Resource Management Organization: Environmental Surveillance
Lab Committee 8 of the International Society for the Methods of Air Sampling and Analysis

Emery, J. F.
ACD Representative: Laboratory Emergency Sample Coordinator
Division Computer Systems Security Officer

Feldman, C.

Fellow: American Society for Testing and Materials

Member: ASTM Committee E-2 on Emission Spectroscopy, Subcommittees on Fundamental Methods, Editorial Practices, and Nomenclature

Ferguson, N. M.

ACD Representative: Energy Systems Environmental Analysis Committee

Glish, G. L.

Associate Editor: *Journal of the American Society for Mass Spectrometry*

Consultant: Finnigan MAT, San Jose, CA

Member: Board of Directors, Asilomar Conference on Mass Spectrometry

ORAU Travelling Lecture Program

Vice-President: American Society for Mass Spectrometry

Griest, W. H.

Consultant: Department of Energy - SBIR Review

Department of Energy - BES

Electric Power Research Institute

Environmental Protection Agency - IERL/TSO

Center for Indoor Research

Guerin, M. R.

Member: Univ. of Kentucky, Tobacco and Health Research Institute Advisory Board

Consultant: SBIR Reviews, DOE, NCI

PHS/Office Smoking and Health Additives

Guiochon, G. A.

Associate Editor: *Analytical Chemistry*

Organizer: 6th International Symposium on Preparative Chromatography, Washington, DC, May 8-10, 1989

Member: Permanent Committee of the International Symposia on Column Liquid Chromatography, HPLC

Board of the Chromatography Subdivision of the Analytical Chemistry Division of ACS

Advisory Boards: *Journal of Chromatography*

Journal of Chromatographic Science

Journal of Liquid Chromatography

Guiochon, G. A.		
	Advisory Boards:	*Chromatographia*
Hettich, R. L.		
	Chairman:	ACD Seminar Committee
	Member:	ORAU Traveling Lecture Program
		Organizing Committee, 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology
Higgins, C. E.		
	Chairman:	ACD Analytical Improvement Council
Holladay, S. K.		
	Member:	ASTM Committee D-34
Howell, P. L.		
	Member:	ASTM C-26 Nuclear Fuel Cycle
		ASQC Energy Division
Ilgner, R. H.		
	ACD Representative:	ACD Environmental Protection Officer
	Consultant:	Fourth Judicial District Court, Monroe, LA
Jenkins, R. A.		
	Consultant:	Federal Trade Commission, Standardized Smoking Practices
		National Institute on Drug Abuse - SBIR Reviews
Jeter, K. O.		
	Member:	ACS Analytical Improvement Committee
Klatt, L. N.		
	Member:	Energy Systems Ph.D. Recruiting Team
		ACD Seminar Committee
Laing, W. R.		
	Chairman:	ASTM Committee C-26, Nuclear Fuel Cycle
	Coordinator:	ACD Quality Assurance Program
		ACD Energy Conservation Program

Laing, W. R.

Fellow:	American Society for Testing and Materials
Member:	ASTM Committee D-33, Protective Coatings
Member:	ASTM Committee D-34, Waste Disposal
	ISO Technical Committee 85, Subcommittee 5
	ORNL Pregrievance Committee
Technical Program Chairman:	31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology

Maskarinec, M. P.

Member:	EPA Working Group on Improvement of TIC Identification

May, M. P.

ORNL Representative:	MMES Technical Training Subcommittee on Analytical Laboratories (Interim Chairman July-Nov.)
Member:	MMES (5-plant) Training Process Review Team
	ACD - Division Training Coordinator
	ACD - Facility 9735 Generator Certification Officer (GCO)

McLuckey, S. A.

Chairman:	Ion Physics and Instrumentation Interest Group, American Society for Mass Spectrometry
Consultant:	Finnigan MAT, San Jose, CA

Ramsey, J. M.

Chairman:	ACS Program Committee of Division of Analytical Chemistry
Editorial Advisory Board:	*Progress in Analytical Spectroscopy*
Member:	Martin Marietta Energy Systems Publication Award Selection Committee

Ramsey, R. S.

Member:	ACD PhD Recruiter
	ORAU Travelling Lecture Program
Consultant:	National Cancer Institute - SBIR Reviews
	Center for Indoor Air Research

Robinson, L.

Member:	ASTM Task Group on Nuclear Methods of Chemical Analysis

Robinson, L.

Co-organizer:	Special Meeting entitled "Analytical Chemists and the Other ANS: The Advanced Neutron Source" for annual meeting of American Nuclear Society, San Francisco, CA, November 26-December 1, 1989
Session Moderator:	1st Southeast Regional Conference of NOBCCHE, Knoxville, TN, Feb. 16-18, 1989

Ross, H. H.

Advisory Board:	*Journal of Radioanalytical and Nuclear Chemistry*
Conference Organizer:	International Conference on New Trends in Liquid Scintillation Counting and Organic Scintillators, Gatlinburg, TN, October 2-5, 1989
Consultant:	Savannah River Site, Aiken, SC
	GPU Nuclear, Three Mile Island, Unit-2, Middletown, PA
Editorial Board:	*Journal of Radioanalytical and Nuclear Chemistry, Letters*
Faculty Member:	Dept. of Chemistry, University of Tennessee, Knoxville (Adjunct Professor, Science Alliance)
Member:	Advisory Committee: International Conference on Liquid Scintillation Science and Technology
	ACS Fellowship Committee, Division of Analytical Chemistry

Rosseel, T. M.

Vice-President:	American Vacuum Society (AVS) Tennessee Valley Chapter (TVC)
Member:	AVS Tennessee Valley Chapter, Scholarship Committee
	X-90 Organizing Committee (15th International Conference on X-ray and Inner Shell Processes), Knoxville, TN, July 9-13, 1990
Treasurer:	AVS Tennessee Valley Chapter
	9th Annual TVC-AVS Symposium & Equipment Exhibit

Shaw, R. W.

Member:	ACD Quality Circle
	Chemical Dispensing Station PIP Committee

Shults, W. D.

Chairman:	ORNL Division/Program Directors Caucus
	Education Committee, ACS Division of Analytical Chemistry
Chairman-Elect:	East Tennessee Section, ACS
Member:	Board of Visitors, Chemistry Department, UT-K
	MMES Analytical Managers Council

Shults, W. D.

Member:	Advisory Committee, Chemistry and Laser Science Division, Los Alamos National Laboratory
	MMES Awards Night Committee (Administrative Support)
	MMES Job Evaluation Committee
	Review Committee, *Analytical Chemistry*
	DOE Analytical Managers Group

Smith, D. H.

Member:	Technical Program Committee, 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology
	ASMS Isotope Ratio Interest Group

Stewart, J. H., Jr.

Member:	ASTM Committee D-34, Waste Disposal
	International Working Group, "Analytical Standards of Minerals, Ores, and Rocks"
	ASTM C-26 Nuclear Fuel Cycle Committee
ACD Coordinator:	Technician Advisory Group

Stokely, J. R.

Chairman:	DOE Site Survey Program RAD Committee
	DOE Technical Safety Appraisal Team
Member:	Future Analytical Support Task Group

Todd, P. J.

Consultant:	National Institutes of Health - General Medicine
	National Institute of Mental Health
Coordinator:	ACD Awards
Secretary:	East Tennessee Mass Spectrometry Discussion Group

Tomkins, B. A.

Member:	ACD Seminar Committee

Wade, J. W.

Site Representative:	Multi-Plant Analytical Committee
	Multi-Plant Procedure Committee

Wise, M. B.
Member: ACD Safety Committee
ORAU Traveling Lecture Program
Judge: Southern Appalachian Science & Engineering Fair, Knoxville, TN

Young, J. P.
ACD Representative: Graduate Fellow Selection Panel, ORNL
Fellow: American Association for the Advancement of Science

Young, J. P.
Member: ACS Program Advisory Committee, Division of Nuclear Chemistry & Technology
Organizer: Symposium on "Lasers in Nuclear Chemistry and Technology", National ACS Meeting, April 1990, Boston, MA

8. 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 non-nuclear energy, new instrumentation and its application, and environmental problems such as monitoring and clean up at ORNL and elsewhere. The multidisciplinary approach required in many such problems is indicated by the number of papers and talks coauthored by members of other ORNL divisions and outside organizations. Such persons are designated by an asterisk.

PUBLICATIONS

Contributions to Books and Proceedings

AUTHOR	AUTHOR, TITLE, AND WHERE PUBLISHED
Asano, K. G.	Glish, G. L.; Van Berkel, G. J.; Asano, K. G.; and McLuckey, S. A., "Multiple Stages of Mass Spectrometry with an Ion Trap," *Advances in Mass Spectrometry, 11A*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 272.
	Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Daughter Ion Formula Determinations by MS^n Experiments on Naturally Occurring Isotopes," *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, May 21-26, 1989, p. 464.
	Goeringer, D. E.; Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Applications of Laser Desorption in an Ion Trap Mass Spectrometer," ibid, p. 1260.
	Glish, G. L.; Asano, K. G.; and McLuckey, S. A., *Daughter Ion Formula Determination by MS^n Experiments on Naturally Occurring Isotopes*, Finnigan MAT Technical Report No. 614, 1989, p. 13.

Buchanan, M. V.	Hettich, R. L.; Buchanan, M. V., "Structural Characterization of DNA Adducts Using Fourier Transform Mass Spectrometry," *Proceedings, DOE Contractor's Meeting on Chemicals with Living Systems*, Albuquerque, NM, November 17-18, 1988, CONF-8811202, p. 56. Hettich, R. L.; Buchanan, M. V., "Laser Ionization Fourier Transform Mass Spectrometry for the Isomeric Differentiation of Alkylated Nucleosides," *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, May 21-26, 1989, p. 86. Stemmler, E. A.;* Buchanan, M. V., "Surface-Catalyzed Reactions of Aromatic Amines with Oxygen and Nitrogen in NICI Mass Spectrometry," ibid, p. 387. Wise, M. B.; Buchanan, M. V.; Ilgner, R. H., "Detection of Trace Organics in Air Using Thermal Desorption ITMS," ibid, p. 1435. Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Detection and Characterization of Fossil-Derived Fuels in Water and Soil Using Direct Purge Ion Trap Mass Spectrometry," ibid, p. 1402. Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Volatile Organics in Water and Soil Using Direct Purge into an ITMS," ibid, p. 1484.
Christie, W. H.	Christie, W. H., "Solids Analysis via Glow Discharge Mass Spectrometry," ibid, p. 1139. James, R. B.* and Christie, W. H., "Pulsed Carbon Dioxide Laser Processing of Thin Ion-Implanted Silicon Layers," *Proceedings of Intl. Conf. on Lasers*, Lake Tahoe, NV, 1989, p. 745.
Dale, J. M.	Hsu, F.*; Shao, M. J.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Surface Effects on Positron Annihilation Characteristics in Cab-O-Sil (SiO_2)," *Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 840.
Donohue, D. L.	Hulett, L. D., Jr.; Lewis, T. A.*; Donohue, D. L.; and Pendyala, S.*, "The Oak Ridge National Laboratory Slow Positron Source," ibid, pp. 586-588.

Donohue, D. L.

Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Hulett, L. D., Jr.; McKown, H. S.; and Pendyala, S.*, "Positron Ionization Mass Spectrometry," ibid, pp. 612.

Lewis, T. A.*; Hulett, L. D., Jr.; and Donohue, D. L., "The Extraction of LINAC-Generated Slow Positrons Using the Single Gap Accelerator Technique," ibid, pp. 589-591.

McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D., Jr.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 22.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.

Eckenrode, B. A.

Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., "Negative Ion Chemical Ionization in an Ion Trap Mass Spectrometer Using Reagent Anions Injected from an External Ion Source," ibid, p. 462.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.

Eckenrode, B. A.; McLuckey, S. A.; and Glish, G. L., "Ion Trajectory Modelling in an Ion Mobility Spectrometer Employing Nonlinear Electric Fields," ibid, p. 1094.

Eckenrode, B. A.; Glish, Gary L.; and McLuckey, S. A., *Negative Ion Chemical Ionization in an Quadrupole Ion Trap Using Reagent Anions Injected from an External Ion Source*, Finnigan MAT Technical Report No. 614, 1989, p. 7.

Flurer, R. A.

Flurer, R. A.; McLuckey, S. A.; and Glish, G. L., "Structures and Energetics of NO_3^- Formed in a Glow Discharge Ionization Source," *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 335.

Glish, G. L.

Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Hulett, L. D., Jr.; McKown, H. S.; and Pendyala, S.*, "Positron Ionization Mass Spectrometry," *Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 612.

Glish, G. L.

Glish, G. L.; Van Berkel, G. J.; Asano, K. G.; and McLuckey, S. A., "Multiple Stages of Mass Spectrometry with an Ion Trap," *Advances in Mass Spectrometry, 11A*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 272.

Glish, G. L. and McLuckey, S. A., "Scan Modes for Hybrid Mass Spectrometers," ibid, p. 274.

Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Selected Reagent Ion Chemical Ionization Using an Ion Trap," ibid, p. 596.

Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Analysis of Porphyrins by Mass Spectrometry," *Advances in Mass Spectrometry, 11B*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 1656.

McLuckey, S. A.; Glish, G. L.; and Grant, B. C., "Explosives Detection with an Ion Trap Mass Spectrometer," *Proceedings of the Third Symposium on Analysis and Detection of Explosives*, Mannheim-Neuostheim, July 10-13, 1989, FRG, p. 25-1.

Conrad, F. J.*; Hannum, D. W.*; Grant, B. C.; McLuckey, S. A.; and Glish, G. L., "The Evaluation of the Oak Ridge MS/MS Explosives Detector," ibid, p. 35-1.

McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 22.

Glish, G. L. and McLuckey, S. A., "Direct Air Monitoring Using an Ion Trap Mass Spectrometer," ibid, p. 77.

Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Charge Separation and Electron Capture Induced Dissociation of Doubly Charged Porphyrin Ions," ibid, p. 234.

Flurer, R. A.; McLuckey, S. A.; and Glish, G. L., "Structures and Energetics of NO_3^- Formed in a Glow Discharge Ionization Source," ibid, p. 335.

Glish, G. L.

Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., "Negative Ion Chemical Ionization in an Ion Trap Mass Spectrometer Using Reagent Anions Injected from an External Ion Source," ibid, p. 462.

Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Daughter Ion Formula Determinations by MS^n Experiments on Naturally Occurring Isotopes," ibid, p. 464.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.

