Chemical and Analytical Sciences Division Progress Report for the Period January 1, 1993, through December 31, 1994

Marvin L. Poutsma
Director
CHEMICAL AND ANALYTICAL SCIENCES DIVISION
PROGRESS REPORT FOR THE PERIOD
January 1, 1993, through December 31, 1994

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FOREWORD

Marvin L. Poutsma

This report provides brief summaries of progress in the Chemical and Analytical Sciences Division (CASD) during 1993 and 1994. The first four chapters, which cover the research mission, are organized to mirror the major organizational units of the division and indicate the scope of the research portfolio. The fifth and sixth chapters summarize the support activities within CASD that are critical for research progress. Finally, the appendices indicate the productivity and recognition of the staff in terms of various forms of external publications, professional activities, and awards.

The defining event during the reporting period occurred on January 1, 1994, when the Analytical Chemistry Division (ACD) and the Chemistry Division (CD) were merged into a single organization, CASD. This consolidation brought together all of the then CD and the major portion of the former ACD, namely the research and special analytical project functions that had not been consolidated into the Lockheed Martin Energy Systems (LMES) Analytical Services Organization that was created in mid-1993 to focus on compliance-driven analytical service work.

The stated mission of the new organization follows:

The Chemical and Analytical Sciences Division provides the leadership and focus at Oak Ridge National Laboratory (ORNL) for chemical research and its application to issues of scientific and technological importance to the Department of Energy (DOE) and the nation. It is committed to producing high quality scientific information and instrumentation, providing chemical expertise for innovative solutions to interdisciplinary problems, maintaining forefront R&D capabilities, and complying with ES&H and ethical standards. Its emphasis areas are chosen to be in congruence with ORNL and DOE missions and supportive of the needs of other federal and international agencies and the industrial and academic sectors. The important elements of CASD’s mission are to perform basic and applied research in the areas of chemical syntheses, properties, structures, transformations, and analyses.

The two precursor divisions had somewhat different subject matter portfolios and research styles. The merger offered an opportunity to merge complementary strengths and experiences. The centerpiece emphasis on analytical chemistry and radioanalytical chemistry within the former ACD carried over to become a major emphasis in CASD, but the research portfolio was broadened by the addition of programs from CD in other subdisciplines of chemistry, including some less traditional areas such as materials chemistry and geochemistry. The two divisions also had somewhat different relative emphases on “basic” and “applied” research projects, and the consolidated portfolio appears closer to the desired balance. A continuing challenge to DOE’s national laboratories is to better integrate basic and applied research in individual research groups in a synergistic and bidirectional fashion, without compromising the specific character of each. The new division is well poised to face that challenge.

A number of organizational changes were made to promote interactions, both in the makeup of individual research groups and in clustering these groups into sections. The Analytical Spectroscopy Section consolidates research activities in diverse aspects of inorganic and organic mass spectrometry, laser spectroscopy and miniaturization of analytical techniques, and surface science. The Nuclear and Radiochemistry Section groups together the major activities that involve radioactive materials, from basic research to special radioanalytical capabilities, and that therefore
require operation of nonreactor nuclear facilities (see below). The Organic Chemistry Section emphasizes organic analytical instrumentation and methodology as well as physical organic research. Finally, the Physical and Materials Chemistry Section contains a variety of research activities that fall into the subdisciplines of physical, inorganic, solution, and materials chemistry.

The support functions of the division were organized into an Office of Environmental, Safety, Health, and Quality Performance and Facilities Operation and an Office of Administrative Services. It was able to draw on the expertise of incumbents from both former divisions and to increase their contributions by typically increasing their span of interactions while focusing their areas of emphasis and expertise. Special attention has been given during the reporting period to improving operations and meeting compliance requirements for the division’s two “nonreactor nuclear facilities,” the Radioactive Materials Analysis Laboratory and the Transuranium Research Laboratory. Although requiring an expanding commitment of time and resources to maintain safe and compliant operation, these facilities continue to provide unique opportunities for significant research and special analytical projects. The division’s performance in the ESH&Q arena has been noteworthy in spite of ever growing regulatory pressures.

The funding profile of CASD includes three major sponsor segments: the DOE (approximately 70%), other federal and private agencies (approximately 10%), and special analytical projects (approximately 20%) for LMES and ORNL programs in isotope production, waste management and environmental restoration, and national security. The single largest DOE sponsor is the Office of Basic Energy Sciences (OBES), with significant contributions as well from the Office of Environmental Management, the Office of Nonproliferation and National Security, and the Office of Energy Efficiency and Renewable Energy.

The division had the opportunity during the reporting period to add a number of new employees, largely by replacement of retirees, who are adding to the creativity and vitality of the research and support staffs. The work of the research staff profits from the presence of numerous long-term guest scientists. For many of them, their assignments in CASD offer valuable educational and professional development opportunities. At any particular time, some 30-35 postdoctoral fellows are in residence, along with numerous graduate and undergraduate students.

Partnerships with academia and industry have been growing as the division has placed more emphasis on making its capabilities available to other sectors of the chemical research enterprise. A number of university professors have spent significant blocks of time as guests of CASD during this reporting period. Currently active mechanisms for industrial interactions include Cooperative Research and Development Agreements (CRADAs), the Advanced Technology Program of the National Institute of Standards and Technology (ATP-NIST), and the Technology Reinvestment Program (TRP) of the Department of Defense (DOD), as well as direct industrial support for special analytical projects.
1. ANALYTICAL SPECTROSCOPY SECTION
S. A. McLuckey, Head

The Analytical Spectroscopy Section is composed of five groups: Inorganic Mass Spectrometry, Optical Spectroscopy, Organic Mass Spectrometry, Secondary Ion Mass Spectrometry, and Surface Chemistry and Heterogeneous Catalysis. Heavy emphasis throughout the section is placed on experimental research and development. Much of the work is centered on advancing the state of the art in chemical measurements with particular emphasis devoted to separations, optical spectroscopy, various forms of mass spectrometry, neutron scattering and positron spectroscopy. The Surface Chemistry Group relies heavily on various surface analysis tools, including ion scattering spectroscopy, with special current emphasis on catalytic reactions of organosulfur molecules. The section and its predecessors have also played an important historical role in the analytical support of a wide variety of research and development programs at Oak Ridge and other DOE facilities. This work is currently concentrated in the Inorganic Mass Spectrometry Group and involves, inter alia, high precision isotope ratio measurements in support of DOE's isotope production programs.

The section is comprised of approximately thirty full-time staff with expertise in physics, instrumentation, computers, and, of course, many subdisciplines of chemistry. Fifteen to twenty-five visitors, including visiting scientists, postdoctoral associates, graduate students, and undergraduates, work with the staff at any given time. These guests benefit from access to state-of-the-art equipment, mentoring by mature scientists, and participation in exciting research activities while at the same time bringing new ideas, new capabilities, and added enthusiasm to the section.

INORGANIC MASS SPECTROMETRY GROUP; D. H. Smith, Leader

Research Activities

Glow Discharge Mass Spectrometry -- An investigation into the cause of anomalously high ion intensities for materials deposited as solutions on the sample cathode led to the conclusion that reactive sputtering was almost certainly the explanation. The utility of using argides, metallic dimers, and +2 species for quantification was demonstrated. ZnAr\(^+\) was observed to be present at anomalously high concentrations (up to 30% of the Zn\(^+\)); the current explanation for this phenomenon is that Zn sputters much more efficiently than the other metals investigated. An evaluation of the ability to measure isotope ratios using a glow discharge source yielded precision as good as \(\pm 0.03\%\); this value was realized with several elements (Pb, Cu) and almost certainly reflects an instrumental limitation. This work is on hold pending arrival of a Fisons Plasma-54 mass spectrometer which is equipped with seven collectors; substantially improved precision is anticipated when a glow discharge cell is interfaced to this instrument. Development of an rf cell for analysis of nonconducting samples continued with design of a cell that accommodates flat specimens (as opposed to the conventional pin shape). A new electrical interface was developed as well. This combination resulted in improved mass resolution and sensitivity in comparison to previous efforts. It offers promise for depth profile analysis of nonconducting films. A glow discharge cell was interfaced to our new Teledyne ion trap. This work is in its early stages; signal-to-noise ratios have been improved; selective ion accumulation has been demonstrated; MS-MS experiments have been performed. The immediate goal of this work is to obtain an elementally pure spectrum free of molecular interferences; if achieved, this capability will have a profound influence on the field of elemental analysis.
Secondary Ion Mass Spectrometry -- A significant advance in the measurement of isotopic ratios from insulating materials was made by using extreme energy filtering to select only those ions of greatest energy. Interfering molecular species are not formed at these high energies, and being able to measure elementally pure beams allowed attainment of unprecedented precision (0.02-0.03% for S⁺; 0.06% for O⁺); these levels reflect the ineluctable limits imposed by counting statistics. This technique has been applied to various geological systems and to studies of corrosion in vessels used in commercial power generation.

Thermal Ionization -- Using the Re overcoating technique developed several years ago, isotopic ratio measurements were made on 10⁷ atoms of Pu. This level of sensitivity compares well with that reported by other laboratories and implies that detection limits are 10⁶ atoms or lower.

Inductively-Coupled Plasma Mass Spectrometry -- Individual tree rings were analyzed by laser ablation to determine the variation of the ratio of Al to Ca over time. This ratio increased as the present day was approached, implying that changes in soil pH caused by acid rain contributed to degradation of the health of trees over the period in question. Electrochemical concentration of various elements prior to introduction to the torch resulted in improvements in detection by factors of 100 (to the mid-ppq [part per quadrillion] region!) for several elements (e.g., Ti). Interference from the matrix was eliminated as well, suggesting that this technique can be exploited to provide enhanced performance in instances where it is needed.

Support Activities

IAEA field trials to evaluate the ability of long established analytical techniques to detect clandestine nuclear activity led to heavy demands on our capacity. Over 100 samples were received and analyzed. A new glow discharge mass spectrometer obtained for support work was delivered in December 1993, but has yet to meet specification. Intense efforts on our part overcame most of the host of problems resulting from the instrument’s original design; we are presently awaiting delivery of a new gas inlet system (designed in the wake of our experience) that we hope will bring the instrument up to expected performance. Our NASA project concluded with evaluation of a gas mass spectrometer for application in pre-lift-off monitoring of various signature gases. Use of our Lu double spiking procedure was enhanced by development of a hot cell chemical separation procedure. Work continued in conjunction with George Swihart (Memphis) in providing high precision analysis of B. ORNL’s Stable Isotopes Program recently contracted to provide ca. 125 g per month of 95% enriched ²²²⁻¹." We provide 4 to 6 weekly isotopic analyses and monthly elemental analyses in support of this project.

Move from Y-12 -- As might be expected, our move is going far more slowly than anyone wants, but progress has been made despite innumerable bureaucratic obstacles. Two of the ORNL designed instruments are now in operation in Building 5505; the third is presently being readied for shipment. We have beneficial occupancy of the clean room (two years behind schedule). The end is in sight, at least with regard to having all operations shifted to X-10; getting free from Y-12 is an entirely different question. About 80% of the space in 9734 and 9735 has been turned over to new owners; it is anticipated that leaving the old Transuranium Laboratory will require years of effort.

Postdoctoral Fellows: B. A. Paterson; Guests: D. Crowe (University of Georgia), K. R. Hess (Franklin and Marshall), E. Jerde (UT Knoxville), K. Johnson (University of Florida), F. L. King (West Virginia University), R. K. Marcus (Clemson University), G. H. Swhart (Memphis University); Student Guests: K. L. Goodner (University of Florida), C. R. Shick (Clemson University), J. Teng (West Virginia University)

OPTICAL SPECTROSCOPY GROUP; J. M. Ramsey, Leader

This group is involved in a broad range of research and development tasks including laser-based measurement techniques that provide ultrahigh sensitivity and/or specificity, microfabrication of chemical processing and measurement devices, and crystallographic molecular structure elucidation.

Work on laser-based measurement techniques continues to include studies of single molecule detection in liquids. Single molecule detection limits by laser induced fluorescence of Rhodamine 6G has been demonstrated in a stream of droplets passing a detector at a 100 Hz rate. These results show the feasibility of performing single molecule measurements at practical analysis rates. The goal is to achieve single molecule detection limits at rates exceeding 1 Khz. Work is also progressing on understanding QED enhancements of fluorescence emission rates in microdroplets and the role of solvent dynamics. Studies of hot filament CVD diamond film growth processes have focused on monitoring of methyl and hydrogen radicals in the boundary layer region. A new frequency doubler has been put in operation to enhance resonance ionization signals of these radicals that are subsequently analyzed by time-of-flight mass spectrometry. A new atmospheric interface has been assembled to allow direct injection of aerosol particles into a quadrupole ion trap mass spectrometer. The first ever tandem mass spectrometry experiments on single microparticles have been completed. In addition, the first demonstration of the ability to use a single electrodynamic trap for both particle trapping and ion trapping was demonstrated. This combination allows nondestructive spectroscopic examination of a single microparticle with subsequent laser desorption/mass spectrometry analysis. Studies also have continued on the use of an all silica fiber optic probe to perform remote spectroscopic analysis of environmental contaminants. Enhancements to this probe are being developed to allow surface enhanced Raman spectroscopy to be performed at the distal end of the probe.

A number of new concepts have been demonstrated with microfabricated devices for chemical analysis. Micellar electrokinetic capillary chromatography (MECC) was demonstrated on a microchip device. This technique allows the separation of neutral species in a capillary electrophoresis (CE) format by including micelles in the buffer which act as a pseudo stationary phase. Separation efficiency and reproducibility were equal to or better than those of conventional capillary experiments. Devices have been fabricated out of new materials, quartz, and BK7 glass that have superior optical properties to the previously used soda lime glass. A preconcentration technique, sample stacking, has been demonstrated “on a chip.” Detection enhancements of more than an order of magnitude have been observed with the worst case scenario, anions. Moreover, the first integrated chemistry devices have been demonstrated that combine chemistry and chemical analysis on a single device. CE was combined with a post-column and pre-column reaction chamber. The pre-column reactor was used to demonstrate the measurement of chemical reaction rates on a microchip device. Kinetic information can be obtained in minutes with procedures under computer control consuming approximately 100 nL of reagents. The ability to integrate chemical processing on microfabricated
devices is significant as it allows manipulation of fluid volumes many orders of magnitude smaller than that possible by using conventional techniques, and the processing is inherently automated.