Van Berkel, G. J.; Tuinman, A. A.*; Glish, G. L.; and McLuckey, S. A., "Porphyrin Pyrrole Sequencing by Low Energy Collision Induced Dissociation of $(M+7H)^+$ Generated in situ During Ammonia Chemical Ionization," ibid, p. 796.

McLuckey, S. A. and Glish, G. L., "The Role of Mass Spectrometry in the Analysis of Explosives," ibid, p. 806.

Grant, B. C.; McBay, E. H.; McLuckey, S. A.; and Glish, G. L., "High Resolution Daughter Ion Analysis Applications in Hybrid Mass Spectrometry," ibid, p. 1029.

Eckenrode, B. A.; McLuckey, S. A.; and Glish, G. L., "Ion Trajectory Modelling in an Ion Mobility Spectrometer Employing Nonlinear Electric Fields," ibid, p. 1094.

Goeringer, D. E.; Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Applications of Laser Desorption in an Ion Trap Mass Spectrometer," ibid, p. 1260.

Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., *Negative Ion Chemical Ionization in a Quadrupole Ion Trap Using Reagent Anions Injected from an External Ion Source*, Finnigan MAT Technical Report No. 614, 1989, p. 7.

Glish, G. L. and McLuckey, S. A., *Direct Air Monitoring Using an Ion Trap Mass Spectrometer*, ibid, p. 11.

Glish, G. L.; Asano, K. G.; and McLuckey, S. A., *Daughter Ion Formula Determination by MS^n Experiments on Naturally Occurring Isotopes*, ibid, p. 13.

Goeringer, D. E.	Goeringer, D. E.; Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Applications of Laser Desorption in an Ion Trap Mass Spectrometer," *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 1260.
Grant, B. C.	McLuckey, S. A.; Glish, G. L.; and Grant, B. C., "Explosives Detection with an Ion Trap Mass Spectrometer," *Proceedings of Third Symposium on Analysis and Detection of Explosives*, Mannheim-Neuostheim, FRG, July 10-13, 1989, p. 25-1.
	Conrad, F. J.*; Hannum, D. W.*; Grant, B. C.; McLuckey, S. A.; and Glish, G. L., "The Evaluation of the Oak Ridge MS/MS Explosives Detector," ibid, p. 35-1.
	Grant, B. C.; McBay, E. H.; McLuckey, S. A.; and Glish, G. L., "High Resolution Daughter Ion Analysis Applications in Hybrid Mass Spectrometry," *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 1029.
Guerin, M. R.	Guerin, M. R., "Formation and General Characteristics of Environmental Tobacco Smoke," *Combustion Processes and the Quality of the Environment*, J. P. Harper, Ed., Air and Waste Management Association, Transactions Series, 1989, p. 173.
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Detection and Characterization of Fossil-Derived Fuels in Water and Soil Using Direct Purge Ion Trap Mass Spectrometry," *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, May 21-26, 1989, p. 1402.
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Volatile Organics in Water and Soil Using Direct Purge into an ITMS," ibid, p. 1484.
Hettich, R. L.	Hettich, R. L., "Generation and Investigation of Aluminum Cluster Ions, Al_n^- (n = 3-50)," *Ohio State University FT/ICR Newsletter*, Alan Marshall, Ed., Spring, 1989.
	Hettich, R. L., "Structural Examination of Aluminum Cluster Ions, Al_n^-, for n = 3-50," *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, May 21-26, 1989, p. 1510.
	Hettich, R. L.; Buchanan, M. V., "Laser Ionization Fourier Transform Mass Spectrometry for the Isomeric Differentiation of Alkylated Nucleosides," ibid, p. 86.

Hettich, R. L.	Hettich, R. L.; Buchanan, M. V., "Structural Characterization of DNA Adducts Using Fourier Transform Mass Spectrometry," *Proceedings, DOE Contractor's Meeting on Chemicals with Living Systems*, Albuquerque, NM, November 17-18, 1988, CONF-8811202, p. 56.
Hulett, L. D., Jr.	Hsu, F.*; Shao, M. J.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Surface Effects on Positron Annihilation Characteristics in Cab-O-Sil (SiO_2)," *Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 840.
	Hulett, L. D., Jr.; Lewis, T. A.*; Donohue, D. L.; and Pendyala, S.*, "The Oak Ridge National Laboratory Slow Positron Source," ibid, p. 586.
	Lewis, T. A.*; Hulett, L. D.; and Donohue, D. L., "The Extraction of LINAC-Generated Slow Positrons Using the Single Gap Accelerator Technique," ibid, p. 589.
	Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Hulett, L. D.; McKown, H. S.; and Pendyala, S.*, "Positron Ionization Mass Spectrometry," ibid, p. 612.
	Hulett, L. D. and Pendyala, S.*, "The Practicality of High Magnification Imaging by Positron Emission," ibid, p. 617.
	Hulett, L. D. and Pendyala, S.*, "A Theorem for the Determination of Resolution Functions for Positron Lifetime Spectrometry," ibid, p. 620.
	McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D., Jr.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 22.
	Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.
Ilgner, R. H.	Wise, M. B.; Buchanan, M. V.; Ilgner, R. H., "Detection of Trace Organics in Air Using Thermal Desorption ITMS," ibid, p. 1435.
McBay, E. H.	Grant, B. C.; McBay, E. H.; McLuckey, S. A.; and Glish, G. L., "High Resolution Daughter Ion Analysis Applications in Hybrid Mass Spectrometry," ibid, p. 1029.

McKown, H. S.

Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Hulett, L. D., Jr.; McKown, H. S.; and Pendyala, S.*, "Positron Ionization Mass Spectrometry," *Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 612.

McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 22.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.

McLuckey, S. A.

Donohue, D. L.; Glish, G. L.; McLuckey, S. A.; Hulett, L. D., Jr.; McKown, H. S.; and Pendyala, S.*, "Positron Ionization Mass Spectrometry," *Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 612.

Glish, G. L.; Van Berkel, G. J.; Asano, K. G.; and McLuckey, S. A., "Multiple Stages of Mass Spectrometry with an Ion Trap," *Advances in Mass Spectrometry, 11A*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 272.

Glish, G. L. and McLuckey, S. A., "Scan Modes for Hybrid Mass Spectrometers," ibid, p. 274.

Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Selected Reagent Ion Chemical Ionization Using an Ion Trap," ibid, p. 596.

Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Analysis of Porphyrins by Mass Spectrometry," *Advances in Mass Spectrometry, 11B*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 1656.

McLuckey, S. A.; Glish, G. L.; and Grant, B. C., "Explosives Detection with an Ion Trap Mass Spectrometer," *Proceedings of the Third Symposium on Analysis and Detection of Explosives*, Mannheim-Neuostheim, FRG, July 10-13, 1989, p. 25-1.

McLuckey, S. A

Conrad, F. J.*; Hannum, D. W.*; Grant, B. C.; McLuckey, S. A.; and Glish, G. L., "The Evaluation of the Oak Ridge MS/MS Explosives Detector," ibid, p. 35-1.

McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 22.

Glish, G. L. and McLuckey, S. A., "Direct Air Monitoring Using an Ion Trap Mass Spectrometer," ibid, p. 77.

Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Charge Separation and Electron Capture Induced Dissociation of Doubly Charged Porphyrin Ions," ibid, p. 234.

Flurer, R. A.; McLuckey, S. A.; and Glish, G. L., "Structures and Energetics of NO_3^- Formed in a Glow Discharge Ionization Source," ibid, p. 335.

Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., "Negative Ion Chemical Ionization in an Ion Trap Mass Spectrometer Using Reagent Anions Injected from an External Ion Source," ibid, p. 462.

Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Daughter Ion Formula Determinations by MS^n Experiments on Naturally Occurring Isotopes," ibid, p. 464.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; McKown, H. S.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," ibid, p. 584.

Van Berkel, G. J.; Tuinman, A. A.*; Glish, G. L.; and McLuckey, S. A., "Porphyrin Pyrrole Sequencing by Low Energy Collision Induced Dissociation of $(M+7H)^+$ Generated in situ During Ammonia Chemical Ionization," ibid, p. 796.

McLuckey, S. A. and Glish, G. L., "The Role of Mass Spectrometry in the Analysis of Explosives," ibid, p. 806.

Grant, B. C.; McBay, E. H.; McLuckey, S. A.; and Glish, G. L., "High Resolution Daughter Ion Analysis Applications in Hybrid Mass Spectrometry," ibid, p. 1029.

McLuckey, S. A.	Eckenrode, B. A.; McLuckey, S. A.; and Glish, G. L., "Ion Trajectory Modelling in an Ion Mobility Spectrometer Employing Nonlinear Electric Fields," ibid, p. 1094.
	Goeringer, D. E.; Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Applications of Laser Desorption in an Ion Trap Mass Spectrometer," ibid, p. 1260.
	Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., *Negative Ion Chemical Ionization in a Quadrupole Ion Trap Using Reagent Anions Injected from an External Ion Source*, Finnigan MAT Technical Report No. 614, 1989, p. 7.
	Glish, G. L. and McLuckey, S. A., *Direct Air Monitoring Using an Ion Trap Mass Spectrometer*, ibid, p. 11.
	Glish, G. L.; Asano, K. G.; and McLuckey, S. A., *Daughter Ion Formula Determination by MS^n Experiments on Naturally Occurring Isotopes*, ibid, p. 13.
Rosseel, T. M.	Hsu, F.*; Shao, M. J.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Surface Effects on Positron Annihilation Characteristics in Cab-O-Sil (SiO$_2$)," *Proceedings of the 8th Intl. Conf. on Positron Annihilation, Positron Annihilation*, L. Dorikens-Van Praect, M. Dorikens, and D. Seegers, eds., World Scientific Press, 1989, p. 840.
	Datz, S.*; Vane, C. R.*; Dittner, P. F.*; Giese, J.*; del Campo, J. Gomez*; Jones, N. L.*; Krause, H. F.*; Rosseel, T. M.; Schulz, M.*; and Schöne, H.*, "Dielectronic Excitation of Hydrogenic Ions in Crystal Channels," *Proceedings of 16th Intl. Conf. on the Physics of Electronic and Atomic Collisions*, New York, NY, July 26-Aug. 1, 1989, p. 793.
Shaw, R. W.	Smith, D. H.; Young, J. P.; and Shaw, R. W., "Diode Laser Application to Resonance Ionization Mass Spectrometry," *Proceedings of the 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 590.
	Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser-Initiated, Two-Color Resonance Ionization Mass Spectrometry of Lanthanum," *Advances in Laser Science IV: Proceedings of the 4th International Laser Science Conference*, Conf. Proceedings 191, Optical Science & Eng'g. Series 10, American Institute of Physics, Atlanta, GA, 1989, p. 288.

Smith, D. H.	Smith, D. H.; Young, J. P.; and Shaw, R. W., "Diode Laser Applications to Resonance Ionization Mass Spectrometry," *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 590. Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser-Initiated, Two-Color Resonance Ionization Mass Spectrometry of Lanthanum," *Advances in Laser Science IV: Proceedings of the 4th International Laser Science Conference*, Conference Proceedings 191, Optical Science and Engineering Series 10, American Institute of Physics, Atlanta, GA, 1989, p. 288.
Van Berkel, G. J.	Glish, G. L.; Van Berkel, G. J.; Asano, K. G.; and McLuckey, S. A., "Multiple Stages of Mass Spectrometry with an Ion Trap," *Advances in Mass Spectrometry, 11A*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 272. Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Selected Reagent Ion Chemical Ionization Using an Ion Trap," ibid, p. 596. Glish, G. L.; Van Berkel, G. J.; and McLuckey, S. A., "Analysis of Porphyrins by Mass Spectrometry," *Advances in Mass Spectrometry, 11B*, P. Longevialle, ed., Heydon & Son, London, 1989, p. 1656. Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Charge Separation and Electron Capture Induced Dissociation of Doubly Charged Porphyrin Ions," *Proceedings of 37th ASMS Conference on Mass Spectrometry and Allied Topics*, Miami Beach, FL, 1989, p. 234. Van Berkel, G. J.; Tuinman, A. A.*; Glish, G. L.; and McLuckey, S. A., "Porphyrin Pyrrole Sequencing by Low Energy Collision Induced Dissociation of $(M+7H)^+$ Generated In Situ During Ammonia Chemical Ionization," ibid, p. 796.
Wise, M. B.	Wise, M. B.; Buchanan, M. V.; Ilgner, R. H., "Detection of Trace Organics in Air Using Thermal Desorption ITMS," ibid, p. 1435. Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Detection and Characterization of Fossil-Derived Fuels in Water and Soil Using Direct Purge Ion Trap Mass Spectrometry," ibid, p. 1402.

Wise, M. B.	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Volatile Organics in Water and Soil Using Direct Purge into an ITMS," ibid, p. 1484.
Young, J. P.	Smith, D. H.; Young, J. P.; and Shaw, R. W., "Diode Laser Application to Resonance Ionization Mass Spectrometry," ibid, p. 590.
	Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser-Initiated, Two-Color Resonance Ionization Mass Spectrometry of Lanthanum," *Advances in Laser Science IV: Proceedings of the 4th International Laser Science Conference*, Conference Proceedings 191, Optical Science and Engineering Series 10, American Institute of Physics, Atlanta, GA, 1989, p. 288.

Articles

Asano, K. G.	McLuckey, S. A.; Glish, G. L.; and Asano, K. G., "The Coupling of an Atmospheric Sampling Ion Source with an Ion Trap Mass Spectrometer," *Anal. Chim. Acta*, 225, 25 (1989).
	Glish, G. L.; Goeringer, D. E.; Asano, K. G.; and McLuckey, S. A., "Laser Desorption Mass Spectrometry and MS/MS with a Three Dimensional Quadrupole Ion Trap," *Int. J. Mass Spectrom. Ion Processes*, 94, 15 (1989).
Blazewicz, P. R.	Blazewicz, P. R.; Whitten, W. B.; and Ramsey, J. M., "Low-Level Detection of Metal Atoms by Multiphoton Ionization in a Low-Pressure Sampling Cell," *Anal. Chem.*, 61, 1010 (1989).
Buchanan, M. V.	Stemmler, E. A.;* Buchanan, M. V., "Negative Ions Generated by Reactions with Oxygen in the Chemical Ionization Source. I. Characterization of Gas-Phase and Wall-Catalyzed Reactions of Fluorene, Anthracene, and Fluoranthene," *Org. Mass Spectrom.* 24, 94 (1989).
	Stemmler, E. A.;* Buchanan, M. V., "Negative Ions Generated by Reactions with Oxygen in the Chemical Ionization Source. II. The Use of Wall-Catalyzed Oxidation Reactions for Differentiation of Polycyclic Aromatic Hydrocarbons and Their Methyl Derivatives," *Org. Mass Spectrom.* 24, 705 (1989).
	Waters, L. C.;* Schenley, R. L.; Owen, B. A.;* Walsh, P. J.;* Hsie, A. W.;* Jolley, R. L.;* Buchanan, M. V.; Condie, W.,* "Biotesting of Wastewater: A Comparative Study Using the *Salmonella* and CHO Assay Systems," *Environ. and Molecular Mutagen.* 14, 254 (1989).
Caldwell, W. M.	Tomkins, B. A.; McMahon, J. M.; Caldwell, W. M.; Wilson, D. L.,* "Liquid Chromatographic Determination of Total Formaldehyde in Drinking Water," *J. Assoc. Off. Anal. Chem.* 72, 835 (1989).
Caton, J. E.	Tomkins, B. A.; Caton, J. E.; Edwards, M. D.;* Garcia, M. E.;* Schenley, R. L.; Wachter, L. J.; Griest, W. H., "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids," *Anal. Chem.* 61, 2751 (1989).

Christie, W. H.	James, R. B.* and Christie, W. H., "Shallow Melting of Thin Heavily Doped Silicon Layers by Pulsed Co_2 Laser Irradiation," *J. Appl. Phys.*, 65, 3655 (1989).
	James, R. B.*; Bolton, P. R.*; Alvarez, R. A.*; and Christie, W. H., "Rapid Heating of Ion-Implanted Silicon by High-Power Pulsed Microwave Radiation," *Mat. Res. Soc. Symp. Proc.*, 124, 207 (1989).
Czok, M.	Jacobson, S.;* Golshan-Shirazi, S.;* Katti, A. M.; Czok, M.; Ma, Z.;* Guiochon, G., "A Theoretical Study of Multi-Component Interferences in Non-Linear Chromatography," *J. Chromatogr.* 484, 103 (1989).
Dale, J. M.	Dale, J. M. and Klatt, L. N., "Principal Component Analysis of Diffuse Near-Infrared Reflectance Data from Paper Currency," *Appl. Spectroscopy*, 43, 1399 (1989).
	Hsu, F. H.*; Shao, M. I.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Three-Photon Yield of Positron Annihilation in Cab-O-Sil (SiO_2)," *J. Phys.: Condens. Matter*, 1, 7453 (1989).
Donohue, D. L.	Young, J. P.; Donohue, D. L.; and Smith, D. H., "Application of Resonance Ionization Mass Spectrometry to the Lanthanide Elements in the Wavelength Range of 430-455 nm," *Spectrochimica Acta B*, 44B, 147 (1989).
	Hulett, L. D., Jr.; Donohue, D. L.; and Lewis, T. A.*, "A High Intensity Monoenergetic Positron Source at Oak Ridge National Laboratory," *Oak Ridger*, September 16, 1989.
Dose, E. V.	Dose, E. V.; Guiochon, G., "The Dependence of Measured UV Absorbance on Spectral Shape and Instrument Bandwidth," *Anal. Chem.* 61, 2571 (1989).
Fleming, G. S.	Marchok, A. C.;* Fleming, G. S.; Tomkins, B. A.; Griest, W. H., "$[^3H]$ Benzo(a)pyrene Utilization in Rats Following Tracheal Implant Exposure," *Toxicol.* 56, 63 (1989).
Glish, G. L.	Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Geoporphyrin Structure Determination Using Chemical Ionization Mass Spectrometry/Mass Spectrometry," *Org. Geochem.*, 14, 203 (1989).

Glish, G. L.	Glish, G. L. and McLuckey, S. A., "Analyzer Scan Modes for Hybrid Mass Spectrometers," *Org. Mass Spectrom.*, **24**, 470 (1989).
	McLuckey, S. A.; Glish, G. L.; and Asano, K. G., "The Coupling of an Atmospheric Sampling Ion Source with an Ion Trap Mass Spectrometer," *Anal. Chim. Acta*, **225**, 25 (1989).
	Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A.; and Tuinman, A. A.*, "Mechanism of Porphyrin Reduction and Decomposition in a High Pressure Chemical Ionization Plasma," *J. Amer. Chem. Soc.*, **111**, 6027 (1989).
	Glish, G. L.; Goeringer, D. E.; Asano, K. G.; and McLuckey, S. A., "Laser Desorption Mass Spectrometry and MS/MS with a Three Dimensional Quadrupole Ion Trap," *Int. J. Mass Spectrom. Ion Processes*, **94**, 15 (1989).
Goeringer, D. E.	Glish, G. L.; Goeringer, D. E.; Asano, K. G.; and McLuckey, S. A., "Laser Desorption Mass Spectrometry and MS/MS with a Three-Dimensional Quadrupole Ion Trap," *Int. J. Mass Spectrom. Ion Processes*, **94**, 15 (1989).
Griest, W. H.	Griest, W. H.; Guzman, C.;* Dekker, M.,* "Packed-Column Supercritical Fluid Chromatographic Separation of Highly Explosive Compounds," *J. Liq. Chromatogr.* **467**, 423 (1989).
	Marchok, A. C.;* Fleming, G. S.; Tomkins, B. A.; Griest, W. H., "[^{3}H] Benzo(a)pyrene Utilization in Rats Following Tracheal Implant Exposure," *Toxicol.* **56**, 63 (1989).
	Tomkins, B. A.; Caton, J. E.; Edwards, M. D.;* Garcia, M. E.;* Schenley, R. L.; Wachter, L. J.; Griest, W. H., "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids," *Anal. Chem.* **61**, 2751 (1989).
Guiochon, G. A.	Golshan-Shirazi, S.;* Guiochon, G. A., "Theoretical Study of System Peaks and Elution Profiles for Large Concentration Bands in the Case of a Binary Eluent Containing a Strongly Solved Additive," *J. Chromatogr.* **461**, 1 (1989).

Guiochon, G. A	Golshan-Shirazi, S.;* Guiochon, G. A., "Experimental Study of System Peaks and Elution Profiles for Large Concentration Bands in the Case of a Binary Eluent Containing a Strongly Solved Additive," *J. Chromatogr.* 461, 19 (1989).
	Guiochon, G.; Ghodbane, S.;* Golshan-Shirazi, S.;* Huang, J. X.;* Katti, A.; Lin, B. C.;* Ma, Z.* "Non-Linear Chromatography. Recent Theoretical and Experimental Results," *Talanta* 36, 19 (1989).
	Lin, B.;* Golshan-Shirazi, S.;* Guiochon, G., "Effect of Mass Transfer Coefficient on the Elution Profile in Non-Linear Chromatography, *J. Phys. Chem.* 93, 3363 (1989).
	Golshan-Shirazi, S.;* Guiochon, G., "Experimental Characterization of the Elution Profiles of High Concentration Chromatographic Bands Using the Analytical Solution of the Ideal Model," *Anal. Chem.* 61, 462 (1989).
	Katti, A.; Guiochon, G., "Optimization of Sample Size and Sample Volume in Preparative Liquid Chromatography," *Anal. Chem.* 61, 982 (1989).
	Golshan-Shirazi, S.;* Guiochon, G., "Analytical Solution for the Ideal Model of Chromatography in the Case of a Pulse of a Binary Mixture with Competitive Langmuir Isotherm," *J. Phys. Chem.* 93, 4341 (1989).
	Ghodbane, S.;* Guiochon, G., "A Simplex Optimization of the Experimental Parameters in Preparative Liquid Chromatography," *Chromatographia* 26, 53 (1989).
	Golshan-Shirazi, S.;* Guiochon, G., "The Theory of Optimization of the Experimental Conditions of Preparative Elution Using the Ideal Model of Chromatography," *Anal. Chem.* 61, 1276 (1989).
	Golshan-Shirazi, S.;* Guiochon, G., "The Theory of Optimization of the Experimental Conditions of Preparative Elution Using the Ideal Model of Chromatography. Influence of Column Efficiency," *Anal. Chem.* 61, 2464 (1989).
	Katti, A.; Ramsey, R. ; Guiochon, G., "Quantitative Extraction of Thymine-Thymine Dimer from a Large Excess of Thymine by Semi-Preparative Liquid Chromatography," *J. Chromatogr.* 477, 119 (1989).

Guiochon, G. A.

Huang, J. X.;* Guiochon, G., "The Applications of Preparative HPLC to the Separation and Purification of Peptides and Proteins," *J. Chromatogr.* 477, 119 (1989).

Golshan-Shirazi, S.;* Guiochon, G., "Influence of Mass Transfer Kinetics on the Separation of a Binary Mixture in Displacement Chromatography," *Anal. Chem.* 61, 1960 (1989).

Golshan-Shirazi, S.;* Lin, B.;* Guiochon, G., "Effect of Mass Transfer Kinetics on the Separation of Two Component Mixtures in Preparative Liquid Chromatography," *J. Phys. Chem.* 93, 6871 (1989).

Lin, B.;* Guiochon, G., "Study of the Influence of Axial Dispersion on the Band Profiles in Non-Linear Chromatography Using the Lax-Wendroff Method," *Sep. Sci. & Technol.* 24, 809 (1989).

Katti, A. M.; Guiochon, G. A., "The Use of an Automatic Fraction Collector-Sampling System for the Experimental Determination of Individual Band Profiles in Preparative Liquid Chromatography," *Am. Lab.* 21, 17 (1989).

Golshan-Shirazi, S.;* Guiochon, G., "Theoretical Study of System Peaks and Elution Profiles for Large Samples of Binary Mixtures Eluted by a Binary Eluent Containing a Strongly Retained Additive," *Anal. Chem.* 61, 2373 (1989).

Golshan-Shirazi, S.;* Guiocnon, G., "Experimental Study of System Peaks and Elution Profiles for Large Samples of Binary Mixtures Eluted by a Binary Eluent Containing a Strongly Retained Additive," *Anal. Chem.* 61, 2380 (1989).

Lin, B.;* Ma, Z.;* Guiochon, G., "Influence of Calculation Errors in the Numerical Simulation of Chromatographic Elution Band Profiles Using a Semi-Ideal Model," *J. Chromatogr.* 484, 83 (1989).

Jacobson, S.;* Golshan-Shirazi, S.;* Katti, A. M.; Czok, M.; Ma, Z.;* Guiochon, G., "A Theoretical Study of Multi-Component Interferences in Non-Linear Chromatography," *J. Chromatogr.* 484, 103 (1989).

Guiochon, G. A.	Golshan-Shirazi, S.;* Guiochon, G., "Analytical Solution of the Ideal Model of Chromatography in the Case of a Pulse of a Binary Mixture with Competitive Langmuir Isotherm. Solution Using the H-Transform," *J. Chromatogr.* 484, 125 (1989).
	Newburger, J.;* Guiochon, G., "Experimental Utilization of a Displacement Effect for the Optimization of the Separation of a Two Component Mixture," *J. Chromatogr.* 484, 153 (1989).
	Lin, B.;* Golshan-Shirazi, S.;* Ma, Z.;* Guiochon, G., "Study of the Representation of Competitive Isotherms and of the Intersection Between Adsorption Isotherms," *J. Chromatogr.* 475, 1 (1989).
	Huang, J. X.;* Guiochon, G., "Competitive Adsorption Behavior in HPLC: Cis- and Trans-Androsterone on Silica," *J. Colloid and Interface Sci.* 128, 577 (1989).
	Remelli, M.;* Blo, G.;* Dondi, F.;* Vidal-Madjar, C.;* Guiochon, G., "Fluidic and Syringe Injection Study by Peak Shape Analysis," *Anal. Chem.* 61, 1489 (1989).
	Dose, E. V.; Guiochon, G., "The Dependence of Measured UV Absorbance on Spectral Shape and Instrument Bandwidth," *Anal. Chem.* 61, 2571 (1989).
Hettich, R. L.	Hettich, R. L., "The Differentiation of Methyl Guanosine Isomers by Laser Ionization Fourier Transform Mass Spectrometry," *Biomed. and Environ. Mass Spectrom.* 18, 265 (1989).
	Hettich, R. L., "Structural Investigations of Aluminum Cluster Ions, Al_n^- ($n = 3$-50)," *J. Am. Chem. Soc.* 111, 8582 (1989).
Higgins, C. E.	Thompson, C. V.; Jenkins, R. A.; Higgins, C. E., "A Thermal Desorption Method for the Determination of Nicotine in Indoor Environments," *Environ. Sci. Technol.* 23, 429 (1989).
Ho, C.-h.	Ramsey, R. S.; Ho, C.-h., "Determination of Pyrimidine Dimers in DNA by High-Performance Liquid Chromatography/Gas Chromatography and Electron Capture Detection," *Anal. Biochem.* 182, 424 (1989).

Hulett, L. D., Jr.	Hulett, L. D., Jr.; Donohue, D. L.; and Lewis, T. A.*, "A High Intensity Monoenergetic Positron Source at Oak Ridge National Laboratory," *Oak Ridger*, September 16, 1989.
	Hsu, F. H.*; Shao, M. I.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Three-Photon Yield of Positron Annihilation in Cab-O-Sil (SiO_2)," *J. Phys.: Condens. Matter*, 1, 7453 (1989).
Jenkins, R. A.	Thompson, C. V.; Jenkins, R. A.; Higgins, C. E., "A Thermal Desorption Method for the Determination of Nicotine in Indoor Environments," *Enviorn. Sci. Technol.* 23, 429 (1989).
Katti, A. M.	Guiochon, G.; Ghodbane, S.;* Golshan-Shirazi, S.;* Huang, J. X.;* Katti, A.; Lin, B. C.;* Ma, Z.* "Non-Linear Chromatography. Recent Theoretical and Experimental Results," *Talanta* 36, 19 (1989).
	Katti, A.; Guiochon, G., "Optimization of Sample Size and Sample Volume in Preparative Liquid Chromatography," *Anal. Chem.* 61, 982 (1989).
	Katti, A.; Ramsey, R. ; Guiochon, G., "Quantitative Extraction of Thymine-Thymine Dimer from a Large Excess of Thymine by Semi-Preparative Liquid Chromatography," *J. Chromatogr.* 477, 119 (1989).
	Katti, A. M.; Guiochon, G. A., "The Use of an Automatic Fraction Collector-Sampling System for the Experimental Determination of Individual Band Profiles in Preparative Liquid Chromatography," *Am. Lab.* 21, 17 (1989).
	Jacobson, S.;* Golshan-Shirazi, S.;* Katti, A. M.; Czok, M.; Ma, Z.;* Guiochon, G., "A Theoretical Study of Multi-Component Interferences in Non-Linear Chromatography," *J. Chromatogr.* 484, 103 (1989).
Klatt, L. N.	Dale, J. M. and Klatt, L. N., "Principal Component Analysis of Diffuse Near-Infrared Reflectance Data from Paper Currency," *Appl. Spectroscopy*, 43, 1399 (1989).
Lyon, W. S.	Lyon, W. S., "Fortieth Anniversary of the New Brunswick Laboratory," *J. Radioanal. Nucl. Chem.*, 137, 1 (1989).
	Lyon, W. S., "The Communication of Science," *Oak Ridger*, August 6, 1989.