The project on crystallographic computing and topology specializes in the use of Morse critical point theory and orbifolds for characterization of crystal chemistry families and simplification of space group symmetry theory applications. Development of an ORNL Orbifold Atlas that can serve as a topological supplement to the International Tables for Crystallography with descriptions of the singular set, underlying topological space, and other topological invariants for each of the 230 crystallographic space groups was started. The computing part of the project completed the software upgrade and testing of the biomolecule x-ray facilities in the Biology Division and the neutron diffraction 4-circle facilities at the High Flux Isotope Reactor (HFIR), which were upgraded in hardware by a previous Laboratory Directed Research and Development (LDRD) project. Neutron diffraction data sets were then collected and processed for 13 compounds in collaboration with users from England, Germany, Canada, and the United States.


ORGANIC MASS SPECTROMETRY GROUP; M. V. Buchanan, Leader

This group conducts fundamental and applied research in organic and biological mass spectrometry, with particular emphasis on trapped ion techniques, both quadrupole ion trap (QIT) and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Investigations of physical processes which occur in the ion trap are being pursued to allow new modes of trap operation to be developed and enhance the analytical utility of this device. Fundamental aspects of collisional activation and dissociation processes are being investigated to provide insight into ion energies and temperatures in a trap during ion storage and resonance excitation. Results to date indicate that resonance excitation acts as a thermal excitation source that produces a relatively slow increase in ion internal energy due to many discrete collisional excitation/relaxation events. Methods and electronics for in situ detection of ions in a QIT have been developed which yield improvements in signal to noise due to the ability to remeasure ion currents from the same population of ions multiple times.

Electrospray (ES) is being investigated to gain insight into the fundamental processes involved in this ionization technique. A series of experiments have demonstrated that ES can be characterized as a two electrode controlled current electrolysis cell. The potential at the metal/solution interface is a function of the ES current and the relative redox potentials and concentrations of the various species in the system, including the metal capillary. Further, the entire process is limited by both the ES current and the solvent flow rate through the capillary. Information gained from these studies is allowing new ways to expand the analytical utility of ES, such as use of ES MS as a highly sensitive and mass selective detector for electrochemical experiments and rapid, on-line electrochemical preconcentration/clean-up techniques for enhanced trace detection of metals, semivolatiles and nonvolatile organics. Electron transfer and chemical reactions have been employed to extend the application of ES to a wider range of organics, such as polycyclic aromatic hydrocarbons, fullerenes,
and others. Investigations have been conducted to increase the sensitivity of ES, especially when combined with on-line capillary electrophoresis. Sheathless electrospray sources using small i.d. gold tipped capillaries have been devised, and detection of attomole quantities of proteins have been achieved. An electrostatic ion guide, consisting of a cylindrical tube with a concentric wire, has been employed to guide ions generated in an ES source through the fringe fields of the 3T magnet of the FTICR. The guide is housed in a vacuum chamber that has three differentially pumped regions. Initial results using a variety of biomolecules have shown that ions may be trapped without the use of a pulse of buffer gas and with low trapping plate voltages, suggesting that the ions arrive at the cell with low kinetic energies. Experiments are now under way to reduce the pressure in the overall system and deflect ions after excitation and detection events to improve mass resolution and other performance characteristics.

Fundamental aspects of matrix assisted laser desorption/ionization are also being investigated using a specially designed time-of-flight instrument. Optical and other methods are being used to probe chemical and physical parameters which affect the success or failure of the MALDI experiment. The results from these studies are being used to extend the mass range and sensitivity of MALDI, especially for oligonucleotides. Other approaches for enhanced MALDI generation of oligonucleotides are also being investigated. Electrophore tags are being attached to the 5'-terminus of an oligonucleotide so electron capture conditions can be used to form ions more efficiently and with less fragmentation than with conventional MALDI conditions. A number of these tags have been synthesized (by Phillip Britt of the Physical Organic Group) and are stable in the MALDI process. The time-of-flight instrument is being modified to permit MALDI under electron capture conditions.

Development of gas phase processes to yield more detailed structural characterization of organics and biomolecules remains a major area of emphasis in the group. Collision induced dissociation processes have been employed with FTICR and MALDI to characterize a series of adducts of DNA oligomers, including identification of the adduct, site of attachment to the nucleobase, and location of the adducted base within the oligomer. New off-resonance excitation techniques have been applied to collisional dissociation studies of MALDI generated ions from oligonucleotides. These new techniques provide increased fragmentation and thus enhanced structural information for these singly charged ions. MALDI FTMS is also being used to identify and structurally characterize a variety of nanoclusters ranging from endohedral fullerenes to gamma radiolysis products of \( \text{C}_60 \). For example, it was found that the ionization potentials of \( \text{La@C}_n \) are substantially lower than the corresponding values for the empty fullerenes, implying that the lanthanum atom donates electron density to the fullerene cage. The relative gas phase acidities for nucleobases have been determined using ES QIT and will be used to understand the decomposition behavior of multiply charged oligonucleotides via collisional activation. This information will provide insight into oligonucleotide sequence. Investigations of ion/ion reactions in a QIT with ES generated multiply charged ions have revealed that these reactions are more energetic, efficient, and rapid than ion/molecule reactions. Further, ion/ion electron transfer has been observed to yield more extensive fragmentation than ion/ion proton transfer. Ion/molecule reactions involving proton transfer with an ion at a specific m/z value have been explored as a means of enhancing mass resolution of ES spectra where individual charge states are not resolved.

Both MALDI and ES are being explored for rapid, confident detection of polymerase chain reaction (PCR) fragments that are widely used in clinical, forensic, biochemical, and other laboratories to
identify people, heritable diseases, and pathogens. Working with a team of researchers from the Biology and Health Sciences Research divisions, we have demonstrated that both ionization techniques may be used to detect synthetic oligomers and PCR products. In the latter case, we have detected DNA fragments diagnostic of cystic fibrosis in humans and fragments specific to *Legionella* bacteria.

The group is actively involved in a number of projects in which the unique capabilities of ion traps are employed for rapid, confident detection of trace compounds and for chemical analysis in the field. We have continued work on the combination of the ORNL atmospheric sampling glow discharge ionization source (ASGDI) with tandem mass spectrometry. Specific attention has been focused on interfacing the source with a small commercial QIT and reducing source pumping requirements by a factor of ten over the normal source. The ORNL ASGDI was recently introduced commercially by Teledyne MEC and exhibited at the Pittsburgh Conference in February. Ion trap instrumentation is being developed as part of a CRADA with the automotive industry to design and build a small, easy to operate instrument for characterization of ultra low emission vehicles (joint with the Instrumentation group). Both ASGDI with NO\(^+\) attachment and *in situ* chemical ionization are being investigated for real-time characterization of emissions from a vehicle being tested on a dynamometer. Methods are also being developed for the rapid detection of target compounds in foods and physiological media using ion traps, especially in combination with new ES techniques. In collaboration with the Knoxville Police Department, we have initiated investigations to help explain why latent fingerprints from children disappear from surfaces faster than those from adults. Initial investigations of the chemical components of fingerprints from children and adults have revealed distinct differences, primarily in the types and molecular weight distribution of compounds that support these observations. Based on these studies, Reza Dabestani and Mike Sigman (Physical Organic Group) will develop an improved method for visualization of fingerprints.

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**SECONDARY ION MASS SPECTROMETRY GROUP;** P. J. Todd, Leader

Research in the Secondary Ion Mass Spectrometry (SIMS) Group centers around development of new analytical capabilities, with special emphasis on spatially resolved analysis (i.e., imaging), along with improvements in ion optics and methods of data acquisition. We receive funding from a variety of sources which covers projects from basic research of fundamental problems to instrumental and data systems development. The interplay among these various projects is such that barriers to progress found in areas of development in one project stimulate basic research to understand and overcome these barriers. Funding sources over the past two years include the DOE Office of Basic Energy Sciences, the Office of Research and Development, the National Institutes of Health, the Laboratory Directed Research and Development Program, and support from the Mass Spectrometry Development Group at Y-12.
We have overcome the fundamental barrier to imaging organic compounds known as the static SIMS limit. This limit is the dose of primary ion (ca. $10^{13}$ primary ions/cm$^2$) beyond which organic compounds cease to emit characteristic secondary ions. This limit has been a profound barrier to mapping the distributions of organic compounds in tissue. Overcoming the static SIMS limit means that the surface of a sample can be cleaned in vacuum, greatly simplifying sample preparation. Furthermore, analysis of dilute samples by summing and averaging data, as well as obtaining depth profiles of organic samples, becomes possible. We accomplished this feat by coordinated use of a primary beam of massive, multiply charged glycerol clusters and our Cs$^+$ ion beam. The Cs$^+$ beam is routinely used for imaging because it can be focused and rastered. The cluster beam can neither be focused nor rastered. However, by alternately turning the Cs$^+$ beam on and off in complement with the cluster beam, images can be obtained with the Cs$^+$ beam and the damaged surface molecules removed with the molecular beam.

Use of the cluster gun has also enabled us to analyze lipids and sugars directly by SIMS without any sample preparation. In fact, we have observed secondary ions characteristic of lipids directly from biologic tissue. These observations represent a major milestone in the application of SIMS to imaging and analyzing biologic tissue. Two major barriers to the ultimate goal of imaging biologic tissue for drugs and their metabolites, namely the static SIMS limit and the lack of characteristic secondary ion emission from tissue, have been overcome.

We have developed a routine and general method of charge compensation for secondary ion imaging of large heterogeneous insulating samples. Most organic samples, in particular biologic tissue samples, are insulators. If the charge which accumulates on the surface of an insulating sample when bombarded by the primary ion beam is not neutralized, analysis by SIMS becomes impossible. With our technique, the secondary ion extraction field is synchronized with a periodic primary Cs$^+$ beam to allow a sheetlike beam of 5 eV electrons to pass over the sample surface. Electrons are attracted to and neutralize any points on the sample that have accumulated positive charge. We now use the technique routinely for static SIMS imaging of biologic and other insulating samples.

We have advanced the field of time-of-flight (TOF) mass spectrometry by experimentally demonstrating that an ion mirror can be constructed which compensates for initial ion kinetic energy distributions in both the ion extraction field as well as the field free drift region. Ion kinetic energy distributions are often the limiting factor in determining mass resolution for TOF mass spectrometers since a distribution of energies (or velocities) leads to a distribution of ion flight times, unless properly compensated for. Conventional ion mirrors compensate only for the drift region. By careful analysis of the entire TOF mass analyzer, we were able to devise a suitable modification to the conventional mirror design and then experimentally demonstrate this capability. The consequence of these measurements is that the ion extraction region no longer needs to be very small relative to the rest of the TOF spectrometer. The removal of this limitation opens the way for development of large field-of-view imaging TOF microprobes and compact TOF SIMS instruments. Although the prototype TOF SIMS instrument compensates for initial kinetic energy distributions in both the extraction field and drift regions, it is very sensitive to small variations in the sample surface potential. In other words, ions (of the same mass) leaving the sample with a distribution of energies have essentially the same flight time through the mass spectrometer, leading to a well defined TOF mass peak. If the sample surface potential changes, however, this peak shifts in the TOF spectrum. We were able to exploit this feature of our TOF spectrometer to measure small changes in the surface potential.
of insulating samples subjected to TOF SIMS analysis. We were able to demonstrate that the equilibrium surface potential reached with charge compensation using low energy electrons could be measured and was a function of the charge compensating electron current. This technique should be useful for fundamental studies of surface charging, as well as a method for evaluating the effectiveness of various charge compensation schemes.

Research Staff: J. M. McMahon, R. T. Short, P. J. Todd; Postdoctoral Fellows: N. Dookeran, X. Guo; Subcontract Support: W. M. Holland; Consultant: J. T. Brenna

SURFACE CHEMISTRY AND HETEROGENEOUS CATALYSIS GROUP; S. H. Overbury, Leader

This group contains two programs. The objective of one program is to understand fundamentals of catalytic reactions of organosulfur molecules occurring at metallic surfaces and to understand how these molecules affect and are affected by the surface structure and composition. The approach is experimental but is complemented by theoretical modeling used as an interpretive tool. Adsorbates chosen for study include thiols, substituted thiophenes, bifunctional molecules such as benzenethiol and mercapto-ethanol, related organic molecules, and partially deuterated derivatives of these molecules. Substrates are metallic and bimetallic single crystals, ultra thin films grown on metal single crystals, and these surfaces following sulfidation or oxidation. The objective of a second program is to develop and apply positron spectroscopy techniques. This involves fundamental studies of the interactions of positrons with materials, applications of the techniques to practical samples, and development of instrumentation and collaborations.

Various methods were applied to study sulfidation of surfaces. High resolution soft x-ray photoemission spectroscopy (SXPS) experiments were performed on the U-13 undulator at the National Synchrotron Light Source to characterize the sulfidation of Ni(111). Combined with other data, a new structural model of the high coverage sulfided surface has emerged and demonstrates the ability of SXPS to determine the bonding environment of S atoms. Low energy alkali ion scattering, ISS, has been used to determine the interaction and structures of co-adsorbed S and Ni on the W(001) surface. The goal of this study was to determine how a strongly bonded adsorbate, sulfur, interacts with a well characterized bimetallic system.

Growth and structural evolution of Ni and C overlayers deposited on W(001) were studied by ISS and W 4f\text{\textit{p}} SXPS. This work allowed comparison between structural details obtained from ion scattering with measurement of the electronic environment sampled by SXPS. The correlation of structural and electronic information shows that the W core levels are less sensitive to the type of nearest neighbors they have than they are to their location relative to the surface. For the carbided surfaces, peaks associated with W atoms bonded to two, three, and four C atoms are evident in the spectra.

ISS studies were undertaken of the structure and surface composition of the (110) and (100) surfaces of FeAl alloy single crystals. First and second layer compositions were determined for each crystal face. An investigation of the structure of clean and Pt covered ZnO by ISS was initiated. To understand supported catalysts it is important to develop new techniques to probe the structure of oxide surfaces and their interaction with metals deposited upon them. Analysis of bulk and thin film oxides will be a major future research emphasis.
Reaction studies of methanethiol, benzenethiol, and dimethyl disulfide (DMDS) on Ni(111) were undertaken during this period. Reaction products, desorption profiles, and preliminary spectroscopic results were obtained. Extensive studies were made of methyl thiolate formed from methanethiol and DMDS. SXPS data proves the presence of two types of molecular intermediates at high coverage. Consideration of HREELS, SXPS, and computational modeling indicates the two intermediates are adsorbed on bridge and hollow sites. Benzenethiol yields only one type of thiolate with C-S bond tilted with respect to the surface normal. Extensive studies of the kinetics of C-S bond scission using SXPS during isothermal anneals provide evidence of hydrogen assisted C-S bond scission in benzenethiol.