Ma, C. Y.	Bayne, C. K.;* Ma, C. Y., "A Comparison of Overlapping Resolution Mapping with Ideal Separation to Optimize the Mobile Phase Composition for High Performance Thin Layer Chromatography, *J. Liq. Chromatogr.* 12, 235 (1989).
Maskarinec, M. P.	Maskarinec, M. P.; Johnson, L. H.;* Bayne, C. K.,* "Preparation of Reference Water and Soil Samples for Performance Evaluation of Volatile Organic Analysis," *J. Assoc. Off. Anal. Chem.* 72, 823 (1989).
McLuckey, S. A.	Glish, G. L. and McLuckey, S. A., "Analyzer Scan Modes for Hybrid Mass Spectrometers," *Org. Mass Spectrom.*, 24, 470 (1989). Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Geoporphyrin Structure Determination Using Chemical Ionization Mass Spectrometry/Mass Spectrometry," *Org. Geochem.*, 14, 203 (1989). McLuckey, S. A.; Glish, G. L.; and Asano, K. G., "The Coupling of an Atmospheric Sampling Ion Source with an Ion Trap Mass Spectrometer," *Anal. Chim. Acta*, 225, 25 (1989). Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A.; and Tuinman, A. A.*, "Mechanism of Porphyrin Reduction and Decomposition in a High Pressure Chemical Ionization Plasma," *J. Amer. Chem. Soc.*, 111, 6027 (1989). Glish, G. L.; Goeringer, D. E.; Asano, K. G.; and McLuckey, S. A., "Laser Desorption Mass Spectrometry and MS/MS with a Three Dimensional Quadrupole Ion Trap," *Int. J. Mass Spectrom. Ion Proc.*, 94, 15 (1989).
McMahon, J. M.	Tomkins, B. A.; McMahon, J. M.; Caldwell, W. M.; Wilson, D. L.*, "Liquid Chromatographic Determination of Total Formaldehyde in Drinking Water," *J. Assoc. Off. Anal. Chem.* 72, 835 (1989).
Moody, R. L.	VoDinh, T.;* Miller, G. H.;* Bello, J.;* Johnson, R.;* Moody, R. L.; Alak, A.,* "Surface-Active Substrates for Raman and Luminescence Analysis," *Talanta*, 36, 227 (1989).

Ramsey, J. M.	Blazewicz, P. R.; Whitten, W. B.; and Ramsey, J. M., "Low-Level Detection of Metal Atoms by Multiphoton Ionization in a Low-Pressure Sampling Cell," *Anal. Chem.*, 61, 1010 (1989).
Ramsey, R. S.	Ramsey, R. S.; Chan, V. W.;* Dittmar, B. M.,* "Retention Modification of Nucleic Acid Constituents in Reversed-Phase High-Performance Liquid Chromatography," *J. Chromatogr.* 486, 167 (1989).
	Ramsey, R. S.; Ho, C.-h., "Determination of Pyrimidine Dimers in DNA by High-Performance Liquid Chromatography/Gas Chromatography and Electron Capture Detection," *Anal. Biochem.* 182, 424 (1989).
	Katti, A.; Ramsey, R. ; Guiochon, G., "Quantitative Extraction of Thymine-Thymine Dimer from a Large Excess of Thymine by Semi-Preparative Liquid Chromatography," *J. Chromatogr.* 477, 119 (1989).
Robinson, L.	Johnson, E.* and Robinson, L., "Neutron Multiple Scattering and Absorption Factors," *Rev. Sci. Inst.*, 60, 3447 (1989).
Rosseel, T. M.	Rosseel, T. M.; Vane, C. R.*; Young, J. P.; Zuhr, R. A.*; and Peterson, R. S.*, "High Resolution HIXSE Studies of the Chemical Environment of Sulfur Implanted in Quartz Glass," *Nucl. Instrum. and Meth. B*, 43, 14 (1989).
	Datz, S.*; Vane, C. R.*; Dittner, P. F.*; Giese, J. P.*; del Campo, J. Gomez*; Jones, N. L.*; Krause, H. F.*; Miller, P. D.*; Schulz, M.*; Schöne, H.*; and Rosseel, T. M., "Resonant Dielectric and Direct-Excitation in Crystal Channels," *Phys. Rev. Letts.*, 63, 742 (1989).
	Datz, S.*; Vane, C. R.*; Dittner, P. F.*; Giese, J. P.*; del Campo, J. Gomez*; Jones, N. L.*; Krause, H. F.*; Miller, P. D.*; Schulz, M.*; Schöne, H.*; and Rosseel, T. M., "Resonant Dielectronic Excitation in Crystal Channels," *Radiation Effects and Defects in Solids*, 110, 95 (1989).
	Hsu, F. H.*; Shao, M. I.*; Hulett, L. D., Jr.; Rosseel, T. M.; and Dale, J. M., "Three-Photon Yield of Positron Annihilation in Cab-O-Sil (SiO_2)," *J. Phys.: Condens. Matter*, 1, 7453 (1989).

Schenley, R. L.

Tomkins, B. A.; Caton, J. E.; Edwards, M. D.;* Garcia, M. E.;* Schenley, R. L.; Wachter, L. J.; Griest, W. H., "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids," *Anal. Chem.* 61, 2751 (1989).

Waters, L. C.;* Schenley, R. L.; Owen, B. A.;* Walsh, P. J.;* Hsie, A. W.;* Jolley, R. L.;* Buchanan, M. V.; Condie, W.,* "Biotesting of Wastewater: A Comparative Study Using the *Salmonella* and CHO Assay Systems," *Environ. and Molecular Mutagen.* 14, 254 (1989).

Shaw, R. W.

Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser Initiated Resonance Ionization Mass Spectrometry of Lanthanum," *Anal. Chem.*, 61, 695 (1989).

Smith, D. H.; Young, J. P.; and Shaw, R. W., "Elemental Resonance Ionization Mass Spectrometry: A Review," *Mass Spectrometry Reviews*, 8, 345 (1989).

Young, J. P.; Shaw, R. W.; and Smith, D. H., "Spectral Study of Promethium and Samarium by Resonance Ionization Mass Spectrometry," *Appl. Spectrosc.*, 43, 1164 (1989).

Young, J. P.; Shaw, R. W.; and Smith, D. H., "Resonance Ionization Mass Spectrometry," *Anal. Chem.*, 61, 1271A (1989).

Shults, W. D.

Shults, W. D., "Analytical Chemistry and Measurement Science," *J. Nucl. Mat. Management*, XVIII (1), 40 (1989).

Smith, D. H.

Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser Initiated Resonance Ionization Mass Spectrometry of Lanthanum," *Anal. Chem.*, 61, 695 (1989).

Young, J. P.; Donohue, D. L.; and Smith, D. H., "Application of Resonance Ionization Mass Spectrometry to the Lanthanide Elements in the Wavelength Range of 430-455 nm," *Spectrochimica Acta B*, 44B, 147 (1989).

Smith, D. H.; Young, J. P.; and Shaw, R. W., "Elemental Resonant Ionization Mass Spectrometry: A Review," *Mass Spectrometry Reviews*, 8, 345 (1989).

Smith, D. H.	Young, J. P.; Shaw, R. W.; and Smith, D. H., "Spectral Study of Promethium and Samarium by Resonance Ionization Mass Spectrometry," *Appl. Spectroscopy*, 43, 1164 (1989). Young, J. P.; Shaw, R. W.; and Smith, D. H., "Resonance Ionization Mass Spectrometry," *Anal. Chem.*, 61, 1271A (1989).
Thompson, C. V.	Thompson, C. V.; Jenkins, R. A.; Higgins, C. E., "A Thermal Desorption Method for the Determination of Nicotine in Indoor Environments," *Environ. Sci. Technol.* 23, 429 (1989).
Todd, P. J.	Cook, K. D.*; Todd, P. J.; and Friar, D.*, "Physical Properties of Matrices Used for Fast Atom Bombardment," *Biomed. and Environ. Mass Spectrom.*, 18, 492 (1989).
Tomkins, B. A.	Marchok, A. C.;* Fleming, G. S.; Tomkins, B. A.; Griest, W. H., "[^{3}H] Benzo(a)pyrene Utilization in Rats Following Tracheal Implant Exposure," *Toxicol.* 56, 63 (1989). Tomkins, B. A.; McMahon, J. M.; Caldwell, W. M.; Wilson, D. L.,* "Liquid Chromatographic Determination of Total Formaldehyde in Drinking Water," *J. Assoc. Off. Anal. Chem.* 72, 835 (1989). Tomkins, B. A.; Caton, J. E.; Edwards, M. D.;* Garcia, M. E.;* Schenley, R. L.; Wachter, L. J.; Griest, W. H., "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids," *Anal. Chem.* 61, 2751 (1989).
Van Berkel, G. J.	Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A.; and Tuinman, A. A.*, "Mechanism of Porphyrin Reduction and Decomposition in a High-Pressure Chemical Ionization Plasma," *J. Am. Chem. Soc.*, 111, 6027 (1989). Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Geoporphyrin Structure Determination Using Chemical Ionization-Mass Spectrometry/Mass Spectrometry," *Org. Geochem.*, 14, 203 (1989).

Van Berkel, G. J.	Van Berkel, G. J.; Quirke, J. M. E.*; and Filby, R. H.*, "The Henryville Bed of the New Albany Shale-II: Comparison of the Nickel and Vanadyl Porphyrins in the Bitumen and Those Generated from the Kerogen During Simulated Catagenesis," *Org. Geochem.*, 14, 129 (1989). Van Berkel, G. J.; Quirke, J. M. E.*; and Filby, R. H.*, "The Henryville Bed of the New Albany Shale-I: Preliminary Characterization of the Nickel and Vanadyl Porphyrins in the Bitumen," *Org. Geochem.*, 14, 119 (1989). Joubert-Castro, A.*; Van Berkel, G. J.; Doolittle, F. G.*; and Filby, R. H .*, "Comparison of Electron Ionization and Fast Atom Bombardment-Mass Spectrometry for the Determination of Nickel, Vanadyl, and Free-Base Porphyrins," *Org. Geochem.*, 14, 193 (1989).
Wachter, L. J.	Tomkins, B. A.; Caton, J. E.; Edwards, M. D.;* Garcia, M. E.;* Schenley, R. L.; Wachter, L. J.; Griest, W. H., "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids," *Anal. Chem.* 61, 2751 (1989).
Whitten, W. B.	Blazewicz, P. R.; Whitten, W. B.; and Ramsey, J. M., "Low-Level Detection of Metal Atoms by Multiphoton Ionization in a Low-Pressure Sampling Cell," *Anal. Chem.*, 61, 1010 (1989).
Young, J. P.	Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser Initiated Resonance Ionization Mass Spectrometry of Lanthanum," *Anal. Chem.*, 61, 695 (1989). Young, J. P.; Donohue, D. L.; and Smith, D. H., "Application of Resonance Ionization Mass Spectrometry to the Lanthanide Elements in the Wavelength Range of 430-455 nm," *Spectrochimica Acta B*, 44B, 147 (1989). Rosseel, T. M.; Vane, C. R.*; Young, J. P.; Zuhr, R. A.*; and Peterson, R. S.*, "High Resolution HIXSE Studies of the Chemical Environment of Sulfur Implanted in Quartz Glass," *Nucl. Instrum. and Meth. B*, 43, 14 (1989). Smith, D. H.; Young, J. P.; and Shaw, R. W., "Elemental Resonant Ionization Mass Spectrometry: A Review," *Mass Spectrometry Reviews*, 8, 245 (1989).

Young, J. P.

Young, J. P.; Shaw, R. W.; and Smith, D. H., "Spectral Study of Promethium and Samarium by Resonance Ionization Mass Spectrometry," *Appl. Spectrosc.*, 43, 1164 (1989).

Wilmarth, W. R.*; Begun, G. M.*; Haire, R. G.*; Young, J. P.; and Peterson, J. R.*, "The Effect of Pressure on the Raman and Absorption Spectra of $PrCl_3$, $PrBr_3$, and $NdBr_3$," *Appl. Spectrosc.*, 43, 1938 (1989).

Young, J. P.; Shaw, R. W.; and Smith, D. H., "Resonance Ionization Mass Spectrometry," *Anal. Chem.*, 61, 1271A (1989).

Reports

Buchanan, M. V.	Buchanan, M. V.; Ma, C. Y., *Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical Characterization of Colored Signal Smokes*, Final Report, ORNL/TM-11195, May 1989.
Carter, J. A.	Smith, D. H.; McBay, E. H.; Mueller, T. R.; Walker, R. L.; and Carter, J. A., *High Precision Isotopic Ratio Measurements of Krypton and Xenon*, Final Report, ORNL/TM-11055, February 1989. Lambert, S. J.* and Carter, J. A., *Uranium-Isotope Systematics in Groundwaters of the Rustler Formation, Northern Delaware Basin, Southeastern New Mexico, I: Principles and Preliminary Results*," SAND87-0388 - UC-721, December 1987 (received 10-2-89). Carter, J. A., *Analytical Chemistry Division Research and Development Summary: Analytical Spectroscopy Section*, ORNL/CF-89/66, March 1989. Carter, J. A., *Analytical Chemistry Division Research and Development Summary: Analytical Spectroscopy Section*, ORNL/CF-89/236, July 1989. Carter, J. A., *Analytical Chemistry Division Research and Development Summary: Analytical Spectroscopy Section*, ORNL/CF-89/332, November 1989.
Christie, W. H.	Stewart, J. H. and Christie, W. H., *Foreign Travel of J. H. Stewart, Jr. and W. H. Christie to Winsford, Cheshire, England*, ORNL/FTR-3488, November 1989.
Costanzo, D. A.	Autrey, J. W.;* Costanzo, D. A.; Griest, W. H.; Kaiser, L. L.;* Keller, J. M.; Nix, C. E.;* Tomkins, B. A., *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*, ORNL/RAP-53, August 1989.
Dyer, F. F.	Kerr, G. D.;* Dyer, F. F.; Emery, J. F.; Pace III, J. V.;* Brodzinski, R. L.;* Marcum, J.,* *Activation of Cobalt by Neutrons from the Hiroshima Bomb*, ORNL-6590, September 26, 1989. Alsmiller, R. G.*; Henderson, D. L.*; Montgomery, B. H.*; Robinson, L.; Dyer, F. F., et al., *Final Report on Seed Money Project 3210-036: Feasibility Study for Californium Cold Neutron Source*, ORNL/TM-11027, October 1989.

Dyer, F. F.	Jenkins, R. A.; Dyer, F. F.; Moody, R. L.; Bayne, C. K.;* Thompson, C. V., *Experimental Evaluation of Selected Field Portable Instrumentation for the Quantitative Determination of Contaminant Levels in Soil and Water at Rocky Mountain Arsenal*, ORNL/TM-11385, October 1989.
Emery, J. F.	Emery, J. F., *Accelerator and Radiation Sources Review Committee Review of the 14 MeV Neutron Generator in Building 2011*, ORNL/CF-89/274, October 1989.
	Kerr, G. D.;* Dyer, F. F.; Emery, J. F.; Pace III, J. V.*; Brodzinski, R. L.*; Marcum, J.*, *Activation of Cobalt by Neutrons from the Hiroshima Bomb*, ORNL-6590, September 1989.
Griest, W. H.	Autrey, J. W.;* Costanzo, D. A.; Griest, W. H.; Kaiser, L. L.;* Keller, J. M.; Nix, C. E.;* Tomkins, B. A., *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*, ORNL/RAP-53, August 1989.
	Ammons, A. K.;* Griest, W. H.; Easterly, C. E.,* *Examination of Field Stock M774 Tank Ammunition Projectile Assemblies*, Report No. Y/PS-957, May 1989.
Guerin, M. R.	Guerin, M. R., *Analytical Chemistry Division Research and Develpoment Summary; February 1989, Organic Chemistry Section*, ORNL/CF-89/85, March 1989.
	Guerin, M. R., *Analytical Chemistry Division Research and Development Summary; June 1989, Organic Chemistry Section*, ORNL/CF-89/276, July 1989.
	Guerin, M. R., *Analytical Chemistry Division Research and Development Summary; October 1989, Organic Chemistry Section*, ORNL/CF-89/359, November 1989.
Holladay, S. K.	Maskarinec, M. P.; Bayne, C. K.;* Johnson, L. H.;* Holladay, S. K.; Jenkins, R. A., *Stability of Volatile Organics in Environmental Water Samples: Storage and Preservation*, ORNL/TM-11300, August 1989.
Jenkins, R. A.	Maskarinec, M. P.; Bayne, C. K.;* Johnson, L. H.;* Holladay, S. K.; Jenkins, R. A., *Stability of Volatile Organics in Environmental Water Samples: Storage and Preservation*, ORNL/TM-11300, August 1989.

Jenkins, R. A.	Jenkins, R. A.; Moneyhun, J. H.; Gayle, T. M.;* Lore, J. D.;* Ross, R. H.,* *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems, Vol. 2: Facility Criteria for the Chemical and Toxicological Characterization of Gun Exhaust*, ORNL-6334/V2, January 1989. Jenkins, R. A.; Dyer, F. F.; Moody, R. L.; Bayne, C. K.;* Thompson, C. V., *Experimental Evaluation of Selected Field Portable Instrumentation for the Quantitative Determination of Contaminant Levels in Soil and Water at Rocky Mountain Arsenal*, ORNL/TM-11385, October 1989.
Keller, J. M.	Autrey, J. W.;* Costanzo, D. A.; Griest, W. H.; Kaiser, L. L.;* Keller, J. M.; Nix, C. E.;* Tomkins, B. A., *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*, ORNL/RAP-53, August 1989.
Klatt, L. N.	Klatt, L. N., *Report of Foreign Travel of L. N. Klatt*, ORNL/FTR-3304, July 1989.
Laing, W. R.	Laing, W. R., *Analytical Chemistry Division Summary Report: Inorganic Chemistry Section*, ORNL/CF-89/50, February 1, 1989. Laing, W. R., *Analytical Chemistry Division Summary Report: Inorganic Chemistry Section*, ORNL/CF-89/254, June 1, 1989. Laing, W. R., *Analytical Chemistry Division Summary Report: Inorganic Chemistry Section*, ORNL/CF-89/311, October 1, 1989.
Ma, C. Y.	Buchanan, M. V.; Ma, C. Y., *Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical Characterization of Colored Signal Smokes*, Final Report, ORNL/TM-11195, May 1989.
Maskarinec, M. P.	Maskarinec, M. P.; Bayne, C. K.;* Johnson, L. H.;* Holladay, S. K.; Jenkins, R. A., *Stability of Volatile Organics in Environmental Water Samples: Storage and Preservation*, ORNL/TM-11300, August 1989. Maskarinec, M. P., *Summary of Analytical and Quality Assurance Requirements of Environmental Regulations*, ORNL/CF-89/207, May 1989.

McBay, E. H.	Smith, D. H.; McBay, E. H.; Mueller, T. R.; Walker, R. L.; and Carter, J. A., *High Precision Isotopic Ratio Measurements of Krypton and Xenon*, Final Report, ORNL/TM-11055, February 1989.
McLuckey, S. A.	McLuckey, S. A., *Report of Foreign Travel of Scott A. McLuckey*, ORNL/FTR-3333, July 20, 1989.
Moneyhun, J. H.	Jenkins, R. A.; Moneyhun, J. H.; Gayle, T. M.;* Lore, J. D.;* Ross, R. H.,* *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems, Vol. 2: Facility Criteria for the Chemical and Toxicological Characterization of Gun Exhaust*, ORNL-6334/V2, January 1989.
Moody, R. L.	Jenkins, R. A.; Dyer, F. F.; Moody, R. L.; Bayne, C. K.;* Thompson, C. V., *Experimental Evaluation of Selected Field Portable Instrumentation for the Quantitative Determination of Contaminant Levels in Soil and Water at Rocky Mountain Arsenal*, ORNL/TM-11385, October 1989.
Mueller, T. R.	Smith, D. H.; McBay, E. H.; Mueller, T. R.; Walker, R. L.; and Carter, J. A., *High Precision Isotopic Ratio Measurements of Krypton and Xenon*, Final Report, ORNL/TM-11055, February 1989.
Robinson, L.	Alsmiller, R. G.*; Henderson, D. L.*; Montgomery, B. H.*; Robinson, L.; Dyer, F. F., et al., *Final Report on Seed Money Project 3210-036: Feasibility Study for Californium Cold Neutron Source*, ORNL/TM-11027, October 1989.
Rosseel, T. M.	Datz, S.*; Vane, C. R.*; Dittner, P. F.*; Giese, J. P.*; del Campo, J. Gomez*; Jones, N. L.*; Krause, H. F.*; Miller, P. D.*; Schulz, M.*; Schöne, H.*; and Rosseel, T. M., *Resonant Dielectronic Excitation in Crystal Channels*, Physics Division Progress Report, ORNL/6508, March 1989.
	Vane, C. R.*; Datz, S.*; Dittner, P. F.*; Giese, J. P.*; Krause, H. F.*; Miller, P. D.*; Schöne, H.*; Schulz, M.*; Rosseel, T. M.; and Peterson, R. S.*, *Radiative Electron Capture by Bare- and One-Electron Ions*, Physics Division Progress Report, ORNL/6508, March 1989.

Rosseel, T. M.	Rosseel, T. M.; Vane, C. R.*; Young, J. P.; Zuhr, R. A.*; and Peterson, R. S.*, *High Resolution HIXSE Studies of the Chemical Environment of Sulfur Implanted in Insulator Matrices*, Solid State Division Progress Report, ORNL/6571, August 1989.
Smith, D. H.	Smith, D. H.; McBay, E. H.; Mueller, T. R.; Walker, R. L.; and Carter, J. A., *High Precision Isotopic Ratio Measurements of Krypton and Xenon*, Final Report, ORNL/TM-11055, February 1989.
	Smith, D. H., *Report of Foreign Travel of D. H. Smith*, ORNL/FTR-3314, July 1989.
Stewart, J. H.	Stewart, J. H. and Christie, W. H., *Report of Foreign Travel of J. H. Stewart, Jr. and W. H. Christie to Winsford, Cheshire, England*, ORNL/FTR 3488, November 1989.
Stokely, J. R.	Stokely, J. R., *Report of Foreign Travel of J. R. Stokely, Section Head, Analytical Chemistry Division*, ORNL/FTR-3292, June 19, 1989.
	Stokely, J. R., *Analytical Chemistry Division Summary Report: Radioactive Materials Analysis Section*, ORNL/CF-89/325, October 1, 1989.
	Stokely, J. R., *Analytical Chemistry Division Summary Report: Radioactive Materials Analysis Section*, ORNL/CF-89/88, April 1, 1989.
Thompson, C. V.	Jenkins, R. A.; Dyer, F. F.; Moody, R. L.; Bayne, C. K.;* Thompson, C. V., *Experimental Evaluation of Selected Field Portable Instrumentation for the Quantitative Determination of Contaminant Levels in Soil and Water at Rocky Mountain Arsenal*, ORNL/TM-11385, October 1989.
Tomkins, B. A.	Autrey, J. W.;* Costanzo, D. A.; Griest, W. H.; Kaiser, L. L.;* Keller, J. M.; Nix, C. E.;* Tomkins, B. A., *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*, ORNL/RAP-53, August 1989.
Walker, R. L.	Smith, D. H.; McBay, E. H.; Mueller, T. R.; Walker, R. L.; and Carter, J. A., *High Precision Isotopic Ratio Measurements of Krypton and Xenon*, Final Report, ORNL/TM-11055, February 1989.
Young, J. P.	Rosseel, T. M.; Vane, C. R.*; Young, J. P.; Zuhr, R. A.*; and Peterson, R. S.*, *High Resolution HIXSE Studies of the Chemical Environment of Sulfur Implanted in Insulator Matrices*, Solid State Division Progress Report, ORNL/6571, August 1989.

ORAL PRESENTATIONS

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

SPEAKER	AUTHORS, MEETING, AND DATE
Asano, K. G.	Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Daughter Ion Formula Determinations by Ms^n Experiments on Naturally Occurring Isotopes," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
Baggett, C. J.	Baggett, C. J. and Keller, J. M., "Analysis of Radioactive Samples by Inductively Coupled Plasma and Atomic Absorption," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Bayne, C. K.*	Bayne, C. K.; Maskarinec, M. P., "Statistical Analysis of Preanalytical Holding Time Data," 5th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, July 24-28, 1989 (invited).
Buchanan, M. V.	Buchanan, M. V.; Wise, M. B.; Guerin, M. R., "Direct Sampling Ion Trap Mass Spectrometry for the Rapid Determination of Volatile Organics in Environmental Matrices," 5th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, July 24-28, 1989 (invited).
	Buchanan, M. V.; Wise, M. B.; Guerin, M. R., "Direct Sampling Ion Trap Mass Spectrometry for Rapid Detection of Trace Organics," SUBWOG 12C Meeting, Oak Ridge, TN, October 3-6, 1989 (invited).
	Buchanan, M. V.; Stemmler, E. A.;* Wise, M. B., "Probing Molecular Structure with Negative Ion Processes," Seminar, Ohio State University, Columbus, OH, November 14, 1989 (invited).
	Buchanan, M. V.; Hettich, R. L., "New Approaches for Determining Molecular Structure with Mass Spectrometry," Massachusetts Institute of Technology, Boston, MA, December 7, 1989 (invited).

Buchanan, M. V.	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Mass Spectrometric Techniques for the Rapid Determination of Trace Organic Compounds in the Environment," U.S. Laboratory Command, Technology Investment Strategy Conference, Oak Ridge, TN, February 27-March 3, 1989.
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Volatile Organics in Wastes and Soil Using Direct Purge Into an ITMS," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Detection and Characterization of Fossil-Derived Fuels in Water and Soil Using Direct Purge Ion Trap Mass Spectrometry," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Volatile Organics in the Environment Using Direct Purge Ion Trap Mass Spectrometry," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
	Buchanan, M. V.; Hettich, R. L.; Ho, C-h., "Differentiation of Alkylated Nucleoside Isomers by Laser Ionization FTMS," 2nd International Symposium on Mass Spectrometry in the Life Sciences, San Francisco, CA, August 27-31, 1989.
	Buchanan, M. V., "Isomers and Intractables: Identification of Bio-Adducts," DOE OHER Review, San Francisco, CA, June 14, 1989.
Carter, J. A.	Carter, J. A., "ORNL Explosives Detection by Mass Spectrometry/Mass Spectrometry - R & D Report," DOE Safeguards and Security Directors and Nuclear Security Information Exchange Group, Albuquerque, NM, Nov. 14-16, 1989.
	Carter, J. A.; Bostick, D. A.; May, M. P.; Walker, R. L.; and Smith, D. H., "Determination of Tank Volumes and Fissile Inventory Employing Lutetium," Permanent Coordinating Group of the PNC (Japan) and DOE, Germantown, MD, Dec. 4-6, 1989.
Ceo, R. N.	Ceo, R. N., "Separation and Physical Characterization of Layers in a Stratified Waste Tank Sludge," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.