SXPS experiments have been conducted on the reaction of methanethiol on ultra thin Ni and C films deposited on W(001). It is found that thin pseudomorphic Ni films increase selectivity for methane production compared to total decomposition, higher from clean W or Ni surfaces. The reactivity of methanethiol can be correlated with the structure of the Ni films on W(001), known from ion scattering measurements. On the C modified surface, selectivity for methane formation is also high, and molecular methanethiol is stabilized to higher temperatures. Isotopic labeling indicates that there is little incorporation of the sulphydryl hydrogen in the methane desorption products. The stability of the thiolates in the bridge sites is also higher than that of thiolates in four-fold sites on the clean surface.

Reactions of thiophene and methyl substituted thiophenes were examined on clean and hydrogen treated Ni(111) surfaces to determine both reaction mechanisms and the effects of hydrogen on the reactions. Thiophenes desulfurize to form mono-unsaturated alkenes. Increasing the availability of hydrogen increases the selectivity toward alkene production but does not result in alkane formation. Steric effects were observed in the reaction as 2,5-dimethyl thiophene underwent rapid cleavage of the methyl groups resulting in only C4 products, while 3-methyl thiophene produced significant pentene. The data are interpreted in terms of either a "metallocycle" intermediate or a π-bonded allyl fragment. Such detailed understanding may allow altered hydrocarbon product selectivity in HDS reactions.

The ability of a laser to remove surface defects from Si(100) was studied by STM. Using sequential, low power, green laser pulses, the dimerized first layer of Si(100) could be mostly removed leaving a vacancy free underlayer with altered structure. This selectivity is believed to be due to the reduced coordination of Si atoms at steps or adjacent to vacancies. This work has implications for possible new methods for the processing of semiconductor surfaces.

Positron and electron induced luminescence were compared to learn more about the mechanisms for positron excitation. Optical spectra of the light emitted from anthracene dissolved in polystyrene were obtained for bombardment by 3 keV positrons or electrons. Differences are attributed to the fact that electron bombardment produces electron hole pairs, while positron excitation can give rise to unpaired holes which ultimately decay with an impurity or defect. Positron induced luminescence may therefore be a useful probe of defects, impurities, and material structures. Measurement of the energy broadening of positron annihilation radiation was tested as a diagnostic probe of paint weathering. It was found that changes due to simulated weathering for periods of a few weeks could be detected compared to control specimens and that there were variations depending upon the presence of pigments and the type of binders. The depth of weather penetration was determined by variation of the energy of the probing positrons. Molecular ionization of gas phase molecules, induced by
positrons with energies from 0.3 to 3 eV, were studied. It was found that positrons with very low
energies, below the threshold for positronium formation, can yield significant fragmentation in large
alkane molecules. The cross section for fragmentation depends upon the size and structure of the
molecule.

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2. NUCLEAR AND RADIOCHEMISTRY SECTION
   J. R. Stokely, Head

The Nuclear and Radiochemistry Section is composed of four groups which perform research, development, and special support for a number of different DOE and LMES programs and a few private corporations. Most of the work conducted by the section involves the handling of radioactive materials in special experimental facilities designed for this purpose. There is considerable variation in the type of work done by the different groups ranging from fundamental chemical R&D to short-term studies needed to meet specific project objectives. Studies and special support are performed in the following general areas: investigation of the fundamental chemical and physical properties of the actinide elements and compounds, characterization of radioactive waste to provide information needed for remediation efforts or environmental compliance, chemical and radiochemical analyses to support the ORNL transuranium element production program, and utilization and advancement of neutron activation analysis for characterization of materials. Applied support and R&D activities within the section often yield new methodology and insight which allow contributions to be made to methods compendii, program reports, or scientific publications or presentations.

NEUTRON ACTIVATION ANALYSIS GROUP; L. Robinson, Leader

The Neutron Activation Analysis (NAA) Group continued conceptual design efforts in support of the Advanced Neutron Source (ANS) project. The ANS project supported personnel for a two week visit to the research reactor at the National Institute of Standards and Technology. During this visit, research was conducted that confirmed the applicability of both thermal and cold neutron prompt gamma ray analysis to the determination of trace elements in soils taken from the Oak Ridge Reservation.

Delayed neutron counting (DNC) was applied in a number of studies in which fissile element content was of interest. Due to a high neutron flux at the High Flux Isotope Reactor (HFIR) and an extremely low delayed neutron background, a detection limit of approximately 10 nanograms per gram was established. This allowed the group to participate in a nuclear nonproliferation study in conjunction with the DOE and the International Atomic Energy Agency (IAEA) designed to determine fissile materials in environmental matrices. Samples included pine needles, tree bark, grasses, mosses, soil, water, and smears from laboratory bench tops. If levels of uranium (or plutonium) were above typical levels for a given matrix, then these materials were subject to additional analysis by mass spectroscopy. Other studies involving the use of DNC were gross fissile content of Gunite Waste Tank samples and transuranium waste samples from ORNL, uranium content of treated soils from the DOE's Fernald and Portsmouth sites, and uranium content in ocean floor sediments. In many of these studies DNC was used in conjunction with conventional NAA to determine the isotopic ratio of $^{238}$U to $^{235}$U.

In 1993 the NAA Group concluded a joint effort with researchers in the Environmental Sciences Division (ESD) to determine baseline concentrations of 35 elements in soil taken from around the Oak Ridge Reservation. This study was a follow-up to the 1991-1992 East Fork Poplar Creek project in which 4000 samples from the creek's floodplain were analyzed for eight elements by NAA. In the
baseline characterization study, about 140 samples were analyzed. The quality assurance standards in both programs were deemed comparable to existing protocols established by the Environmental Protection Agency (EPA) for the Contract Laboratory Program (CLP).

A Monte Carlo integration method has been developed to solve the integral form of the solution of the Boltzmann transport equation. The approach is used to treat neutron transport in a system with a californium-252 neutron source. The flux of cold neutrons is studied as a function of the moderator and cooling materials and as a function of the geometry of the system. This appears to be the first time that a Monte Carlo method has been used to obtain such results. These results are compared with those from the diffusion form of the solution of the Boltzmann equation and from experiments. The relationship between the momenta of two particles before and after collision are written in a new way. This relationship is that imposed by the conservation of energy and momentum in an elastic collision. These calculations could serve as the basis for the development of an actual cold neutron source which would have applications in trace element analysis and moderator development.

Neutron activation analysis continues to be used to detect ppm concentrations of $^{129}$I in spent reactor fuel rods. Following chemical separation of unwanted fission products, iodine is retained on an ion exchange resin loaded directly in a small irradiation insert. These inserts are loaded directly into rabbits, irradiated, and counted the following day.

A neutron activation analysis procedure was developed to determine sub-ppb levels of molybdenum and tungsten in high purity silica gel. This work was prompted by a Work-For-Others (WFO) request by the General Electric Company (GE). GE fabricates quartz optical fibers from the silica gel, and apparently the presence of Mo and W causes embrittlement of the fibers. This project will help GE to select raw materials of the highest purity and to find sources of contamination in their manufacturing process.

A project to assist the Southwest Naval Engineering Command to determine naturally occurring radionuclides in building materials continues. Materials analyzed include gravel, sand, soil, rocks, cement, and finished concrete. Among the radioisotopes measured by high resolution gamma ray spectroscopy are $^{40}$K, $^{238}$U, and $^{232}$Th. Radon emanation rates are determined by storing samples in dessicators for several days and sampling the air inside the dessicator with a Lucas cell. The Lucas cell has a zinc sulfide coating on one face, and light pulses produced in the cell by alpha particles are measured in a phototube.

A novel method for the determination of aluminum and phosphorus in biological material has been developed. It is extremely difficult to determine microscopic amounts of aluminum in the presence of macroscopic amounts of phosphorus due to the production of $^{28}$Al from fast neutron reactions in stable $^{31}$P. This new method takes advantage of the uniquely different neutron flux spectra of the two pneumatic tube systems at HFIR. The apparent Al production rates are determined in both systems using standards. Samples are then irradiated and counted similarly. Final concentrations of Al or P are determined from the solution of a set of simultaneous equations. This method has been validated using standard reference materials. Over 100 biological samples have been analyzed including brain, kidney, liver, and fingernails.

The application of NAA to geology and geochemistry continued via the group collaboration with geochemists from The University of Tennessee at Knoxville. Over 150 geological and lunar samples
have been analyzed. This association has led to two publications and the dissertation of one graduate student.

Since 1991 the NAA Group has collaborated with researchers in the ESD on a program to monitor airborne mercury levels in the vicinity of the Y-12 plant. Samples are taken by pumping a metered amount of filtered air through iodated charcoal traps. The charcoal in these traps is placed in high purity graphite rabbits and irradiated for up to five minutes. Radioactive $^{203}$Hg is measured three to four weeks later.

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### RADIOACTIVE MATERIALS ANALYSIS LABORATORY GROUP; J. M. Keller, Leader

The Radioactive Materials Analysis Laboratory (RMAL) develops new methodology for the inorganic and radiochemical analysis of radioactive materials. Most of the current work is directed toward the characterization of radioactive waste from underground storage tanks and radioactive sludge stored in drums. In addition, the group provides technical and analytical support to numerous programs and special projects within the laboratory. Over the past year the group has expanded to include a number of special projects involving environmental levels of radioactivity which include wildlife monitoring and a Noble Gas Monitoring System for the HFIR stack. A selection of the special projects and programs are discussed below.

Method development studies for the clean-up of radioactive waste samples for characterization are sponsored by the Analytical Services Division (ASD) of DOE/HQ. The purpose of the project is to develop more efficient methods for the characterization of radioactive waste samples from DOE facilities and to distribute these methods to potential users. Traditional methods are not well adapted to the handling of high levels of radioactivity in samples. Also, the standard method cannot handle interferences from the complex sample matrices typical of DOE radioactive wastes. Improved methods must consider as low as reasonably achievable (ALARA) practices, waste minimization, and contamination control. These improvements involve methodologies that reduce or replace hazardous reagents/solvents, can be performed remotely, require less time, and can be easily adapted to automation. These studies are presented in the form of procedures which are included in the *DOE Methods for Evaluating Environmental and Waste Management Samples* (DOE Methods Compendium), a compendium of sampling and analysis procedures for DOE waste samples, published by the ASD.

During 1993, method development studies focused on three main areas: clean-up of radioactive samples for (1) metals determination by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), (2) alpha spectrometry, and (3) radioactive strontium determination. These studies resulted in the development of new methods using extraction chromatography which reduce waste, time, and personnel exposure as compared to traditional techniques using solvent extraction and precipitation techniques. Results of these studies were presented at the 44th Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy in
Atlanta, Georgia, and at the 1993 Analytical Chemistry Information Meeting Poster Session in Oak Ridge, Tennessee. The studies on metal determinations were published as an ORNL Technical Report, *Separation Techniques for the Clean-up of Radioactive Mixed Waste for ICP-AES/ICP-MS Analysis*, in March 1993. As a result of the strontium determination studies, a procedure, *Determination of Total Radioactive Strontium Using Extraction Chromatography*, was submitted to the ASD and included in the DOE Methods Compendium.

During 1994, studies concentrated on the determination of $^{99}$Tc in radioactive wastes and contaminated oils. The studies of $^{99}$Tc in radioactive wastes were combined with 1993 studies and presented at the American Chemical Society (ACS) National Meeting in Washington, D.C. The oral presentation has been submitted for publication in the proceedings of the national meeting. A new sample preparation method for $^{99}$Tc, *Determination of $^{99}$Tc in Oils Using a Muffle Furnace and Extraction Chromatography*, was also submitted to the ASD for inclusion in the DOE Methods Compendium.

The GAAT Treatability Study is a large program being conducted by the LMES Environmental Restoration Division for Environmental Restoration and Waste Management (ERWM)/LMES to determine the options for removing radioactive waste from the inactive gunite storage tanks located within the ORNL Waste Area Grouping (WAG) 1. RMAL became involved with this project in the summer of 1994, and we are currently funded at about $800 K/year for analytical and technical support on the physical, inorganic, and radiochemical characterization of the tank waste. The data generated by the project will support planning in the areas of waste management, risk assessment, safety, design, and structural integrity.

RMAL is the lead analytical laboratory for the DOE Waste Isolation Pilot Plant (WIPP) Transuranic (TRU) Waste Characterization Program (TWCP). This work is supported by the DOE Carlsbad Area Office (DOE/CAO) and is currently funded at $1.5 M/year. Waste characterization data will be collected to support regulatory compliance programs associated with the WIPP facility.

The TWCP requirements for WIPP involved the upgrade of facilities, procurement of analytical instruments and equipment, and the development of many procedures and project plans. The procurement and installation of several GC and GC/MS systems, new glove boxes, high pressure microwave dissolution systems, a mercury cold vapor AA system, and a data management system were completed during the 1993-94 time frame. Also completed during this period were the upgrades to several laboratories and modifications to the HVAC system for new glove box installations. The required procedures were developed, written, and approved during the past year. Quality assurance (QA) documents were prepared which included the development of the *Radioactive Materials Analysis Laboratory-Oak Ridge National Laboratory (RMAL-ORNL) Quality Assurance Project Plan (QAPjP) for the Transuranic Waste Characterization Program (TWCP)*. This QAPjP was submitted for review and approval to Idaho National Engineering Laboratory (INEL) in September 1994.

RMAL personnel provide radiological support and collaboration to LMES/TWRA/DOE for monitoring wildlife throughout the Oak Ridge reservation. These efforts mostly include the annual deer hunts held each fall and monitoring/tagging studies done on geese and turkeys. The total number of deer taken during the 1994 hunts was 495, consisting of 309 bucks and 186 does. The total number of deer not released to the hunter over the past two years is fifteen, which is below the average
retention percentage of about 3% for all hunts. Of the deer retained during the 1994 hunts, two were kept because of $^{137}$Cs being present above the release limit of 5 pCi/g. This was the first time in ten years that deer were retained due to $^{137}$Cs contamination (all other retained deer were due to $^{90}$Sr contamination).