Christie, W. H.	Christie, W. H., "A Sensitivity Factor Approach to Quantitative Analysis with the Glow Discharge Mass Spectrometer," Pittsburgh Conference and Exposition, VG Workshop, Atlanta, GA, March 6-10, 1989 (invited).
	Christie, W. H., "Solids Analysis Via Glow Discharge Mass Spectrometry," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Christie, W. H., "Secondary Ion Mass Spectrometry," Chemistry Department, Univ. of Tennessee at Chattanooga, Feb. 24, 1989 (invited).
	Christie, W. H. and Fassett, J.*, "Multiphoton Resonate Ionization," Seventh International Conference on Secondary Ion Mass Spectrometry, Monterey, CA, Sept. 3-8, 1989 (invited).
	Christie, W. H., "Glow Discharge Mass Spectrometry as a Quantitative Analysis Technique," FACSS Meeting, Chicago, IL, Oct. 1-6, 1989 (invited).
	Christie, W. H., "Glow Discharge Mass Spectrometry," DOE/BES Site Review, Oak Ridge, TN, April 23-25, 1989.
Dale, J. M.	Dale, J. M. and Klatt, L. N., "Counterfeit Currency Detection by Principal Component Analysis of Near-Infrared Reflectance Data," Pittsburgh Conference and Exhibition, Atlanta, GA, March 6-10, 1989.
Dihel, D. L.	Dihel, D. L.; Wade, J. W.; and Scott, T. G., "The Determination of Radium-223, 224, 226 in Environmental Samples," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Donohue, D. L.	Donohue, D. L., "Positron Ionization Mass Spectrometry," ORNL Chemical Physics Seminar, Oak Ridge, TN, June 19, 1989.
	Donohue, D. L.; Hulett, L. D.; McLuckey, S. A.; Glish, G. L.; and Eckenrode, B. A., "Initial Results of Positron Ionization Mass Spectrometry," Workshop on Positron Annihilation in Gases, Green Belt, MD, July 21, 1989.

Donohue, D. L.	Donohue, D. L.; Hulett, L. D., Jr.; Glish, G. L.; McLuckey, S. A.; and Eckenrode, B. A., "Positron Ionization Mass Spectrometry," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10, 1989.
Dyer, F. F.	Dyer, F. F., "Proposed Analytical Facilities for the Advanced Neutron Source," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Eckenrode, B. A.	Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., "Negative Ion Chemical Ionization in an Ion Trap Mass Spectrometer Using Reagent Anions Injected from an External Ion Source," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 1989.
	Eckenrode, B. A.; Glish, G. L.; and McLuckey, S. A., "Ion Trajectory Modelling in an Ion Mobility Spectrometer Employing Nonlinear Electric Fields," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 1989.
	Eckenrode, B. A.; McLuckey, S. A.; and Glish, G. L., "Improved Design of an Ion Mobility Spectrometer for Trace Analysis," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Eldridge, J. S.	Eldridge, J. S., "Radiological Characterization of Soils," Workshop on the Management of Contaminated Soils, Knoxville, TN, November 10, 1989.
	Eldridge, J. S., "Radioanalytical and QA Concepts for Environmental Surveillance," Health Physics Society Annual Meeting, Albuquerque, NM, June 25-29, 1989.
Glish, G. L.	Glish, G. L., "Ion Trap Research at Oak Ridge," Naval Research Laboratory, Washington, DC, January 12, 1989 (invited).
	Glish, G. L.; McLuckey, S. A.; and Van Berkel, G. J., "The Ion Trap Mass Spectrometer: It's Not Just a GC Detector Anymore," North Jersey Mass Spectrometry Discussion Group, New Brunswick, NJ, January 16, 1989 (invited).
	Glish, G. L., "MS/MS: A New Dimension in Mass Spectrometry," ORSES Program, Oak Ridge, TN, February 22, 1989 (invited).

Glish, G. L.

Glish, G. L., "Progress in Organic Mass Spectrometry," DOE/BES Site Review, Oak Ridge, TN, April 24, 1989.

Glish, G. L., "MS/MS: Increasing the Dimensions of Mass Spectrometry," University of North Carolina, Chapel Hill, NC, May 1, 1989 (invited).

Glish, G. L., "The Quadrupole Ion Trap: Big Performance from a Little Mass Spectrometer," Triangle Area Mass Spectrometry Discussion Group, Chapel Hill, North Carolina, May 1, 1989 (invited).

Glish, G. L. and McLuckey, S. A., "The Ion Trap: A Multi-Purpose Mass Spectrometer," Plenary lecture at Finnigan MAT Users Forum, Miami Beach, FL, May 21, 1989 (invited).

Glish, G. L. and McLuckey, S. A., "Direct Air Monitoring Using an Ion Trap Mass Spectrometer," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989 (invited).

Glish, G. L. and McLuckey, S. A., "The MS/MS Advantage: Tailoring Instrument Design to the Application," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989 (invited).

Glish, G. L. and McLuckey, S. A., "Progress in Explosives Detection at Oak Ridge," FAA Vapor Technology Symposium, Atlantic City, NJ, June 6-7, 1989 (invited).

Glish, G. L. and McLuckey, S. A., "Use of an Ion Trap Mass Spectrometer for Real-Time Air Monitoring," 31st Rocky Mountain Conference on Analytical Chemistry, Denver, CO, July 31-August 2, 1989 (invited).

Glish, G. L.; McLuckey, S. A.; and Asano, K. G., "New Signature Detection," LAGER Meeting on Effluent Research, Washington, DC, August 15, 1989.

Glish, G. L. and McLuckey, S. A., "Real-Time Air Monitoring for Explosives and Other Compounds," Meeting on Analytical Chemistry of Weapons Materials, Oak Ridge, TN, October 3-6, 1989 (invited).

Glish, G. L.	Glish, G. L. and McLuckey, S. A., "Recent Developments in Explosives Detection at Oak Ridge," FBI Meeting on Explosives Detection, Quantico, VA, October 11, 1989 (invited).
	Glish, G. L. and McLuckey, S. A., "Non-Conventional Hybrid Instruments: The Whats and Whys of 'Reverse' Thinking," Workshop on Hybrid Mass Spectrometers, Lake Louise, Canada, November 30-December 2, 1989 (invited).
Goeringer, D. E.	Goeringer, D. E.; Christie, W. H.; and Valiga, R. E., "Inorganic SIMS," BES Site Review, Oak Ridge, TN, April 24-25, 1989.
	Goeringer, D. E.; Glish, G. L.; Asano, K. G.; and McLuckey, S. A., "Applications of Laser Desorption in an Ion Trap Mass Spectrometer," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Goeringer, D. E.; Glish, G. L.; Asano, K. G.; McLuckey, S. A.; Whitten, W. B.; and Ramsey, J. M., "Developments in Laser-Based Techniques for Ion Trap Mass Spectrometry," FACSS Meeting, Chicago, IL, Oct. 1-6, 1989 (invited).
Grant, B. C.	Grant, B. C.; McBay, E. H.; McLuckey, S. A.; and Glish, G. L., "High Resolution Daughter Ion Analysis Applications in Hybrid Mass Spectrometry," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
Griest, W. H.	Griest, W. H.; Ho, C.-h.; Stewart, A. J.;* Tyndall, R. L.;* Tan, E.;* Guerin, M. R., "Characterization of Explosives Processing Waste Decomposition Due to Composting," Workshop on Composting Development, New Orleans, LA, September 6-8, 1989 (invited).
	Griest, W. H.; Tomkins, B. A.; Schenley, R. L.; Caton, J. E.; Fleming, G. S.; Edwards, M. D.;* Harmon, S. H.; Wachter, L. J.; Garcia, M. E.,* "Determination of Organic Compounds in Radioactive Nuclear Wastes," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
	Griest, W. H.; Ho, C.-h.; Stewart, A. J.;* Tyndall, R. L.;* Tan, E.;* Guerin, M. R., "Toxicological and Chemical Characterization of Composted Explosives Processing Waste," 14th Annual Army Environmental R&D Symposium, Williamsburg, VA, November 14-16, 1989 (invited).

Guerin, M. R.	Guerin, M. R.; Griest, W. H.; Ho, C.-h., "Health Related Chemical Properties of Crude Oil," Conference on the Alaskan Crude Oil Spill and Human Health, Seattle, WA, July 28-30, 1989 (invited).
Guiochon, G. A.	Guiochon, G. A., "Optimizing Large Scale Production in Chromatography," 5th International Symposium on Separation Science and Biotechnology, Fort Lauderdale, FL, January 19, 1989.
	Guiochon, G. A.; Ma, Z.;* Lin, B.,* "Physical-Chemical Measurement in Nonlinear Chromatography: Parameter Estimation," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Huang, J.-X.,* "Experimental Verification of Semi-Ideal Model of Chromatography for Displacement Chromatography," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Ghodbane, S.,* "Optimization of Experimental Parameters in Preparative HPLC," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Golshan-Shirazi, S.,* "Experimental Verfication of Analytical Solution of Large Concentration Band in the Case of the Langmuir Isotherm," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Czok, M.; Huang, J.-X.,* "Gradient Elution Under Overload Conditions," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Schudel, J. V. H., "Characterization of Some Commercially Available Stationary Phases in HPLC," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guiochon, G. A.; Aubel, M. T., "Characterization of Reversed-Phase LC Stationary Phases Using Ribonuclease A," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Guinchon, G. A., "Prediction of Band Profiles in Non-Linear Chromatography," Pittsburgh Conference and Exposition, March 5-10, 1989.

Guiochon, G. A.

Guiochon, G. A.; Huang, J.-X.,* "Competitive Adsorption Behavior in HPLC (II): Proteins on TSK DEAE Anion Exchanger," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.

Guiochon, G. A.; Dose, E. V.; Roles, J. L., "Gas Chromatographic Study of Ceramic Materials Surface Properties," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.

Guiochon, G. A., "Non-Linear Chromatrography," University of North Carolina, Chapel Hill, NC, March 27, 1989.

Guiochon, G. A, "Preparative Liquid Chromatography," Research Triangle Chromatography Discussion Group, Raleigh, NC, March 28, 1989.

Guiochon, G. A., "Recent Progress in Preparative Liquid Chromatography," Tennessee Eastman, Kingsport, TN, April 7, 1989.

Guiochon, G. A., "Non-Linear Chromatography. Recent Theoretical and Experimental Results," Distinguished Lectures in Chemistry Series, San Jose State University, San Jose, CA, April 25, 1989.

Golshan-Shirazi, S.;* Guiochon, G. A., "The Theory of Optimization of the Experimental Conditions of Preparative Elution Using the Ideal and Semi-Ideal Models of Chromatography," 6th International Symposium on Preparative Chromatography, Washington, DC, May 8, 1989.

Guiochon, G. A., "Purification of Peptides and Proteins by Preparative Liquid Chromatogrpahy," Department of Chemistry, East Tennessee State University, Johnson City, TN, September 29, 1989.

Guiochon, G. A., "Purification of Peptides and Proteins by Preparative Liquid Chromatography," Department of Chemistry, Georgetown College, Georgetown, KY, October 19, 1989.

Guiochon, G. A.; Czok, M., "New Packing Materials for Size Exclusion Chromatography," 197th National Meeting, American Chemical Society, Dallas, TX, April 13, 1989.

Guiochon, G. A.

Guiochon, G. A.; Golshan-Shirazi, S.;* Katti, A. M.; Czok, M., "The Theory of Non-Linear Chromatography," 13th International Symposium on Column Liquid Chromatography, Stockholm, Sweden, June 30, 1989.

Guiochon, G. A.; Golshan-Shirazi, S.;* Katti, A. M., "Optimization of Experimental Conditions for Maximum Production Rate in Preparative Liquid Chromatography," Chromatographie Symposium in Memoriam Istvan Halasz, Saarbruecken, Federal Republic of Germany, July 3, 1989.

Guiochon, G. A.; Golshan-Shirazi,* "Optimization of Column Design and Operation Parameters for Preparative Scale High Performance Liquid Chromatography," Eastern Analytical Symposium, New York, NY, September 25, 1989.

Guiochon, G. A.; Golshan-Shirazi,* "Optimization of Column Design and Operation Parameters for Preparative Scale High Performance Liquid Chromatography," Separation and Energy Symposium, Knoxville, TN, October 25, 1989.

Guiochon, G. A., "The Optimization of Experimental Conditions in Preparative High Performance Liquid Chromatography," 1989 Annual Meeting, American Institute of Chemical Engineers, San Francisco, CA, November 6, 1989.

Newburger, J.;* Guiochon, G. A., "The Utility of Sample Self-Displacement as a Routine Preparative Separation Technique," 6th International Symposium on Preparative Chromatography, Washington, DC, May 8, 1989.

Newburger, J.;* Guiochon, G. A., "The Utility of Sample Self-Displacement as a Routine Preparative Separation Technique," 13th International Symposium on Column Liquid Chromatography, Stockholm, Sweden, June 27, 1989.

Golshan-Shirazi, S.;* Guiochon, G. A., "On the Theory of Optimization of the Experimental Conditions of Preparative Chromatography," 13th International Symposium on Column Liquid Chromatography, Stockholm, Sweden, June 27, 1989.

Hettich, R. L.

Hettich, R. L., "Characterization of Photo-Induced Pyrimidine Cyclobutane Dimers by Laser Ionization Fourier Transform Mass Spectrometry," ASMS Workshop on Mechanisms in Desorption Ionization, Sanibel Island, FL, January 23, 1989.

Hettich, R. L.

Hettich, R. L., "Characterization of Alkylated Nucleosides by Laser Ionization Fourier Transform Mass Spectrometry," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.

Hettich, R. L., "Structural Examination of Aluminum Cluster Ions, Al_n^- for $n = 3\text{-}50$," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.

Hettich, R. L.; Buchanan, M. V., "Laser Ionization Fourier Transform Mass Spectrometry for the Isomeric Differentiation of Alkylated Nucleosides," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.

Hettich, R. L.; Buchanan, M. V., "Differentiation of Alkylated Nucleoside Isomers by Laser Ionization Fourier Transform Mass Spectrometry," 2nd International Symposium on Mass Spectrometry in the Health and Life Sciences, San Francisco, CA, August 27-31, 1989.

Hettich, R. L.; Buchanan, M. V. "Structural Examination of DNA Adducts by Laser Ionization Fourier Transform Mass Spectrometry," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.

Hettich, R. L.; Buchanan, M. V., "Structural Characterization and Isomeric Differentiation of DNA Adducts," Massachusetts Institute of Technology, Boston, MA, December 7, 1989 (invited).

Ilgner, R. H.

Ilgner, R. H.; Buchanan, M. V., "Automated Thermal Desorption of Trace Organics in Air Using a New Sample Handling System," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.

Ilgner, R. H.; Wise, M. B.; Buchanan, M. V., "Direct Thermal Desorption MS/MS Analysis of Selected Organophosphonates with an Ion Trap Mass Spectrometer," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.

Jenkins, R. A.

Jenkins, R. A.; Dyer, F. F.; Moody, R. L., "Performance of a Commercial Portable X-Ray Fluorescence Unit for Field Analysis of Contaminated Soil and Water," 198th American Chemical Society National Meeting, Miami Beach, FL, September 10-15, 1989 (invited).

Katti, A. M.	Katti, A. M.; Huang, J.-X.;* Guiochon, G. A., "Experimental Verification of Semi-Ideal Model of Chromatography for Displacement Chromatography," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Katti, A. M.; Guiochon, G. A., "Mass Overload in Liquid Chromatography: A Theoretical and Experimental Approach," 6th International Symposium on Preparative Chromatography, Washington, DC, May 8, 1989.
	Katti, A. M.; Guiochon, G. A., "Mass Overload in Liquid Chromatogrpahy: A Theoretical and Experimental Approach," 13th International Symposium on Column Liquid Chromatography," Stockholm, Sweden, June 27, 1989.
	Katti, A. M.; Guiochon, G. A., "A Study of Binary Separations by Overloaded Elution and Displacement," 1989 Annual Meeting, American Institute of Chemical Engineers, San Francisco, CA, November 6, 1989.
Keller, J. M.	Keller, J. M.; Costanzo, D. A.; and Autrey, J. W.*, "Radiochemical and Inorganic Characterization of the ORNL Inactive Tanks for Radioactive Liquid Waste," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Klatt, L. N.	Klatt, L. N., "A Microcomputer Controlled Hot-Cell Titration System," 2nd Karlsruhe International Conference on Analytical Chemistry in Nuclear Technology, Karlsruhe, Federal Republic of Germany, June 5-9, 1989.
	Klatt, L. N., "Instrumentation Developments," International Atomic Energy Agency Safeguards Analytical Laboratory, Seibersdorf, Austria, June 12, 1989.
	Klatt, L. N., "Instrumentation Developments," Kernforschunszentrum Karlsruhe, Institut für Radiochemie, Karlsruhe, Federal Republic of Germany, June 14, 1989.
	Dale, J. M. and Klatt, L. N., "Can the Counterfeit Bill Be Detected?" Eastern Analytical Symposium, New York, NY, September 25-29, 1989 (invited).
Laing, W. R.	Laing, W. R., "Is There QA Life After the DOE Survey," Argonne National Laboratory, Argonne, IL, Chemical Technical Division Seminar, April 6, 1989.

Lyon, W. S.	Lyon, W. S., "Neutron Activation Analysis and Gamma Ray Spectrometry," New Brunswick Laboratory 40th Anniversary, Argonne National Laboratory, Argonne, IL, April 3, 1989 (invited).
McLuckey, S. A.	McLuckey, S. A., "Explosives Detection at ORNL," MMES Engineering Meeting, Oak Ridge Y-12 Plant, January 19, 1989 (invited).
	McLuckey, S. A. and Glish, G. L., "Ion Injection and MS/MS Studies with a 3-Dimensional Quadrupole," Pittsburgh Conference and Exhibition, Atlanta, GA, March 8, 1989 (invited).
	McLuckey, S. A. and Glish, G. L., "Explosives Detection with MS/MS," Entry Control Technology Review for DOE Facilities, Albuquerque, NM, April 19, 1989.
	McLuckey, S. A.; Glish, G. L.; Donohue, D. L.; Hulett, L. D., Jr.; and McKown, H. S., "Ionization by Positrons: What's the Matter with Anti-Matter?" 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 22, 1989 (invited).
	McLuckey, S. A. and Glish, G. L., "The Role of Mass Spectrometry in the Analysis of Explosives," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 24, 1989 (invited).
	McLuckey, S. A.; Glish, G. L.; and Eckenrode, B. A., "The Study of Negative Ions using a Three Dimensional Quadrupole," Triennial International Dynamic Mass Spectrometry Symposium, Salford, England, July 3-5, 1989.
	McLuckey, S. A.; Glish, G. L.; and Grant, B. C., "Explosives Detection with an Ion Trap Mass Spectrometer," Third International Symposium on Analysis and Detection of Explosives, Mannheim, FRG, July 10-13, 1989.
	McLuckey, S. A. and Glish, G. L., "Explosives Detection by Mass Spectrometry," FACSS XVI, Chicago, IL, October 1-6, 1989 (invited).
	McLuckey, S. A.; Glish, G. L.; Van Berkel, G. J.; Eckenrode, B. A.; Flurer, R. A.; Asano, K. G.; and Goeringer, D. E., "Ion Trap Mass Spectrometry with Unconventional Ionization Methods," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.

Ramsey, J. M.

Ramsey, J. M., "Nonlinear Analytical Laser Spectroscopy," Varian Research Center, Palo Alto, CA, February 17, 1989 (invited).

Ramsey, J. M.; Blazewicz, P. R.; and Whitten, W. B., "Spectrochemical Analysis by Multiphoton Ionization in a Low Pressure Sampling Interface," Pittsburgh Conference and Exhibition, Atlanta, GA, March 6, 1989 (invited).

Ramsey, J. M., "Non-Linear Optics and Spectrochemical Analysis," Randolph T. Major Memorial Lecture Series, University of Connecticut, Storrs, CT, April 7, 1989 (invited).

Ramsey, J. M., "Progress in Laser Spectroscopy," DOE/BES Site Review, ORNL, Oak Ridge, TN, April 25, 1989.

Ramsey, J. M. and Whitten, W. B., "Looking for Single Molecules in Small Droplets," 198th National American Chemical Society Meeting, Miami Beach, FL, September 11, 1989 (invited).

Ramsey, J. M.; Whitten, W. B.; and Blazewicz, P. R., "One and Two Color Multiphoton Ionization in a Low Pressure Sampling Cell," 1989 FACSS Meeting, Chicago, IL, October 2, 1989 (invited).

Goeringer, D. E.; Whitten, W. B.; and Ramsey, J. M., "Photoionization Spectroscopy in an Ion Trap Mass Spectrometer," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11, 1989.

Ramsey, J. M., "Laser Analytical Atomic Spectroscopy," Analytical Chemistry Division Seminar, Oak Ridge, TN, October 24, 1989 (invited).

Ramsey, J. M., "Spectrochemical Analysis in Electrodynamic Traps: Particles, Neutrals, and Ions," Department of Chemistry, University of Tennessee, Knoxville, TN, October 26, 1989 (invited).

Ramsey, R. S.

Ramsey, R. S.; Ho, C.-h.; Row, K. H.,* "The Determination of UV-Induced Lesions in DNA by HPLC/GC," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.

Ramsey, R. S.	Ramsey, R. S., "Chromatography Isolation and Measurements," U.S. DOE/OHER Toxicology Research Review, San Francisco, CA, June 13, 1989.
	Ramsey, R. S.; Katti, A. M., Guiochon, G. A., "The Quantitative Sampling of Thymine Dimer from Excess Thymine as Predicted Using a Semi-Ideal Chromatography Model," 16th Annual FACSS Meeting, Chicago, IL, October 1-6, 1989 (invited).
Robinson, L.	Robinson, L.; Dyer, F. F.; and Emery, J. F., "Neutron Activation Facilities in the Advanced Neutron Source," American Nuclear Society 1989 Winter Meeting, San Francisco, CA, November 26-30, 1989.
	Robinson, L.; Dyer, F. F.; West, C. D.*; and Montgomery, B. H.*, "Design and Use of a Proposed Californium Cold Neutron Source," Nuclear Analytical Methods in the Life Sciences International Conference, Gaithersburg, MD, April 17-21, 1989.
	Robinson, L., "An Expert System for Gamma-Ray Spectroscopy," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
	Robinson, L., "Neutron Activation" and "Careers in Science and Engineering," a series of lectures and panel discussions, Lincoln University, Philadelphia, PA, April 13-14, 1989.
Ross, H. H.	Ross, H. H., "Photon Scattering Effects in Heterogeneous Scintillator Systems," International Conference on New Trends in Liquid Scintillation Counting and Organic Scintillators, Gatlinburg, TN, October 2-5, 1989.
Rosseel, T. M	Rosseel, T. M.; Young, J. P.; Zuhr, R. A.*; Vane, C. R.*; Jones, N. L.*; and Peterson, R. S.*, "High Resolution X-Ray Studies of the Chemical Environment of Ions Implanted in Insulators," Symposium on Chemical Applications of Particle Accelerators, American Chemical Society National Meeting, Dallas, TX, April 9-14, 1989.
	Rosseel, T. M., "High Resolution Studies of the Chemical Environment of Sulfur Implanted in Insulator Matrices," DOE/BES Site Review, Oak Ridge National Laboratory, Oak Ridge, TN, April 24-25, 1989.

Shaw, R. W.	Shaw, R. W.; Young, J. P.; and Smith, D. H., "Resonance Ionization Mass Spectrometry," DOE/BES Site Review, Oak Ridge, TN, April 23-25, 1989.
	Shaw, R. W.; Young, J. P., and Smith, D. H., "Diode Laser-Initiated Resonance Ionization Mass Spectrometry," DOE/OHER/OBES Workshop on Advanced Laser Technology for Chemical Measurements, Argonne, IL, May 9-11, 1989.
	Shaw, R. W.; Young, J. P.; and Smith, D. H., "Diode Laser Resonance Ionization Mass Spectrometry," Fifth Interdisciplinary Laser Science Conference, Stanford University, Palo Alto, CA, August 27-31, 1989.
Shults, W. D.	Shults, W. D., "Recent Advances in Detection of Organic Vapors," Second Karlsruhe International Conference on Analytical Chemistry in Nuclear Technology, Karlsruhe, FRG, June 5-9, 1989 (invited).
	Shults, W. D., "Analytical Chemistry and Measurement Science," New Brunswick Laboratory 40th Anniversary Symposium, Argonne, Illinois, April 3-5, 1989 (invited).
	Shults, W. D., "The Excitement of Analytical Chemistry in a Multipurpose National Laboratory," Pittsburgh Conference and Exhibition, Atlanta, GA, March 6-10, 1989 (invited).
Smith, D. H.	Smith, D. H.; Young, J. P.; and Shaw, R. W., "Diode Laser Applications to Resonance Ionization Mass Spectrometry," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
Stemmler, E. A.*	Stemmler, E. A.;* Buchanan, M. V., "Surface-Catalyzed Reactions of Aromatic Amines with Oxygen and Nitrogen in NICI Mass Spectrometry," 37th Annual Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Stemmler, E. A.;* Buchanan, M. V., "Gas-Phase and Surface-Catalyzed Reactions of PAH in Negative Ion Chemical Ionization Mass Spectrometry," 16th Annual FACSS Meeting, Chicago, IL, October 1-6, 1989.

Stokely, J. R.	Stokely, J. R., "Characterization of Mixed Radioactive/Chemical Waste for Regulatory Classification and Remedial Action," Second International Conference on Analytical Chemistry in Nuclear Technology, Karlsruhe, Germany, June 5-9, 1989.
Thompson, C. V.	Thompson, C. V.; Edwards, M. D.;* Maskarinec, M. P., "A New Method for the Sampling and Analysis of Volatile Organics in Soils," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1989.
Todd, Peter J.	Todd, Peter J., "Solute Introduction and Liquid Secondary Ion Emission," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Todd, Peter J., "Origin of Secondary Ions Emitted from Liquids," SIMS VII - 7th Intl. Conf. on Secondary Ion Mass Spectrometry, Monterey, CA, Sept. 3-8, 1989.
Tomkins, B. A.	Tomkins, B. A.; McMahon, J. M.; Caldwell, W. M.; Wilson, D. L.,* "Ultratrace Determination of Formaldehyde in Potable Water," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
Van Berkel, G. J.	Van Berkel, G. J.; Tuinman, A. A.*; Glish, G. L.; and McLuckey, S. A., "Porphyrin Pyrrole Sequencing by Low Energy Collision Induced Dissociation of $(M+7H)^+$ Generated in situ During Ammonia Chemical Ionization," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Van Berkel, G. J.; Glish, G. L.; and McLuckey, S. A., "Charge Separation and Electron Capture Induced Dissociation of Doubly Charged Porphyrin Ions," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
	Van Berkel, G. J., "Geoporphyrin Analysis Using an Ion Trap Mass Spectrometer," 197th National Meeting of the American Chemical Society, Dallas, TX, April 9-14, 1989 (invited).
Whaley, K. S.	Whaley, K. S. and Lindahl, P. C.*, "Assessment of Inorganic Analysis Data Quality in the DOE Environmental Survey," 31st ORNL/DOE Conference on Analytical Chemistry in Energy Technology, October 10-12, 1989.

Wise, M. B.	Wise, M. B.; Ilgner, R. H.; Buchanan, M. V., "Direct Thermal Desorption MS/MS Analysis of Selected Organophosphonates with an Ion Trap Mass Spectrometer," Pittsburgh Conference and Exposition, Atlanta, GA, March 5-10, 1989.
	Wise, M. B.; Buchanan, M. V.; Ilgner, R. H., "Detection of Trace Organics in Air Using Thermal Desorption ITMS," 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21-26, 1989.
Wise, M. B.	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Direct Sampling Mass Spectrometry for the Detection of Trace Organics in the Environment," Gas Research Institute Bioengineering Conference, Knoxville, TN, February 22, 1989 (invited).
	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "New Mass Spectrometric Techniques for the Rapid Determination of Organic Compounds in Water and Soils," 19th International Symposium on Environmental Analytical Chemistry, Jekyll Island, GA, May 22-24, 1989 (invited).
	Wise, M. B.; Higgins, C. E.; Ilgner, R. H.; Guerin, M. R., "Rapid Determination of Nicotine in Ambient Air Using Thermal Desorption Ion Trap Mass Spectrometry," 43rd Tobacco Chemists' Research Conference, Richmond, VA, October 2-5, 1989.
	Wise, M. B.; Higgins, C. E.; Ilgner, R. H.; Guerin, M. R., "Evaluation of Ion Trap Mass Spectrometry for the Determination of Ambient Nicotine," EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Raleigh, NC, May 2-5, 1989.