TRANSURANIUM ANALYSIS GROUP; C. D. Parks, Leader

The Transuranium Analysis Group (TAG) is located in the Radiochemical Engineering Development Center (REDC), Building 7920. The group is currently made up of four staff members, four technical support members, and two subcontractor employees. The primary objectives of the group are to provide around-the-clock analytical support to the transuranium isotope production efforts by the REDC of the Chemical Technology Division (CTD) and to provide monitoring of radioactive and non-radioactive process waste streams for the Waste Operations Section of the Waste Management and Remedial Action Division (WMRAD). In addition, the group provides analytical support to a variety of laboratory programs including waste tank characterization projects, remedial action programs, radioactive waste solidification projects, and support of health physics throughout the laboratory for the identification of nuclides from various contamination events.

The analytical support provided for the REDC/CTD throughout CY 1993 and for much of the first half of CY 1994 entailed Mark-42 Fuel Assembly processing and development. The Mark-42 Fuel Assemblies were irradiated at the DOE Savannah River Site and are processed for the recovery of plutonium, americium, and curium. The first two of a planned ten fuel assemblies to be processed were completed during this period. Development support on the Mark-42 processing included a series of PUREX experiments to characterize the separation of plutonium from other transuranic elements and TRUEX experiments intended to validate the computer model (developed at Argonne National Laboratory) of the process which removes transuranic elements from waste solutions. The TAG also conducted experiments in conjunction with researchers from CTD on the removal of high levels of cesium from the MK-42 waste solutions using a resorcinol formaldehyde resin in order that the waste stream resulting from the processing is not as highly radioactive when discharged to the waste tanks. The level of support for the MK-42 processing included the analysis of 1,400 samples with approximately 17,000 analytical determinations during the period.

During the second half of CY 1994 and into CY 1995, analytical support provided for the REDC/CTD involved TRU Campaign #69. The TAG performed a wide variety of chemical and radiochemical analyses in support of the processing and purification of curium, berkelium, californium, einsteinium, and fermium. The transcurium actinides are produced through the irradiation of curium targets in the HFIR, and radiochemical analyses are required throughout the purification to verify the processing steps and to quantify the amounts of material present. Development work during the campaign included the testing and implementation of a procedure to separate berkelium from cerium using EICrom's TEVA•Spec extraction chromatography resin. The effort provided by the group for TRU Campaign #69 included the analysis of 941 samples with approximately 8,300 analytical
determinations. During the period CY 1993 and CY 1994, the total number of samples analyzed in support of TRU Campaign operations was 2,344 with approximately 19,000 analytical determinations performed.

The TAG performs both chemical and radiochemical analyses in support of ORNL's Waste Operations monitoring of various waste streams at the laboratory. Among the streams monitored are waters prior to release to the Clinch River, various ponds and creeks inside the laboratory for possible releases of radioactivity, and process water in areas prior to work. Routine samples are also taken from the Low Level Liquid Waste (LLWW) Facility to monitor the effectiveness of columns used on the LLLW stream to remove radioactive constituents. Samples from various nonradiological streams (Process Water Treatment Plant, Sewage Treatment Plant, etc.) are also monitored to ensure that activity is not being introduced. During the period CY 1993 and CY 1994, the TAG performed nearly 93,000 analyses on 30,000 samples received from the WMRAD.


TRANSURANIUM ELEMENT CHEMISTRY GROUP; R. G. Haire, Leader

The Transuranium Element Chemistry Group's objective is to perform systematic investigations regarding the fundamental chemistry, physics, and materials science of actinide metals, alloys, and compounds. The goals are to advance the basic science of these materials and to provide information conducive to technologies that are relevant to various missions of the DOE.

The experimental research focuses on vapor and solid state science of the f-elements, with the emphasis being on the actinides through fermium. Several scientific disciplines are employed in the experimental studies; these include high pressure x-ray diffraction and/or spectroscopy, high temperature x-ray diffraction and mass spectrometry, laser ablation mass spectrometry, thermal analyses, solid state spectroscopy (Raman, absorption, fluorescence), and novel synthetic techniques. The chemistry of the actinides and transactinides is also considered theoretically using quantum and statistical mechanics.

Our high pressure studies explore the effects of pressure on materials. One of the principal effects of pressure is to decrease the atomic separations in materials, which can induce large changes in their chemical and physical properties and provide insight into their fundamental science. Collaborative investigations with the Institute for Transuranium Elements during this period have involved x-ray diffraction and resistivity studies of americium and einsteinium metals as well as several actinide bismuthides. For the metals, the focus was on the delocalization of the f-electrons and the occurrence of a metallic valence change due to pressure. From such studies we have established pseudo Hill limits, which are very useful for interpreting the behaviors of actinide compounds. Studies of the actinide monobismuthides searched for potential valence fluctuations brought about by pressure and allowed systematic comparisons to be made between their pressure behaviors and those of other actinide monopnictides or monochalcogenides. Attempts were made to explain the structural transformations and volume collapses observed in terms of the electronic configurations of atoms comprising the compounds.
We have also pursued high temperature studies of f-elements which concern thermochemical and physicochemical properties of vapors and condensed phases. These studies have involved the actinide elements, alloys and compounds, and dealt with gas-solid reactions of uranium halides and technetium compounds; the vaporization and phase behaviors of actinide oxides; and the high temperature physicochemical properties of several actinide alloys systems.

High temperature gas solid chemical studies probed materials in special environments, revealing novel species and bonding not encountered under conventional conditions. Mass spectrometric Knudsen cell studies involving reactive gases with both technetium and uranium have identified aspects of their chemistries that may be problematic in remediation technologies. New vapor species of technetium have been identified (e.g., TcO_4^Br, TcO_4^I, etc.), some of which have no known Mn/Re analogs. Although extensively studied, some fundamental aspects of uranium halide chemistry remain enigmatic. We have now synthesized and identified new gaseous halides, UF_4Cl and UF_4Cl_2, which help clarify the bonding concepts for mixed uranium halides.

Oxides are one of the primary compounds of the actinides; yet many have not been characterized thoroughly, and even less was known about their high temperature vaporization/decomposition behaviors. Knudsen cell mass spectrometry and X-ray diffraction were employed in high temperature systematic studies to determine their vaporization/decomposition behaviors, which were found to be controlled by underlying roles of the element's electronic configurations and promotion energies. A relationship was devised that allowed us to correlate actinide monoxide dissociation energies with the f-electron promotion energies, which established predictions and correlations for the vaporization behaviors of all the actinides. Supplemental studies of phase behaviors at elevated temperatures complemented these vaporization studies. Such data have important implications for the speciation encountered in immobilization technologies (e.g., glasses), the vapor diffusion of actinides during high temperature processes, new synthetic concepts, etc.

The alloying behaviors of actinide metals with other f-element and transition metals illuminates bonding and electronic structures in metallic systems (e.g., roles of 5f-electrons in intermetallic bonding); they are also important for understanding and/or predicting the behaviors of actinide materials in technological applications pertinent to remediation applications, medical uses, separations, etc. Our studies of such actinide alloys have employed primarily differential thermal analysis and x-ray diffraction. We have shown that the Np-Zr system differs significantly from the U-Zr system. The Np-Fe phase diagram was found to be similar to those for U-Fe and Pu-Fe but exhibited characteristics which could not be quantitatively predicted. Similar studies were initiated for other Np-transition metal alloy systems.

Another area of research has involved the chemistry and mechanisms of laser ablation and two dimensional (mass optical) spectrometry. The fundamental insights derived from these investigations are important for understanding and predicting the behaviors of actinides in multiple chemical situations, as well as probing a new dimension in actinide chemistry. Pulsed laser ablation of solids efficiently produces vapor species for a variety of investigations. In developing experimental techniques for actinide materials, we have discovered that ablation of lanthanide oxalates produces novel lanthanide oxide clusters (Ln_{m}O_{n}^{+}, with m up to 64 and n = 3/2 m). These clusters exhibit remarkable stoichiometry/valence variations that reflect subtle distinctions between the electronic structures of the different lanthanides. Other ablation techniques are being developed to probe spectroscopic properties and metal ion molecule reactions.
We have frequently used solid state spectroscopy (Raman, luminescence, absorbance, etc.) to investigate a wide range of structural, electronic, and chemical properties of f-element materials. One area of investigation incorporating spectroscopy was the characterization (valence state identification, speciation, etc.) of f-elements in glass matrices. Another was the generation and characterization of divalent states of f-elements in a tetraborate host. Following confirmation of published work on the stabilization of divalent Eu, Sm, and Yb in SrB₄O₇ hosts, it has been possible to stabilize the divalent states of Tm, Nd, Dy, and Cf in this matrix. This procedure provides access to the divalent state of f-elements for other studies and will be pursued to determine the limit of stabilization afforded by this host.

Developments in quantum and statistical mechanics approaches, and in computers and software, have provided greater capabilities for computational and theoretical chemistry. Topics addressed recently include the eigenstates of Am, quantum mechanical calculations for element 106, statistical mechanical molecular dynamics calculations, and neutron transport calculations. Several electron excitation energies for Am have been derived, and the results show that some spectroscopic terms assigned presently to experimental levels are probably incorrect. These calculated excitation energies will be highly beneficial for assigning experimental spectra and understanding electronic transitions in Am. Calculations on diatomic molecules have determined bond energies for molecular ions formed between argon and several transition metals during glow-discharge mass spectroetry studies. These energies were employed for interpreting the experimental data. A new technique for calculating neutron transport properties has been developed for the design and development of Californium-252 cold neutron sources. Our calculations were in good agreement with available experimental data and with results calculated via a diffusion approach.

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The Organic Chemistry Section performs fundamental and applied research, technology and analytical methods development, and specialty analytical support involving organic chemicals and materials. Chemical research addresses the structure and reactivity of organic chemicals in their native environments. Coals, lignin, biomass, and surface bound chemicals are receiving primary attention. Thermal and photolytic transformation chemistries for solids and water, respectively, are of special interest. Work on the chemistry of solids and surfaces is enhanced by related research in solid state nuclear magnetic resonance and chromatography based surface characterization. Applied chemical research currently addresses the development and demonstration of low emission diesel fuels and improved technologies for processing wood of promise to the pulp and paper industry. Analytical research and development addresses advanced instrumentation, high sensitivity sampling and analysis methods, and the fundamentals of chromatographic separation. Ion trap mass spectrometry continues as the primary area of instrumentation development with particular attention given to fieldable and continuous monitoring instruments. Solid sorbent air sampling and solid phase extraction of aqueous samples are combined with ion trap and chromatographic methods of analysis to yield part-per-trillion sensitivities. Specialty analytical support in this period has included direction of a national survey of exposure to environmental tobacco smoke, characterizing the headspace of underground storage tanks containing radioactive wastes, and establishing a facility for analyzing mixed wastes.

ANALYTICAL METHODS GROUP; W. H. Griest, Leader

The objectives of the Analytical Methods Group are the development of organic chemical separations and measurements methods, and their application to scientific questions and programmatic issues. Group expertise includes sample preparation, chromatographic separations and measurements, spectrometric identifications, specialty sample matrices, unusual analytes, and ultratrace determinations. The group is funded mainly by the DOE and the DOD (U.S. Army), but also is supported by other federal agencies (National Cancer Institute and U.S. Forest Service).

The analysis of environmental materials is a major focus of the group for several sponsors. Two major problems in the accurate analysis of volatile organic compounds (VOCs) in soils are the preservation of VOCs during sample shipment and their incomplete extraction in analysis. Optimum refrigerant packing conditions which preserve samples in coolers for shipment up to five days have been identified and demonstrated in a field study, and a hot methanol extraction method which recovers VOCs from soil more efficiently than the EPA purging protocol has been developed. It is suspected that VOCs sequestered in micropores and fissures of soil particles are displaced and released more efficiently by the hot polar solvent than by the bubbling action of the conventional gas purge.

Unusual environmental contaminants determined for military sponsors include a rocket propellant and phosphorus- and sulfur-containing chemical warfare agent decomposition products and
manufacturing byproducts. The method for determining N,N-dimethylnitrosamine (a propellant constituent) in groundwater was developed, certified, and applied with excellent results to approximately 50 groundwater and water treatment process research samples. The 2 parts-per-trillion level of sensitivity is unmatched by any other method or laboratory. It is achieved by the novel combination of a large volume injection (0.2 mL of a 1 mL solvent extract concentrate from 1 L of water) using a solid phase sorbent column and a short path thermal desorber, and gas chromatography (GC) with a chemiluminescence detector operated in the nitrosamine selective mode. More recent work aims to replace the 24-hour continuous solvent extraction with a carbonaceous solid phase sorbent. Development and certification is nearly complete for the alkylphosphonic acids method (detection limit of ca. 1 ppb in water), which features solid phase extraction with a quaternary amine anion exchanger substituted column medium, elution with an alkaline derivatizing agent which forms the methyl esters upon injection into the GC inlet, and detection/quantitation using a phosphorus selective flame photometric detector.

Explosives also are an important focus of method development and applications. The standard method for determination of explosives in soils requires an overnight ultrasonic extraction using acetonitrile, followed by high performance liquid chromatography (HPLC) with diode array ultraviolet absorbance detection. Initial investigations into a faster method based upon supercritical fluid extraction (SFE) provided evidence for the first time that nitramine explosives (important as a component of plastic explosives and some propellants) could be extracted by SFE. The important factors were a relatively high SFE temperature and a polar modifier in the supercritical fluid.

An unusual law enforcement related environmental analytical activity conducted for the U.S. Forest Service was the identification of unique compounds which could be used for the rapid detection at a distance of marijuana gardens (ideally, using airborne direct sampling ion trap mass spectrometry [DSITMS]). In a study conducted in collaboration with the Instrumentation Group and the Environmental Monitoring Group, air samples were collected within an experimental marijuana garden maintained by the U.S. Department of Agriculture and were analyzed using several techniques including GC-MS and DSITMS. Two sesquiterpenes, beta-caryophyllene and (-)-isocarophyllene, were identified as very promising indicators because of their relatively high abundance. Monoterpenes were not unique and were found in background sources such as pine and cedar.

Analytical methods for and investigations of hazardous and mixed wastes also are a major focus of the group. The efficiency of composting for decontaminating and detoxifying explosives laden soils and sediments has been investigated in a multidisciplinary study led by this group for the U.S. Army. Analyses of explosives and their microbial metabolites in soils and composts and determinations of the bacterial mutagenicity and leachable aquatic toxicity showed greater than 98% reductions in explosives content and similar decreases in toxicity by the composting process. The fate of the major explosive, 2,4,6-trinitrotoluene (TNT), also was briefly investigated. The TNT was not mineralized (converted to carbon dioxide, water, and nitrogen oxides), but rather biotransformed into an insoluble product which resists release into the environment. The evidence suggested that an amino derivative of TNT was covalently bound to humic substances in the soil. These findings were instrumental in the acceptance by the State of Oregon and EPA Region X of windrow composting for remediating explosives lagoon sediments at the Umatilla Army Depot activity site.
Not only explosives but also munitions have been the subject of analytical methods development and programmatic investigations. Studies for the Army demonstrated that adhesive joint failure in combustible cartridge case munitions is caused by an interdependent, multifactorial mechanism including heat and nitroester migration into the case wall from the propellant charge. A method for micro-sampling and analyzing the case wall without destroying the structural integrity of the round was developed. Current methods of sampling and analysis damage the round and make it unsuitable for further testing or firing. The nitroester migration in the case wall of M829 antitank rounds was mapped and found to be uniform circumferentially around the round but varied along the length of the round. This prompted the development of a prototype nitroester indicator patch which could signal the accumulation of nitroesters from the propellant in the case wall and identify rounds which are unsafe and liable to structural failure.

The group has developed many analytical methods for characterization of radioactive mixed wastes (RMWs) and is part of the unique analytical capabilities of the RMAL. For several years, EPA and other analytical methods have been adapted and their performance validated for their application to RMW analysis in glove box, hot cell, and radiochemical hood operations. Methods for extracting and analyzing volatile organic compounds, Resource Conservation and Recovery Act Toxicity Characteristic ("TCLP") semivolatiles and pesticides have been adapted, validated, and published in a DOE manual of methods for waste and environmental sample analysis. A particularly difficult achievement was the development, production, and performance validation of the prototype equipment for conducting the TCLP zero head-space extraction (ZHE) of VOCs. The equipment developed for the ZHE of RMW was found to perform better than the EPA TCLP protocol ZHE in preserving and recovering VOCs from wastes. The second phase of the project is now focusing on modifying state-of-the-art methods and instrumentation such as GC-ITMS and HPLC-MS to RMW analyses. It has been demonstrated that the GC-ITMS is $10^2$-$10^3$ more sensitive in the analysis of semivolatile organic compounds than is the EPA protocol GC-quadrupole MS, and allows smaller sample amounts or more diluted extracts to be analyzed.

A unique laboratory has been set up at the RMAL for the preparation and organic chemical analysis of transuranic wastes on a custom production scale. Sample extraction, purification, and solvent concentration equipment has been set up in glove boxes and radiochemical hoods. A custom volatile purging apparatus has been obtained and installed in a glove box and interfaced to a trap/desorption module and GC-MS located outside of the box. Other GCs and a GC-MS for analysis of semivolatile organics, nonhalogenated/water soluble volatiles, and PCBs have been set up in radiochemical hoods or laboratories. Method performance demonstration and procedure documentation are under way in preparation for regulatory analyses of transuranic waste sludges to be placed in the WIPP.

The development of methodologies for health effects issues and bioanalytical chemistry included the investigation of volatile organic carcinogens in food, the search for dibenzo(a,l)pyrene (DbalP, the most carcinogenic polycyclic aromatic hydrocarbon [PAH] yet discovered) in materials relevant to human exposure, and a mutagenic antibiotic that only affects female germ cells. A unique blender purge and trap device was developed to allow the accurate analysis of benzene and other VOCs in foods at low to sub-ppb concentrations. The method was demonstrated to be highly reliable and accurate, and the benzene content of many raw and cooked foods was determined. Of particular interest was the observation of a linear correlation between the benzene content and the level of
gamma irradiation (for preservation) of chicken meat. However, the levels of benzene were in the low ppb range even at the highest dose of irradiation (1.77 ppb at 3 KGy). A very extensive 16-step method consisting of solvent and pH partitioning, sorption column chromatography, and sequential HPLC on reverse phase/size exclusion/reverse phase columns was developed to isolate a very narrow PAH subfraction extending in ring size from benzo(ghi)perylene to anthanthrene in complex mixtures. Application to tobacco, charcoal and coal smoke particulates, a coal liquefaction heavy oil, and roofing tar indicated that DbaP concentrations are very low, and definitive evidence for its presence is exceedingly difficult to obtain. The upper limits to its concentration ranged from 75 ppb in combustion particulates from Chinese smoky coal to 4 ppb in tobacco smoke condensate. The main difficulty was the complexity of the isolate and the very low relative concentration of DbaP, which prevented positive ultraviolet spectral identification.

The antibiotic bleomycin affects female (but not male) germ cells. Means of detecting it in female germ cells are needed for studies of its mode of action. Methods were developed and demonstrated to harvest large numbers of oocytes from mice, expose them \textit{in vitro} to bleomycin, extract bleomycin taken up by the cells, and detect it using matrix assisted laser desorption ionization time-of-flight mass spectrometry.


\textbf{ENVIRONMENTAL MONITORING GROUP; R. A. Jenkins, Leader}

The Environmental Monitoring Group conducts applied research on the development and application of analytical methods for the determination of toxic species in complex matrices, with special emphasis on airborne and environmental mixtures. An important additional specialty is the area of enhanced biomass processing and fuels chemistry, with particular emphasis on process optimization. The group is funded primarily by the DOE, but is also supported by the Westinghouse Hanford Co., the DOD, and the Center for Indoor Air Research (CIAR).

A long term focus of the group has been the generation, sampling, and/or chemical characterization of complex airborne matrices. For example, we have developed sampling and analytical methodology bases for the determination of airborne organic species in the underground storage tanks at DOE's Hanford Site. The technology has been based on the collection of organics of a very wide range of volatilities on traps containing sequentially packed multiple sorbents, followed by gas chromatographic/mass spectrometric analysis. Fugitive emissions from these tanks over the years have resulted in a number of flammability and worker exposure concerns. To date, we have applied the methodology to the headspace characterization of more than 35 tanks at the site.

We have been conducting studies through a large CRADA with Cincinnati Milacron (CM). CM is one of the country's largest providers of machining fluids for the metal working industry. Aerosols of the fluids resulting from the machining process can often be irritating to workers. Studies in our laboratories have been directed toward the determination of particle size distribution of fluid aerosols
generated for inhalation toxicology studies of these fluids. Cascade impaction has been employed to provide size fractionation, relying on UV or fluorescence spectrophotometry for quantification of stage loading. In addition, we have been using HPLC to determine distribution of aerosol components as a function of particle size. Results to date have indicated a wide range of size distributions, depending on specific fluid compositions.

One of our most interesting recent studies has been the determination of human exposure to environmental tobacco smoke (ETS). Approximately 100 subjects were recruited from each of 16 cities around the country to wear personal sampling systems, both at work and away from work. Samples were analyzed for eight components of ETS, and individual samples of saliva were collected and analyzed for a metabolite of nicotine (cotinine) to assess smoker status and to compare individual ETS nicotine exposure with levels of salivary cotinine. The field phase of the study was concluded in June 1994, and data evaluation is ongoing. Preliminary conclusions from the study are that individuals living with smokers receive a greater ETS exposure at home than do individuals who are exposed in the workplace. In addition, the fraction of individuals who misreport their smoking status (i.e., claim to be lifetime never smokers but are in fact current active smokers) is much higher than that reported in previous studies. The latter finding has profound implications for the assessment of risk to lung cancer from ETS exposure.

A second focus of our group is the development and evaluation of technologies for more rapid and/or complete characterization of sites contaminated with organic wastes. To this end, we have been developing two subsurface sampling systems. One of these, the multisorbent arrayed sampler, consists of an array of six multisorbent traps, identical to those validated for the tank headspace characterization studies described above, in a remotely operated assembly designed to function in conventional 4" diameter monitoring wells. The sampler has an integrated packer so that the zone being sampled in the well can be isolated. Quantitative samples of vadose (unsaturated) zone soil gas can be collected on the sorbent traps and returned to the surface for analysis by a variety of analytical techniques. The sampler was deployed during two field trials each at DOE’s Savannah River and Hanford sites. As a result of the Hanford deployments, several previously unreported semivolatile contaminants of the subsurface were identified. The DOD has been supporting the development of a membrane interface sampling system for both vadose and saturated zone implantation. This system is designed to be deployed with the Army’s cone penetrometer system and permits contaminants, which pass through the interface, to be swept to the surface where they can be analyzed in real time using a direct sampling ion trap mass spectrometer. Unique features of this system will permit quantitative determination of soil gas levels of contaminants, independent of the soil permeability. We are exploring the patentability of the interface system. Laboratory evaluations are nearing completion, and the system is due to be field tested in the first half of CY 1995.

Another aspect of our enhanced site characterization efforts has been the evaluation of field analytical technologies, with the end product of the studies being the development of SW-846-type analytical methods for inclusion in the DOE Methods Compendium. During the past two years, we have tested and developed methods for several immunoassay kits for the determination of PCBs, mercury, and fuel components in soil and water, and colorimetric test strips for the determination of lead, chromate, nickel, and nitrate in water. In addition, we have developed methods for the determination of selected VOCs in water and soil, using the Bruel and Kjaer Model 1302 photoacoustic infrared monitor. All of these methods have been submitted and reviewed and are now a part of the Compendium.
A final focus of our group is on the development of environmentally friendly technologies. Research areas include low emission diesel fuels which incorporate biomaterials, wood processing technologies which lower process chemical use, and development of effective electrochemical methods for decontaminating and recycling metals from gaseous diffusion plants. Efforts to formulate and evaluate emission reducing diesel fuels have been funded by a variety of sources, including DOE/EE, in-house support (LDRD and seed money), and a USCAR partnership. Stable diesel fuels which have conventional performance, contain 20% or more renewables, and reduce NO\textsubscript{x} by 25% have been formulated and evaluated. A thermal pretreatment technology which increases chemical penetration into whole wood has been under development with LDRD support. This technology permits direct hydrolysis of individual constituents within whole, bark-on wood by chemical catalysts and biocatalysts. Results of kraft pulping tests indicate substantial increases in yield (up to 10%) coupled with reductions in lignin content (30-50%) and effective alkali (25%). Longer term funding for this research will be sought in 1995. Methods for removing radioactive contaminants (\textsuperscript{60}Co, \textsuperscript{99}Tc, and U) from gaseous diffusion plant scrap are being evaluated. It appears that a combination of purification methods and electrochemical processing could purify the nickel sufficiently for reuse at DOE facilities. The availability of effective process technology could decrease the DOE's costs of maintaining contaminated nickel as a legacy waste.

An important addition to our specialty facilities during this period has been the installation of a room sized controlled experimental atmosphere chamber in Building 5507. The chamber has interior stainless steel walls and an air recirculation system capable of maintaining a wide range of temperatures and relative humidities at a variety of circulation conditions. To date, the facility has been used to generate dilute atmospheres of typical subsurface environmental contaminants and homogeneous atmospheres of environmental tobacco smoke. However, its capabilities afford the opportunity to perform large scale monitoring instrument validations, enclosure of bench scale chemical processing to assess fugitive emissions, and generation of battlefield obscurant and security related aerosols.


INSTRUMENTATION GROUP; M.B. Wise, Leader

The Instrumentation Group conducts basic and applied research in the area of analytical instrument development and novel applications of existing analytical technologies. Projects span all aspects of instrument evolution including concept, design, construction, testing, validation, and technology transfer. Special capabilities exist particularly in the areas of mass spectrometry, quadrupole ion trap mass spectrometry, sampling hardware and techniques, computers, electronics, and field instrumentation. Areas which are currently being emphasized include instrumentation and methods for on-site field analysis of organic pollutants, automated instrumentation for process monitoring, mass spectrometry detection of chemical warfare agents and precursors, and downsized instrumentation for man portable and specialized applications.
Many of the ongoing projects in the Instrumentation Group are related to the development and application of DSITMS. DSITMS is a combination of sampling and measurement technologies for the rapid determination of organic pollutants in a wide range of samples including air, water, soil, and waste media. With this technology, low levels of pollutants can be quickly determined without the need for extensive sample preparation or compound separation methods. Demonstrated detection limits range from 10 pptt to 10 ppb, depending on the analyte, the sample matrix, and the exact analytical method used. Sample analysis time is generally less than 5 minutes, allowing the results to be available to the customers almost immediately and greatly reducing the cost relative to conventional laboratory analysis.

The application of DSITMS to the rapid analysis of organic pollutants in the environment has been a major thrust of our research during the last several years. This work has been sponsored by the DOE Office of Technology Development (EM-50), the DOE Waste Management (EM-40), the U. S. Army Environmental Center (AEC), the Program Manager for Rocky Mountain Arsenal, and the LMES ERWM programs. Much of this project has a special focus on the development of DSITMS instruments which can be operated either in a laboratory or in the field for site characterization, compliance monitoring, and remediation monitoring activities. The benefits of rapid on-site analysis capability include more thorough site investigations, quick access to analytical results by site engineers and geologists, and reduced analytical costs by minimizing the number of samples which must be shipped to an off-site laboratory for routine analysis. Field demonstrations of the DSITMS technology have been successfully conducted at a number of DOE and DOD sites across the country. In addition, DSITMS instruments are currently deployed for routine use at the Oak Ridge site, the Savannah River site, and Rocky Mountain Arsenal. Gaining acceptance of the DSITMS technology by regulatory agencies continues to be a focus area of the environmentally related projects. A DSITMS method for screening VOCs in groundwater was approved by the EPA Office of Solid Waste Organic Methods Working Group during July 1994 for tentative inclusion in a future update of the SW-846 manual. Commercialization of the technology is currently being addressed by Teledyne Electronic Technologies as the result of the ARPA Technology Reinvestment Program (TRP). This TRP also includes as partners ORNL, Monsanto, Phillips Petroleum, Scientific Instrument Services, Inc., and Synergist, Inc.

Current work for the U.S. AEC involves the development of DSITMS methods for environmental contaminants of special interest to DOD including explosives, chlorinated solvents, and fuels. In addition, DSITMS is being tested in conjunction with the Army's cone penetrometer truck which is used for rapid site characterization. The cone penetrometer is a hydraulic system for pushing sensors and sampling probes into soil and groundwater, and is a low cost alternative to conventional soil boring and well drilling. The DSITMS is being evaluated as a real time monitor for the characterization of volatile organic compounds in soil gas which is sampled through the tip of the cone penetrometer as it is pushed into the ground. The fast response and high sensitivity of the ion trap should provide the ability to produce high resolution depth profiles of VOCs in soil.

In addition to the environmental applications described above, there are several other projects in the Instrumentation Group which utilize variations of ion trap technology for other applications. One of these projects is funded by the Edgewood Research Development and Engineering Center (ERDEC) and is focused on using ion trap mass spectrometry for the on-site detection of chemical warfare
agents and precursors for treaty verification purposes. This project primarily involves evaluating the performance characteristics of a fieldable ion trap mass spectrometer which is manufactured for ERDEC by Bruker-Franzen.