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Amer. J. Public Hlth.	Anal. Chem.	Biomed. & Env. Mass Spec.	Cancer Research	Energy & Fuels	Env. Sci. & Tech.	Health Physics	Int. J. Mass Spec.	J. Amer. Chem. Soc.	J. Amer. Soc. Mass Spec.	J. of Chromatography	J. of Phys. Chem.	Org. Mass Spectrometry	Proposals	Other	Total
Buchanan, M. V.		6	5		2					1			3	21	1	39
Carter, J. A.														8		8
Christie, W. H.		1													1	2
Dale, J. M.														1		1
Donohue, D. L.		4												1	1	6
Dose, E. V.		5										1			1	7
Dyer, F. F.														2		2
Eldridge, J. S.							3									3
Feldman, C.		3														3
Glish, G. L.		3	1					3		1				2	6	16
Goeringer, D. E.															1	1
Griest, W. H.		2				1								4		7
Guerin, M. R.	1			1		1								5	1	9
Guiochon, G. A.		250*									18	2		6	4	280
Hettich, R. L.										1				1		2
Ho, C. H.														3		3
Hulett, L. D.															2	2
Jenkins, R. A.						2								5	1	8
Klatt, L. N.		2												1	1	4
Laing, W. R.															6	6
Maskarinec, M. P.						1									1	2
McLuckey, S. A.		3							1	2					2	8
Mueller, T. R.														2		2
Ramsey, J.M.		3												2		5
Ramsey, R. S.		3												3	2	8
Ross, H. H.														3	61	64
Rosseel, T. M.														2		2
Shaw, R. W.		1												2		3
Smith, D. H.		2												1		3
Stewart, J. H.															6	6
Stokely, J. R.														2		2
Todd, P. J.										2				41		43
Tomkins, B. A.		1													1	2
Van Berkel, G. J.										1					2	3
Whitten, W. B.														1		1
Young, J. P.		2												2	1	5
Totals	1	291	6	1	2	5	3	3	1	8	18	3	3	121	102	568

*As Associate Editor

SUMMARY OF ANALYTICAL SERVICE WORK

	Number of results reported by				
Organization	Analytical Spectroscopy	Radioactive Materials Analysis	Organic Chemistry	Inorganic Chemistry	Total
ORNL Unit					
Analytical Chemistry	1046	3938	9206	2471	16661
Central Management		1439	276	135	1850
Chemical Technology	2850	4870	967	13955	22642
Chemistry	240	65	388	1033	1726
Energy		704	719	6108	7531
Enginering Physics and Mathematics	22	32	341	5	400
Engineering Technology		66	105	210	381
Environmental and Health Protection	5610	46020	59037	31578	142245
Environmental Sciences		1360	16965	53000	71325
Finance and Materials		14	76	405	495
Fuel Recycle	2141	87	109	61	2398
Fusion Energy	161	64	541	97	863
Health and Safety Research	56	570	1088	129	1843
Instrumentation and Controls		38	242	79	359
Metals and Ceramics	3416	276	2390	1386	7468
Physics	136	75	397	8	616
Plant and Equipment	158	484	5855	773	7270
Research Reactor		78	1321	332	1731
Solid State	142	54	559	180	935
Others					
DOE Environmental Survey Program		1120	5546	1820	8486
K-25	2173	1195	1523		4891
Miscellaneous	1841	1777	787	6	4411
Paducah Gaseous Diffusion Plant			672		672
Savannah River Laboratory	276				276
Work for Others	1833				1833
Y-12		65	372		437
TOTAL	22101	64391	109482	113771	308981

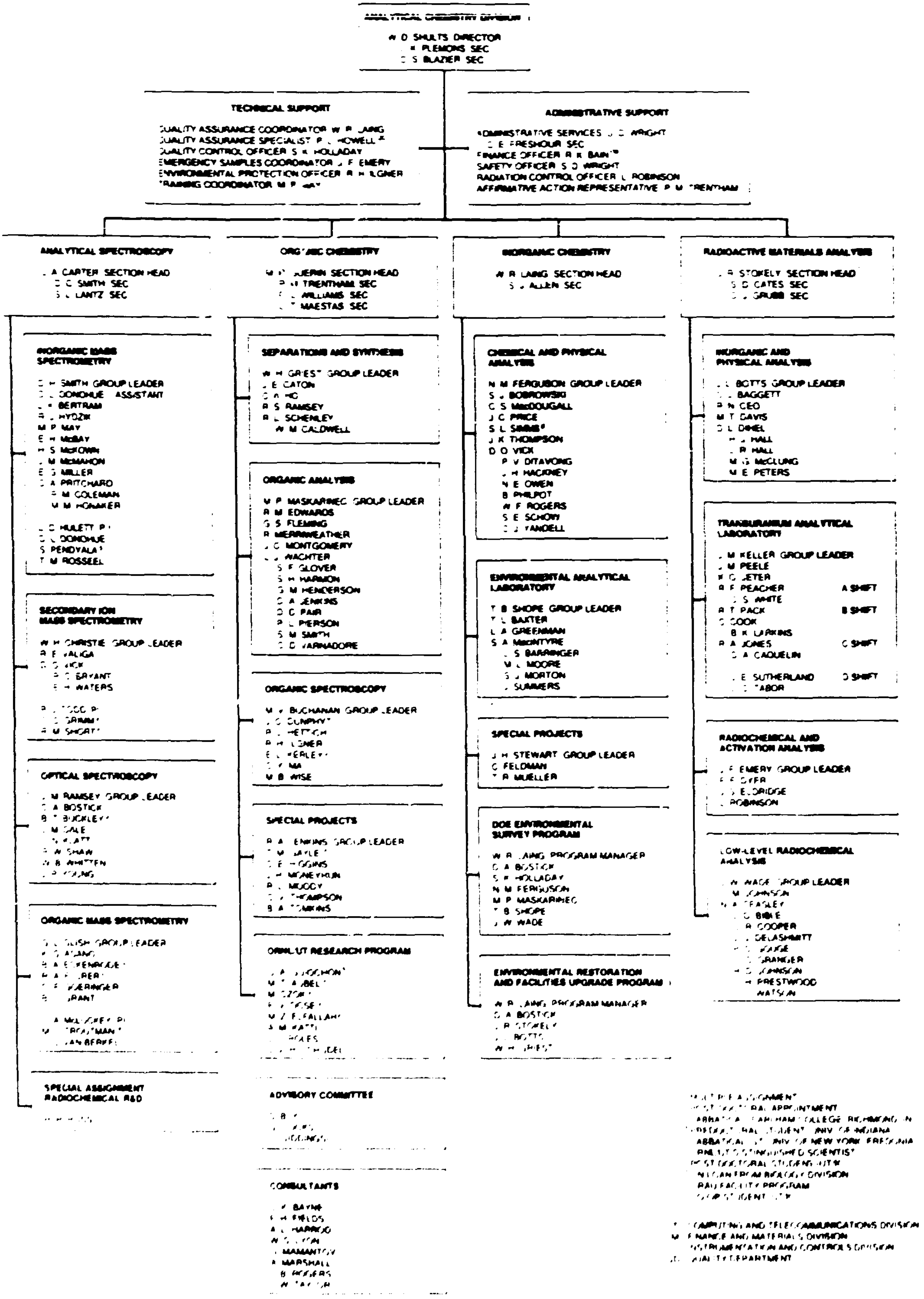
DIVISIONAL MANPOWER AND FINANCIAL SUMMARY
FY 1989

Source	$K	PY[a]
DOE programs		
Energy Research		
Basic Energy Sciences	1,775	13.6
Health and Environmental Research	572	4.6
Environmental Survey	738	7.2
Safeguards and Security	518	5.0
Nuclear Energy	245	2.1
Multi-program Facilities Support	733	7.2
Fossil Energy	80	0.7
Miscellaneous	175	1.7
Total DOE programs	4,836	42.1
Work for others - federal agencies		
Department of Defense	1,312	9.4
National Cancer Institute	307	2.2
Department of State	35	0.3
Environmental Protection Agency	44	0.3
National Institute of Health	50	0.3
Miscellaneous	26	0.1
Total WFO - federal agencies	1,774	12.6
Work for others - nonfederal agencies		
Protective Coating Companies	34	0.1
Uranium Ore Testing Companies	28	0.1
Center for Indoor Air Research	80	0.7
Miscellaneous	372	3.4
Total WFO - nonfederal agencies	514	4.3
Support/Services		
Other ORNL Divisions/Programs	6,057	85.1
Other Clients	630	8.9
Total Support/Services	6,687[b]	94.0
TOTAL FINANCIAL PLANS	13,811	153.0

---

[a] Person Years

[b] Does not reflect Laboratory general and administrative expense or general plant services.


ANALYTICAL CHEMISTRY DIVISION
W D SHULTS DIRECTOR
PLEMONS SEC
S BLAZIER SEC
TECHNICAL SUPPORT
QUALITY ASSURANCE COORDINATOR W R LAING
QUALITY ASSURANCE SPECIALIST HOWELL
QUALITY CONTROL OFFICER S K HOLLADAY
EMERGENCY SAMPLES COORDINATOR F EMERY
ENVIRONMENTAL PROTECTION OFFICER ILGNER
TRAINING COORDINATOR M P MAY
ADMINISTRATIVE SUPPORT
ADMINISTRATIVE SERVICES WRIGHT
E FRESHOUR SEC
FINANCE OFFICER R K BAIN
SAFETY OFFICER S D WRIGHT
RADIATION CONTROL OFFICER ROBINSON
AFFIRMATIVE ACTION REPRESENTATIVE P M TRENTHAM
ANALYTICAL SPECTROSCOPY
A CARTER SECTION HEAD
C SMITH SEC
LANTZ SEC
ORGANIC CHEMISTRY
GUERIN SECTION HEAD
TRENTHAM SEC
WILLIAMS SEC
MAESTAS SEC
INORGANIC CHEMISTRY
W R LAING SECTION HEAD
S ALLEN SEC
RADIOACTIVE MATERIALS ANALYSIS
R STOKELY SECTION HEAD
S D CATES SEC
GRUBB SEC
INORGANIC MASS SPECTROMETRY
SMITH GROUP LEADER
DONOHUE ASSISTANT
BERTRAM
HYDZIK
M P MAY
E McBAY
S McKOWN
M McMAHON
E MILLER
A PRITCHARD
M COLEMAN
M M HONAKER
HULETT
DONOHUE
S PENDYALA
T M ROSSEEL
SECONDARY ION MASS SPECTROMETRY
W H CHRISTIE GROUP LEADER
R E VALIGA
BRYANT
WATERS
TODD
GRIMM
R M SHORT
OPTICAL SPECTROSCOPY
M RAMSEY GROUP LEADER
A BOSTICK
B BUCKLEY
M GALE
R W SHAW
W B WHITTEN
P YOUNG
ORGANIC MASS SPECTROMETRY
GLISH GROUP LEADER
EDKENRODE
GRANT
TROUTMAN
VAN BERKEL
SPECIAL ASSIGNMENT RADIOCHEMICAL R&D
SEPARATIONS AND SYNTHESIS
W H GRIEST GROUP LEADER
E CATON
HO
R S RAMSEY
R L SCHENLEY
W M CALDWELL
ORGANIC ANALYSIS
M P MASKARINEC GROUP LEADER
R M EDWARDS
G S FLEMING
R MERRIWEATHER
C MONTGOMERY
WACHTER
S F GLOVER
S H HARMON
M HENDERSON
A JENKINS
C PAIR
PIERSON
S M SMITH
D VARNADORE
ORGANIC SPECTROSCOPY
M V BUCHANAN GROUP LEADER
DUNPHY
HETTICH
ILGNER
KERLEY
MA
M B WISE
SPECIAL PROJECTS
R A JENKINS GROUP LEADER
HIGGINS
MONEYHUN
MOODY
THOMPSON
B A TOMKINS
ORNL-UT RESEARCH PROGRAM
FALLAHI
ADVISORY COMMITTEE
CONSULTANTS
BAYNE
FIELDS
A HARROD
MAMANTOV
MARSHALL
B ROGERS
TAYLOR
CHEMICAL AND PHYSICAL ANALYSIS
N M FERGUSON GROUP LEADER
S BOBROWSKI
C S MacDOUGALL
J C PRICE
S L SIMMS
J K THOMPSON
D O VICK
P V DITAVONG
H HACKNEY
N E OWEN
B PHILPOT
W F ROGERS
S E SCHOW
YANDELL
ENVIRONMENTAL ANALYTICAL LABORATORY
T B SHOPE GROUP LEADER
BAXTER
L A GREENMAN
S A MacINTYRE
S BARRINGER
MOORE
MORTON
SUMMERS
SPECIAL PROJECTS
J H STEWART GROUP LEADER
C FELDMAN
R MUELLER
DOE ENVIRONMENTAL SURVEY PROGRAM
W R LAING PROGRAM MANAGER
C A BOSTICK
S K HOLLADAY
N M FERGUSON
M P MASKARINEC
T B SHOPE
J W WADE
ENVIRONMENTAL RESTORATION AND FACILITIES UPGRADE PROGRAM
W R LAING PROGRAM MANAGER
C A BOSTICK
R STOKELY
BOTTS
W H GRIEST
INORGANIC AND PHYSICAL ANALYSIS
BOTTS GROUP LEADER
BAGGETT
R N CEO
M T DAVIS
L DIKEL
HALL
R HALL
M G McCLUNG
M E PETERS
TRANSURANIUM ANALYTICAL LABORATORY
M KELLER GROUP LEADER
M PEELE
C JETER
R F PEACHER
A SHIFT
S WHITE
R T PACK
B SHIFT
COOK
B K LARKINS
R A JONES
C SHIFT
A CAQUELIN
E SUTHERLAND
D SHIFT
TABOR
RADIOCHEMICAL AND ACTIVATION ANALYSIS
F EMERY GROUP LEADER
DYER
ELDRIDGE
ROBINSON
LOW-LEVEL RADIOCHEMICAL ANALYSIS
W WADE GROUP LEADER
M JOHNSON
BEASLEY
BIBLE
R COOPER
DELASHMITT
GRANGER
JOHNSON
PRESTWOOD
WATSON
MULTIPLE ASSIGNMENT
POSTDOCTORAL APPOINTMENT
SABBATICAL EARLHAM COLLEGE RICHMOND IN
DOCTORAL STUDENT UNIV OF INDIANA
SABBATICAL UNIV OF NEW YORK FREDONIA
DISTINGUISHED SCIENTIST
POSTDOCTORAL STUDENT
BIOLOGY DIVISION
FACILITY PROGRAM
STUDENT
COMPUTING AND TELECOMMUNICATIONS DIVISION
FINANCE AND MATERIALS DIVISION
INSTRUMENTATION AND CONTROLS DIVISION
QUALITY DEPARTMENT