The high sensitivity and rapid response capabilities of the ion trap have also made this technology a major cornerstone in a project cofunded by the U.S. Forest Service and the DOE which is aimed at the remote detection of hidden marijuana gardens. This has been a joint project between the Instrumentation Group, the Environmental Monitoring Group, and the Analytical Methods Group. The goal of this work has been to collect and characterize samples of airborne vapors from marijuana plants with the intent of identifying unique markers or a combination of markers which might be used to help locate illegal marijuana gardens planted in the national forests.

Another collaborative project is being conducted in conjunction with the Environmental Research Consortium and personnel from McClellan Air Force Base. This project is part of a CRADA with the U.S. automotive industry and will result in a prototype hydrocarbon and oxygenated hydrocarbon speciation monitor based on an ion trap mass spectrometer with low to sub-ppb detection limits. The target compounds were selected because of their toxicity or contribution toward smog. The ORNL focus is on ion source design (i.e., atmospheric sampling glow discharge and in situ chemical ionization), characterizing ion chemistry (i.e., proton transfer, NO+ attachment), methods development, and providing input on overall system design. Experiments have been performed on static samples to demonstrate instrumental capabilities, and experiments in a dynamometer test facility using the prototype instrument are scheduled for early 1996.

Although applications of ion trap mass spectrometry constitute much of the work in the Instrumentation Group, there is also a significant effort which is devoted entirely to advancing the state of the art of ion trap technology. One project which is funded by the DOE (NN-20) is being conducted in conjunction with the Analytical Spectroscopy Section. This work is aimed at the development of new modes of ion trap operation which could improve the analytical speed, specificity, selectivity, and detection limits. Work which has been specifically conducted in the Instrumentation Group has focused on characterizing the performance of ion trap mass spectrometers using air as a buffer gas as opposed to helium. The results have clearly demonstrated that there are operating parameters outside of the normal operating conditions in which the use of air as a buffer gas does not seriously degrade the instrument performance for compounds with molecular weights of less than 200 amu. This could be a significant advantage in terms of increasing the portability of the instrument and reducing the complexity of sample inlets. In addition, operational conditions have been discovered which permit improved performance for the ion trap in its more traditional mode of operation using helium as the buffer gas.

Another related project is also funded by the DOE, NN-20, and is aimed at the development of a full featured, man portable ion trap. This project is being conducted in collaboration with Phil Hemberger at Los Alamos National Laboratory. The final product will be an instrument which has all of the capabilities of a research grade laboratory ion trap, yet is packaged in a case which can be carried on board an aircraft. Los Alamos will be contributing to the design and construction of the mass analyzer hardware and control software. Work at ORNL will involve completion of the analyzer hardware, the design and construction of the vacuum system, interfacing of the sample inlets, final packaging, and development of interactive software for instrument control and data reduction.
Both of the projects which are aimed at the development of advanced ion traps are also supporting the development of a general purpose analytical instrument control and data manipulation system which is based on the VXI bus. This system will provide generic hardware for controlling and acquiring data from ion traps and, in principle, other types of analytical devices. The VXI bus provides an industry standard which is used for a variety of applications including process control and monitoring. Modular devices are linked together by the VXI bus in order to form a functioning control and data system. Software for control of the system is being written using LabView, which provides a convenient means of interacting with the VXI modules. For the advanced ion trap projects, the VXI system will provide an upgradable and customizable data acquisition and control platform for implementing and evaluating new ion trap operating modes which would be difficult to investigate using the commercial ion trap hardware and software.

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PHYSICAL ORGANIC CHEMISTRY GROUP; A. C. Buchanan, III, Leader

The Physical Organic Chemistry Group conducts research that addresses the structure and reactivity of organic chemicals and materials, particularly in complex settings. An integrated approach is employed that involves chemical synthesis, product analysis, determination of reaction kinetics and mechanisms, structural interrogation via spectroscopic methods, and computational methods. Emphasis areas include structure and reactivity of fuel materials such as coal, kerogen, and biomass; development of advanced NMR spectroscopic methods for analysis of complex carbonaceous solids such as fossil fuels, polymers, and fullerenes; thermal or catalyzed decomposition reactions for organic compounds, polymers, and surface-bound organic films; photochemical reactions of hazardous organic compounds at environmentally related solid-air and solid-liquid interfaces, and in aqueous solutions; development and investigation of photocatalysts for degradation of organic chemicals; and optical spectroscopic investigation of organics in heterogeneous environments. Major projects are summarized below.

The objective of our fuel related research is to gain new knowledge on the chemical structure and reactivity of coal, lignin, and biomass. This research contributes to the scientific foundations required for the commercial development of novel processes for the conversion of fossil and renewable resources into chemicals or fuels in an environmentally acceptable manner. Reaction mechanisms that underpin thermal and catalyzed reactions of coal and lignin have been explored through the use of representative organic model compounds. Silica immobilized compounds are employed to study interfacial reactions in dispersed solids, and dramatic effects of clay minerals on thermochemical reaction pathways for coal and lignin model compounds have been observed. The impact of restricted mass transport on reaction pathways involving free radicals has also been addressed, and a novel radical relay mechanism involving serial hydrogen transfers on a surface has been demonstrated. Hydropyrolysis reactions have been investigated isothermally and by temperature programmed reduction (TPR) with online detection by mass spectrometry. High pressure TPR experiments on immobilized organosulfur model compounds have permitted an analysis of the
corresponding sulfur species in coals and kerogens. Pyrolysis pathways for model compounds containing key coal heteroatom functionality such as ethers and sulfides have been investigated in fluid phase and silica immobilized forms. Model compounds and polymers containing carboxylic acid functionality have been prepared and their pyrolysis behavior investigated to reveal reaction pathways associated with low temperature cross-linking events observed in the pyrolysis of low rank coals. Solid state NMR methods are being developed to obtain structure/reactivity information in chemically modified coals and lignins. NMR techniques under development include high resolution solid state 19F-NMR, and triple resonance 13C-NMR techniques that exploit the 13C-19F dipolar interaction to reveal information on local structure in 19F-labeled organic molecules, polymers, and coals. Fluorination chemistry under investigation included the conversion of specific oxygen functional groups in low rank coals into fluoride derivatives using diethylaminosulfur trifluoride and sulfur tetrafluoride. The combined fluorination and NMR approach provided the first evidence for primary alcohols in a lignite and also provided a novel method for differentiation of aliphatic and aromatic carboxylic acids.

The emphasis of our photochemistry program is on fundamental investigations into the influence of local chemical environment on the photochemistry of hazardous organic materials. Studies of photochemical events at interfaces (solid/liquid and solid/gas) and in aqueous media are of central importance to this research. Results from these studies enhance the basic understanding of photochemical processes occurring in industrially and environmentally important settings. In addition, the research will lead to an improved understanding of the factors that control the environmental fate and residence times of these organics. The photochemistry of polycyclic aromatic hydrocarbons (PAHs) has been the focal point for recent studies because of connection between these materials and fossil fuel production and consumption, and the status of many PAHs as EPA priority pollutants. Product analysis and in situ spectroscopic techniques are the primary methods used in the investigations. A systematic study of PAH structure has allowed the elucidation of contributions from electron transfer and singlet molecular oxygen mediated PAH oxidation pathways. Highly polar surfaces, such as that of SiO2, have been shown to have dramatic effects on the photochemistry of weakly interacting organics, as typified by unsubstituted PAHs. Investigations using spectroscopic interfacial probes have revealed PAH pairing effects on the surface and permitted a quantitative measure of the nature of PAH surface interactions. Likewise, water has been shown to be a medium that exerts significant influence on the rates and product distributions observed for PAH photochemistry. Photooxidations of several PAHs have been observed principally to involve energy transfer mechanisms with singlet oxygen as a key intermediate. Recently, semi-empirical SCF calculations have been employed which indicate that the pathway for singlet oxygen addition to phenanthrene andacenaphthalene is through a peroxirane intermediate. In related research, photocatalysts are being designed to photooxidize PAHs in waste waters that are difficult to bioremediate. Immobilized photosensitizers have been prepared that can oxidize dilute aqueous solutions of PAHs under solar irradiation. This research helps form the foundations for development of new remediation schemes.

A collaborative project with the Organic Mass Spectrometry Group aims to develop a new DNA sequencing technique based on matrix assisted laser desorption time-of-flight MS coupled with DNA labeling. Synthetic methods have been developed for derivatization of aminohexyl modified DNA with several electrophore tags. MS characterization of electrophore tagged 17-mers have shown that the derivatives are stable under the analysis conditions. Research continues to focus on improvements in the MS desorption/ionization efficiency for these derivatives.
In an attempt to derive a method for characterizing the surfaces of pulverulent materials, we have studied the distributions of the adsorption energies (AED) of different probes on the surface of adsorbents. These AEDs are derived from experimental data acquired by gas GC. The adsorption isotherms of the probes are calculated from nonlinear elution profiles obtained by GC, using the characteristic points method of finite concentration chromatography. The AED is then calculated from the classical linear Fredholm integral equation of adsorption using these adsorption isotherms. The problem is mathematically ill posed. It is solved with an iterative maximum likelihood method called expectation-maximization (EM). The algorithm was programmed and run on a massive parallel supercomputer. Parallelization and use of the matrix-vector routines supplied by the vendor provide substantially faster run times than that executed with the sequential code by other mainframe computers, allowing the economical use of the EM algorithm for these types of problems. Theoretical models for the local adsorption include the Langmuir, Jovanovic, Fowler-Guggenheim (both random and patchwise), and Brunauer-Emmett-Teller local isotherms.

Experimentally, porous layer open tubular capillary columns (PLOT) are prepared from a slurry of the adsorbent powder in a compatible solvent. The column, filled with the slurry and closed at one end, is slowly coiled inside an oven at a temperature slightly above the solvent boiling point. A thin homogeneous layer is obtained. The performance of these columns was to be considerably better than that of packed columns in terms of their ability to supply accurate isotherm data and AEDs. The effect of the finite column efficiency and the limited loading factor on the accuracy of the estimated energy distributions was investigated. It was shown that the accuracy decreases with decreasing efficiency and that approximately 5000 theoretical plates are needed (PLOTs have consistently more than 20,000 plates) when the loading factor, \( L_f \), equals 0.56 for sampling of a unimodal Gaussian distribution. Increasing \( L_f \) further increases the contribution of finite efficiency to the AED and causes a divergence at the low energy endpoint if too high. This occurs as the retention time approaches the holdup time. These results indicate that the accuracy of estimated AEDs with respect to the true underlying distribution of the surface is poor for most studies of this nature.

The adsorption energy distributions of the molecular probes are calculated from their adsorption isotherms using the expectation-maximization (EM) method of parameter estimation. EM does not require prior knowledge of the distribution function or the isotherm, requires no smoothing of the isotherm data, and converges with high stability toward the maximum likelihood estimate. The method is therefore robust and accurate at high iteration numbers. The EM algorithm was tested with
known energy distributions corresponding to unimodal Gaussian, bimodal Gaussian, Poisson distributions, and the distributions resulting from Misra isotherms, using a procedure which simulates the whole determination process. The results are contrasted to those obtained with conventional methods and shown to be superior in terms of both robustness, accuracy, and information theory. The effect of undersampling of the high pressure/low energy region of the adsorption is reported and discussed for the EM algorithm, as well as the effect of signal-to-noise ratio on the degree of heterogeneity that may be estimated experimentally.

The estimation of adsorption energy distributions on DAVISIL, IMPAQ, and VYDAC silica samples was considered in detail. Chemical derivatization of these samples was also considered. The adsorbates studied include diethylether, methanol, ethanol, tetrahydrofuran, pyridine, and heptane. The effects of temperature and maximum solute partial pressure on the AED estimation were studied. The validity of the technique is assessed, and it was concluded that adsorption energy distributions may only be calculated accurately and without bias for systems in which the majority of the adsorption energy is 10 kJ/mol greater than the heat of vaporization of the solute. For adsorption energies less than this, intermolecular interactions decrease the accuracy and confidence of the results. Other experimental parameters, including the detector range and resolution and the injection profile, also limit the scope of studies of this kind. The major obstacle is the difficulty in sampling the entire range of adsorption energies, especially the low energies which correspond to the required measurement of the retention times corresponding to high solute partial pressures.

The determination of the thermodynamic data required for the modeling of chromatography must be done with an accuracy which seems to exceed what the current level of column-to-column reproducibility of these data permits at present. An investigation of this important scale-up problem is ongoing. Isotherm data were measured by frontal analysis and elution by characteristic points for 2,6-dimethylphenol, 3-phenyl-1-propanol, and methyl benzoate on columns packed with four commercial octadecyl silica (KROMASIL, VYDAC, YMC, and ZORBAX, all average particle size, 10 μm), using methanol/water (45 x 55, v/v) solutions as the mobile phase. Seven 10 x 0.46 cm and two 25 x 0.46 cm columns were packed for each phase. The column efficiencies and capacity factors were also determined for a series of compounds: m-cresol, benzyl alcohol, methyl benzoate, benzyl acetate, and 2-isopropylphenol, all eluted under infinite dilution conditions. The average total column porosities were derived from the uracil retention volume, the internal and external porosities by reversed size exclusion chromatography, from the calibration curve obtained with a series of polystyrene standards with molecular weights ranging from 456 to 20,600,000 Dalton.

The retention factors and isotherm coefficients depend on the packing density which varies markedly from column to column and is also a function of the column length. This observation is consistent with the results of previous work, which has shown that the beds of packing materials in conventional packed columns consolidate to a marked extent during an initial period. Therefore, a procedure for the accurate and precise determination of the external porosity of columns is necessary. The internal and external pore volumes (hence, porosities) of the columns can easily be determined with accuracy from the plots of the logarithm of the molecular weight of the probes versus their retention volume. Corrections of isotherm data based on the difference between column retention factors and phase
ratios do not compensate correctly for the deviations observed. Corrections based on the difference of external porosities of the columns do better.

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4. PHYSICAL AND MATERIALS CHEMISTRY SECTION  
R. E. Mesmer, Head

The research in this section represents a mix of basic and applied research in the areas of chemical separations, geochemistry, high temperature aqueous chemistry, inorganic materials chemistry, and polymer science. There are 23 Ph.D. and 3 B.S. and M.S. staff in this section. The principal sponsors include the Office of Basic Energy Science (Divisions of Chemical, Materials, and Geosciences), Office of Technology Development, Office of Energy Efficiency and Renewable Energy, Electric Power Research Institute, and Office of Health and Environmental Research.

The Chemical Separations Group addresses solvent extraction/ion exchange of cations, anions, and ion pairs; design, synthesis, and evaluation of macrocyclic ligands for molecular recognition; structures of extraction complexes; and separations in environmental restoration. The Geochemistry Group addresses experimental studies of hydrothermal and magmatic systems; crustal materials and fluid-rock interactions; metal ion complexing; stable isotope geochemistry; and high temperature thermodynamics of C-H-O-N systems. The High Temperature Aqueous Chemistry Group addresses thermodynamic properties and reaction thermodynamics of solutes in water at high temperature; experimentation and modeling; nonideal electrolyte behavior; and applications to energy production and waste treatment. The Inorganic Materials Chemistry Group addresses the synthesis and characterization of ceramic, optoelectronic, and superconducting materials; thin films; sol-gel synthesis of multicomponent oxides; reactive sputtering for nanocomposites; and CVD. The Polymer Science Group addresses experimental and computational characterization of polymer structure and dynamics; semicrystalline and amorphous materials; polymer blends; and use of molecular dynamics and neural networks in materials science.

CHEMICAL SEPARATIONS GROUP; B. A. Moyer, Leader

CASD's Chemical Separations Group strives to elucidate principles of chemical recognition and separations and to develop applications supporting the missions of its sponsors, including DOE programs in Basic Energy Sciences (BES), Office of Environmental Management (OEM), and the Office of Health and Environmental Research (OHER). Research themes primarily deal with the coordination chemistry of synthetic organic ligands designed to selectively complex metal ions and effect their separation from complex matrices. Within this broad area, the group has earned an international reputation as a leader in solvent extraction and ion exchange, both in fundamental and applied aspects. In large part, the special strength that the group has developed in the area of crown ethers, macrocyclic compounds, and designed ligands has been responsible for this success and has led to a number of noteworthy accomplishments in recent years. One recent applied accomplishment, for example, has been the development of a novel solvent extraction process that uses crown ethers for removing the radioactive contaminant technetium from aqueous waste. In addition to waste treatment, potential applications of the systems developed by the group include groundwater remediation, hydrometallurgy, nuclear separations, analytical chemistry, and biotechnology. Systems selective for such metals as lithium, sodium, cesium, strontium, barium, radium, manganese, copper, and zinc have been characterized. Further, the binding of lanthanides and actinides is a major topic in several projects.
To accomplish its mission, the Chemical Separations Group has assembled a uniquely equipped, multidisciplinary team of scientists. In a typical R&D cycle, individual problems are analyzed, and the appropriate ligands are designed, synthesized, tested for efficacy, and probed in detail. Molecular mechanics calculations are employed in the design of extractants. The performance of extraction systems is assessed by distribution studies aided by computer modeling. Analytical tools employed in characterizing separations include ICP spectrometry, scintillation counting, ion chromatography, HPLC, capillary electrophoresis, electrochemistry, and luminescence spectroscopy. For a complete understanding of systems at a molecular level, details of structure and bonding are obtained by x-ray crystallography, NMR spectrometry, FTIR spectrophotometry, calorimetry, and other physical techniques. The group's own modeling program, SXLSQI, developed by C. F. Baes, Jr., is the most powerful and informative program available for modeling solvent extraction data.

Under the group's largest program, "Chemical and Structural Principles in Solvent Extraction," sponsored by the Division of Chemical Sciences/OBES/DOE, the molecular level behavior of crown ethers as selective extractants for several classes of metal ions has received major emphasis. The primary thrust has entailed the factors governing the ability of crown ethers to recognize the alkali metals according to size, especially at the extrema represented by environmentally important lithium and cesium. Illustrative of the many systems studied, a family of 14-crown-4 ethers having various hydrocarbon substituents has been shown to extract lithium with selectivity factors exceeding 50:1 vs. sodium ion. This ability, however, depends markedly on the particular substituents on the ring. X-ray crystallography reveals the binding of lithium cations in basket-like complexes, though the free crowns adopt twisted shapes. Significantly, calculations by molecular mechanics performed at Pacific Northwest Laboratories (B. P. Hay) show that the energy cost to "untwist" one of the substituted 14-crown-4 ethers correlates with its lithium extraction ability. To test this exciting structure-function relationship, the extraction behavior of a representative case, nonamethyl-14-crown-4, has been examined. The stoichiometry of extraction has been determined in 1-octanol by distribution measurements and $^7$Li NMR, and strong solvation effects have been observed. Two dimensional NMR has aided the understanding of crown ether conformation, especially as applied to the role of functionalized sidearms attached to rigid dibenzo-14-crown-4 lariat ethers. In contrast to such small macrocycles, crown ethers having 21 or more ring atoms exhibit selectivity for the large alkali metals, cesium and rubidium. Selectivities exceeding 100:1 over sodium have been obtained, and the underlying extraction equilibria have been determined by modeling studies. Crystal structures of a number of the crown ethers with cesium salts have elucidated the roles of ring size and benzo substituents. New crown ethers bearing triptyceno and anthraceno substituents have been synthesized.

A new project entitled "Selective In-Situ Sorption of Tc from Groundwater" has been initiated under the U.S. DOE Efficient Separations and Processing (ESP) Cross-Cutting Program of the Office of Technology Development/OEM. The objective entails the development of improved resins for the removal of technetium from groundwater as targeted to the contamination problems found at the gaseous diffusion plants, especially Portsmouth and Paducah. Through collaboration with Professor S. D. Alexandratos of The University of Tennessee, Knoxville, a series of promising resins have been synthesized, and more efficient uptake of technetium than possible with commercial resins has indeed been achieved.

A new process for the removal of technetium from defense tank wastes such as found at Hanford has been developed. Under the ESP funded project "Alkaline-Side Extraction of Technetium and Acti-
Crown Ethers and Other Extractants\textsuperscript{a} initiated in FY 1993, it was shown that crown ethers extract technetium as pertechnetate ion from alkaline media containing high concentrations of sodium nitrate and other salts. The crown ethers offer the key advantage that the extraction cycle can be completed with an economical stripping step employing only water. Efficient conditions for the extraction cycle have been identified. In related work involving collaboration with Professor R. B. Robinson of The University of Tennessee, the extraction of technetium has also been demonstrated in supported liquid membranes. The problem of decontaminating alkaline waste solutions containing complexed actinides has also been examined, and an extraction system capable of removing trivalent actinides and lanthanides has been identified.

The group's expertise in ligand synthesis and coordination chemistry has been productively applied to the attachment of metal ion reporter groups to oligonucleotides for DNA sequencing. In projects supported by the DOE OHER Human Genome Program, the photon antenna function of aromatic groups attached to chelated lanthanide ions was demonstrated to enhance the luminescence detection of the lanthanide ions. The principle has been applied to the laser luminescence detection of a Eu(III)-labelled oligonucleotide by capillary electrophoresis. Alternatively, ferrocene groups can be attached to DNA fragments for electrochemical detection by capillary electrophoresis. A series of ferrocene and stannane reporter groups employing isotopically pure iron and tin, respectively, have been demonstrated in mass based detection schemes.


GEOCHEMISTRY GROUP; D. J. Wesolowski, Leader

The Geochemistry Group conducts basic and applied research on the geochemical controls of matter and energy transfer in the Earth's crust, as these relate to such issues as fossil and geothermal energy resource formation, discovery, and exploitation; nuclear and toxic waste disposal and remediation; and the effects of energy utilization on the lithosphere/atmosphere/hydrosphere system such as global climate change, acid rain and acid mine drainage, and groundwater quality. Our principal approach is to conduct experimental studies of earth materials (minerals, rocks, and fluids), including their physicochemical properties and the chemical reactions among them, using a variety of state-of-the-art and/or unique facilities which enable the simulation of subsurface conditions from room temperature and pressure to 1200°C and 10,000 atmospheres. Our efforts are focused in four main categories:
(1) the speciation of elements in high temperature brines and the chemical reactions of natural brines with minerals and rocks; (2) the partitioning of the stable isotopes of hydrogen (D/H), oxygen (\(^{18}O/^{16}O\)), carbon (\(^{13}C/^{12}C\)), and sulfur (\(^{34}S/^{32}S\)) among minerals and fluids as a function of temperature and salinity; (3) the thermodynamic properties of natural gas and deep Earth fluids (\(CO_2-CH_4-H_2O-N_2\) gas mixtures); and (4) the thermodynamic properties of silicate minerals and melts.

Highlights of our recent research projects are described in the next few paragraphs.

In collaboration with the High Temperature Aqueous Chemistry Group, we make extensive use of unique pressure vessel systems fitted with platinum-hydrogen electrodes that enable extremely precise measurement of pH in aqueous solutions from 0 to 300°C. Much of our recent work with these systems has focused on the acid dissociation constants and thermal stabilities of organic acids found in natural waters and their ability to complex metal ions. These acids, which are produced by biological activity and decomposition of buried organic material in soils, aquifers, and hydrocarbon reservoirs, may play important roles in the migration of wastes as well as economically valuable metals, and may influence the hydrodynamics of groundwater and geothermal systems by enhancing permeability through selective dissolution of certain minerals. In the past two years we have determined the formation constants of Nd\(^{3+}\)-acetate complexes to 250°C in 0.1 molal NaCl solutions, Cd\(^{2+}\)-malonate and oxalate complexes in 0.1-5.0 molal sodium trifluoromethanesulfonate solutions to 75 and 125°C, respectively, and Al\(^{3+}\)-malonate complexes to 75°C in 0.1-5.0 molal NaCl solutions.

We have also initiated a detailed study of the thermal stabilities of malonic, succinic, and oxalic acids using the platinum hydrogen cells to continuously monitor the pH during the decomposition process. Finally, these facilities have been used to study several inorganic reactions, including (1) the determination of Al\(^{3+}\) complexes with SO\(_4^{2-}\) in 0.1 to 1.0 molal NaCl solutions from 0 to 125°C, relevant to acid rain and acid mine drainage environmental problems; and (2) the surface charge and H\(^+\) sorption properties of the mineral rutile (TiO\(_2\)) in 0.01 to 3.0 molal NaCl solutions from 25 to 250°C, the first such direct measurements ever conducted at temperatures above 100°C.

In a collaborative effort involving our group and the Inorganic Mass Spectrometry and Secondary Ionization Mass Spectrometry groups, we have been utilizing ion microprobes to investigate the trace element and stable sulfur and oxygen isotope distributions in minerals formed during fluid migration sedimentary rocks of the Western Canada oil and natural gas province. Ion probes permit examination of the chemical and isotopic signatures of fluid (aqueous and hydrocarbon) sources and flow paths on the scale of individual mineral grains, which aids in the development of improved hydrocarbon exploration and development models. Innovative stable isotope measurement techniques have been developed which enable us to demonstrate that H\(_2\)S-rich "sour" gas and oil accumulations within the province are a result of thermogenic reduction of pore water sulfate in portions of the sedimentary basin subjected to very deep burial. This collaborative team has obtained a substantial LDRD grant to design, construct, and test a unique ion microprobe specifically optimized for the measurement of the stable isotope ratios of O, C, H, and S in geological materials, ceramics, and metal corrosion products, with micron scale spatial resolution.

The Geochemistry Group also conducts extensive experimental studies of stable isotope partitioning among geological minerals and fluids. Current efforts involve a detailed investigation of the rates of oxygen and carbon isotope exchange between H\(_2\)O-CO\(_2\) fluids and the minerals calcite, quartz, and feldspar, the three most abundant minerals in the Earth's crust. We have also determined the
equilibrium fractionation of oxygen isotopes between water and the minerals magnetite (Fe₃O₄) and hematite (Fe₂O₃) in the 300-400°C range by employing a variety of novel in situ reactions. These iron oxides, which form in a variety of geological environments, contain a wealth of information about the sources, redox states, and temperatures of aqueous and hydrocarbon fluids associated with geothermal and hydrocarbon energy resources. A promising line of recent investigation involves determination of the stable oxygen isotope compositions of magnetite corrosion products formed on both the steam side and the fire side of steel tubing in fossil fuel burning power plants. These measurements, funded by the ORNL seed money program and performed on samples provided by the Electric Power Research Institute, indicate that the mechanisms of corrosion and the nature and diffusion rates of the corrosive oxidants (O₂ versus H₂O) can be determined by appropriately constrained laboratory and field experiments.

We are heavily involved in detailed studies of several key geochemical processes which play a pivotal role in modeling geothermal systems. Applied studies of these systems are funded by DOE's Division of Geothermal Technology Development, and these are closely coordinated with more generic, long-term studies funded by the OBES/Geoscience Research Program. Current efforts are focused on (1) the geochemistry of aluminum in geothermal systems, with recent results including the measurement of boehmite (AlO(OH)) solubility in NaCl brines to 250°C with in situ pH monitoring in our platinum hydrogen cells (the first measurements of this type ever reported); (2) the effect of dissolved salts in the system Na-K-Mg-Ca-Cl-SO₄ on the partitioning of hydrogen and oxygen isotopes between aqueous brines and coexisting water vapor and minerals to 350°C, as well as the pure water liquid vapor partitioning of both isotopes from the freezing to the critical point; and (3) the solubility of water in silicate melts (the heat engine for most active geothermal systems) and the chemical composition of separate aqueous fluids in equilibrium with granitic silicate melts as a function of temperature, pressure, and melt composition.

Finally, we have developed a unique, high temperature and pressure, vibrating tube densimeter for the determination of the pressure-volume-temperature relationships of C-O-H-N gas mixtures. This facility has produced some of the world's most accurate data on the densities of CO₂-CH₄-N₂ mixtures (the main components of natural gas) in the range of 50-300°C and 100-1,000 atmospheres.

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HIGH TEMPERATURE AQUEOUS CHEMISTRY GROUP; R. E. Mesmer, Leader

The High Temperature Aqueous Chemistry Group conducts basic and applied research on aqueous systems at high temperatures and pressures of importance to DOE energy related activities. Basic research is aimed at establishing fundamental principles governing chemical and thermodynamic behavior of aqueous solutions of broad classes of solutes to high temperatures and pressures through state-of-the-art laboratory studies using an exceptional arsenal of unique equipment developed over many years at ORNL. Results in this program are also advancing the disciplines of solution
chemistry and hydrothermal chemistry, as well as having important applications in several applied programs supported by DOE and other agencies.

The combination of results from measurements with potentiometry, electrical conductance, flow calorimetry and densimetry, as well as isopiestic and phase studies, provide definitive information on chemical processes occurring in aqueous solutions at high temperature. These include the equilibrium reactions ion association, hydrolysis, adsorption, precipitation, metal ion complexation with inorganic and organic species, and finally the distribution of solutes between the liquid and vapor phases. Information is being produced on the thermodynamics of reaction equilibria, especially those involving charged species, that yields models for prediction and data fitting of the complex temperature-pressure-composition relationships, particularly the divergences seen in near-critical and highly dilute solutions. The intractable nonidealities of electrolyte solutions are being systematically studied to provide input for ion interaction models for computations on real mixtures occurring in natural and technological settings such as geothermal reservoirs, power plants and steam generators, waste disposal and processing facilities, and mineral deposition processes in nature.

In this and the next few paragraphs, some highlights of both the basic and applied research efforts will be discussed. First, we have undertaken a broad research program to investigate and quantify metal complexation using the unique hydrogen electrode concentration cell developed in this program which provides an accurate measure of pH from 0 to 300°C, even in highly saline solutions. For example, the formation of zinc sulfate complexes that play a role in PWR primary side corrosion was investigated to 250°C. Similarly, the highly stable cadmium(II) complexes with naturally occurring organic acids are being measured to determine the environmental impact of releasing cadmium from waste sites. The thermodynamics of dissolved aluminum in the presence of sulfate and organic acids and kinetics of dissolution of aluminum solid phases are being investigated by potentiometry, spectroscopy, and solubility measurements to understand how aluminum is released to the environment. The first study of the complexation of a rare earth metal ion, neodymium, with an organic acid to high temperatures has now been completed. Finally, as part of an effort to quantify the adsorption of toxic metals onto mineral surfaces over the ranges of temperature, pH, and salinity found in nature, the first study of the adsorption/desorption of hydrogen ions on an oxide surface (TiO₂) has been completed to 275°C.

The isopiestic method has proven to be one of the most productive approaches to measurement of the excess thermodynamics of aqueous electrolytes; the ORNL facility is the only one capable of measurement above 100°C. During this period, new results were obtained on alkali bromides to add to the extensive list of chlorides, sulfates, hydroxides, and phosphates that have been previously studied. Preliminary examination shows similar trends with cation size as for the chlorides. Completion of a comprehensive analysis of the alkali bisulfates demonstrates that lower activity coefficients are observed for this class than for the two halides. This unique apparatus is now being readied for study of water adsorption by geothermal reservoir materials in an attempt to provide necessary data for the evaluation of reservoir behavior and lifetimes.

Electrical conductivity, as a tool to explore association behavior of electrolytes, has been pioneered in this program, especially at high temperatures, and is currently being applied to the study of the important class of alkali hydroxides in addition to NaCl(aq) and sodium triflate. Results for NaOH(aq) and KOH(aq) show association similar in type to NaCl(aq) but intermediate in magnitude between
NaCl(aq) and HCl(aq). Attempts to make measurements near the critical point demonstrated the need for greater precision, which is being sought with an improved cell design in a collaboration with the University of Delaware group of R. H. Wood.

Flow calorimetry is our best tool for measurement of excess thermodynamic properties through measurements of heats of dilution, and it has the widest temperature range of operation. The ORNL calorimeter has recently been used in studies on MgCl$_2$(aq) over a wide concentration range and on NaCl(aq) in the dilute range. An important and unexpected observation was the transport and redeposition of metallic platinum in one of the capillary lines caused by incomplete removal of oxygen. Also, to improve the quality of the measurements, new heat exchanger designs have now been tested, and there is evidence for the need to preheat solutions for greatest accuracy above 300°C. In a related activity, the high temperature vibrating tube densimeter previously constructed in the program is being modified to add a capability for heat capacity measurements to supplement the heats of dilution results and give standard state heat capacities.

Currently, emphasis is being given to the study of the volatility of electrolytes for two major applications. Geothermal steam systems include varying levels of electrolytes in water and steam at high temperatures, and certain solutes in steam (e.g., HCl) are highly corrosive to piping and turbine systems (a problem of interest to the Office of Energy Efficiency and Renewable Energy of DOE). Corrosion and deposition of salts lead to problems even in the much cleaner fossil fired steam cycle (Electric Power Research Institute). We have recently determined equilibrium constants for the partitioning of electrolytes such as HCl, NaCl, Na$_2$SO$_4$, NaHSO$_4$, H$_2$SO$_4$, NaOH, NH$_4$Cl, and NH$_4$HSO$_4$, as well as some mixtures, between water and steam at high temperatures. Combined with data obtained in this program on excess thermodynamic properties (e.g., activity coefficients) in high temperature brines, these results yield models for calculating the composition of coexisting brine and steam phases over wide ranges of temperature and solute concentration. The models take into account both the production of solute contaminated steam and the formation of varying amounts of condensate liquids from the steam, and can be used to track the changing composition of condensate with varying initial boiler water concentrations, steam formation and condensation temperatures, and extent of condensation. The models are currently being used to estimate steam formation conditions in geothermal reservoirs to address the feasibility of various methods for mitigation of corrosive steam production in geothermal power cycles, and as input for revision of guidelines for the operation of fossil fired steam generator cycles in large power plants.

For the purpose of gaining an understanding of some of our macroscopic observations on a microscopic scale, an effort has been initiated on computer simulations of electrolyte solutions with P. T. Cummings and A. Chialvo. Both experimental results and quantitative empirical models based on those results are important sources of data for comparison with thermodynamic quantities calculated from molecular dynamics simulations of high temperature aqueous solutions. Recently, simulations have been carried out which give values of the equilibrium constant at infinite dilution for the formation of ion pairs in model aqueous sodium chloride at a supercritical temperature and near the critical density of the solvent. Some disagreement was found that appears largely to be due to the difference between the simulation result for the dielectric constant of the pure solvent as compared with the corresponding value for water under these conditions. When a comparison is made between quantities which are less dependent on the solvent dielectric constant, the agreement is within the combined uncertainties of the simulation and of the experimental determination. This promising
result is being pursued through simulation studies at addition state points, and testing of improved potential models.

Finally, this group is involved in a technology transfer project through a CRADA with Modell Environmental Corporation to assist in the development of the supercritical water oxidation (SCWO) process for treatment of mixed wastes, hazardous and radioactive, for DOE. The work is CRADA protected but involves laboratory phase studies on in situ neutralizers and an effort with CTD to upgrade the ASPEN Plus Code for aqueous electrolytes at SCWO conditions.

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**CHEMISTRY OF ADVANCED INORGANIC MATERIALS; D. B. Beach, Leader**

The Chemistry of Advanced Inorganic Materials Group is primarily engaged in the synthesis of inorganic solid state materials by nonclassical synthetic techniques. Classical synthesis of inorganic materials by solid-solid reaction requires long reaction times at high temperatures and often extensive grinding and mixing, the so-called “heat it and beat it” approach to synthesis. These extreme conditions are required because of slow diffusion of reactants in the solid state and often preclude the use of these materials in many technological applications. To overcome the limitations of classical synthetic techniques, we are currently using a number of techniques including aerosol pyrolysis of mixed metal nitrates as precursors to cuprate superconductors, plasma assisted chemical vapor deposition and plasma sputtering of oxide and nonoxide ceramic materials, pseudomorphic conversion of oxide ceramics to nonoxide ceramics using gas-solid reactions, ion implantation to produce electrocatalytic electrodes, and sol-gel and metal organic chemical vapor deposition of titanates for electronic applications.

**High Tc Superconductors --** Studies of complex cuprate superconductors with high critical temperatures were carried out in collaboration with the Solid State and Metals and Ceramics divisions of ORNL as part of the Superconductivity Technology Center. Our primary goal was the synthesis of materials with the potential for high current applications in significant magnetic fields. To these ends, we explored the synthesis of powders of [(Bi,_,Pb,)Sr,Ca,Cu,O,]_, Bi,Pb-2223, using aerosol pyrolysis of nitrate solutions to produce fine grain, intimately mixed materials. These powders were then used for the synthesis of Powder in Tube (PIT) conductors with performance superior to those made by other methods. Aerosol pyrolysis was also used to prepare powders of Ba,Ca,Cu,Ago,Oy for subsequent thallination using a multizone thallination furnace which allowed the independent control of thallium oxide vapor pressure and substrate temperature. The resulting TIBa,Ca,Cu,Oy, Ti-1223, materials, both powders and thin films, showed excellent superconducting properties. Spray pyrolysis using nitrate solutions and subsequent thallination were used to prepare Ti-1223 films with relatively high critical currents. Finally, a sol-gel synthesis of Ti-1223 films using an all alkoxide chemistry was developed.
In addition to these more applied studies, new superconductors were synthesized for basic structure and property studies. Several recently discovered mercury containing superconductors were synthesized of the general formula \( \text{HgBa}_x\text{Ca}_2\text{Cu}_2\text{O}_{y} \) (henceforth referred to as Hg-1223). Thermopower and resistivity measurements of Hg-1223 prepared with various degrees of oxygen doping indicated that the measured \( T_c \) of 134 K could be raised further by high pressure oxygen annealing. Samples of the quaternary intermetallic superconductor \( \text{YNi}_2\text{B}_2\text{C} \) were prepared, and its structure was determined by neutron diffraction.

**Plasma Synthesis** -- Plasma synthesis of thin films provides energy for chemical reactions without having to heat the deposition surface. Plasma assisted chemical vapor deposition (CVD) was used to generate nonoxide ceramic coatings such as SiC. In addition to CVD, plasma synthesis was also used to prepare a variety of novel nanocomposite materials by physically sputtering targets of alloys in a reactive gas ambient. For example, by sputtering a target containing gold and silicon with an oxygen plasma, a gold oxide/silicon oxide nanocomposite was formed. By heating the sample, gold oxide decomposed to form gold nanoclusters less then 100 Å in diameter. These gold nanoclusters were dispersed in an amorphous insulating matrix of silicon dioxide. Other systems studied included gold/gallium in a nitrogen plasma and gold/aluminum in a nitrogen plasma. The gold/silicon oxide system showed interesting optical and dielectric behavior, and the gold/aluminum nitride system was studied for nonlinear optical effects.

**Pseudomorphic Synthesis** -- This technique starts with an inexpensive, easily synthesized oxide ceramic with a desirable morphology such as a whisker or a needle and converts this oxide to a carbide or nitride by a gas solid reaction to produce a difficult to prepare ceramic material with hopefully the same morphology as the starting oxide. An example would be tungsten carbide whiskers from whiskers of sodium tungsten bronze.

**Preparation and Characterization of Electro catalytic Surfaces** -- Ion implantation was used to prepare ruthenium oxide/titanium oxide electrodes by implanting ruthenium into titanium and then anodizing/oxidizing the electrode to form an electrode to model those used for electrocatalysis of brine in the chlor-alkali process. A number of analytical techniques including Rutherford backscattering spectroscopy (RBS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used to characterize these electrodes.

**High Dielectric Constant Titanates** -- Work was started on the synthesis of very thin films of lead lanthanum titanate (PLT) for use as capacitors in microelectronics. The films were prepared by sol-gel techniques using a complex mixture of alkoxide precursors. Films were annealed by rapid thermal processing so as to minimize damage to the electrode and unwanted interfacial diffusion. Films with dielectric constants as high as 600 at 1000 Å of thickness were prepared.

**Basic Research and Development of Radioactive Waste Management** -- This research was funded by the Army to explore the basic chemistry of titanates as storage forms for the transuranic elements. The compound \( \text{Pu}_x\text{Ti}_2\text{O}_7 \) was synthesized, and its solid solubility in lanthanide dititanates was studied. The compounds \( \text{Pu}_{x+y}\text{Ln}_x\text{Ti}_2\text{O}_{y+7} \) (Ln - Gd, Er, and Lu), \( \text{Pu}_2\text{Ti}_7\text{O}_{17} \) and \( \text{Sr}_{x}\text{Pu}_{y/3}\text{Ti}_4\text{O}_{12} \) were also synthesized. Work on analogous compounds but containing americium was started.
In this program, we pursue fundamental structural and dynamic studies with the intent of providing a better understanding of advanced polymeric materials. To characterize the structure of bulk polymers and fibers at the molecular level, we use small angle and wide angle x-ray and neutron scattering; the motion and disorder in polymers is probed by NMR and neutron spectroscopy; scanning tunneling, atomic force, and optical microscopies can map out surface morphologies; and the bulk mechanical, transport, and thermodynamic properties are characterized with thermal and mechanical analysis. The theoretical aspects are addressed with state-of-the-art molecular dynamics and neural networks to simulate chain conformations, dynamics, and energy flow in polymers, with the simulations closely linked to experiment.

Wide angle x-ray (WAXS) and neutron (WANS) scattering are used to study the structure of liquids, polymer melts, and polymer blends to obtain fundamental information on the intra- and intermolecular interactions between molecules in these systems. For the first time, the partial H-H radial distribution functions (RDF) were obtained for three alkanes using the neutron isotopic substitution method without recourse to models of the intramolecular structure. Good agreement with molecular dynamics calculations was obtained. WAXS RDF measurements on a number of vinyl polymers were undertaken in an attempt to understand the general prediction of a "pre-peak" in the intermolecular C-C structure function by PRISM theory for vinyl polymers. The lack of a pre-peak in isotactic-polypropylene (i-PP) seems to suggest that the accepted Rotational Isomeric State (RIS) model for i-PP may be incorrect, and that it may have a structure different from other vinyl polymers. The intramolecular structure of vinyl polymers is of interest in modeling the structure of polymer blends.

A series of tetra-n-dialkylammonium salts (TAAH) have been examined with thermal analysis, solid state NMR, atomic force microscopy, wide angle x-ray powder diffraction (Rietveld analysis), and single crystal analysis. The interest in these materials stems from the fact that these relatively small molecules display some of the same mesophases encountered in polymers. The twenty TAAHs studied undergo numerous transitions as a function of temperature, and the phases could be classified as ordered crystals, plastic crystals, or conformationally disordered (condis) crystals. Both stable and nonequilibrium behavior was analyzed. The method for distinguishing between plastic and condis crystals has already been applied to other disordered semicrystalline materials.

The ability of atomic force microscopy (AFM) to image structure at the atomic level is well established for many materials with good surface order. We have been using AFM to examine atomic scale defects, friction effects in ion implanted graphite and polystyrene, nonwoven polymer textiles, polymeric filtration materials, and the relationship of surface morphology to phase separation in alkane mixtures and polymer blends.

The mechanism of large scale irreversible deformation of semicrystalline polymers is a matter of controversy. One of the proposed explanations is that the crystalline regions must melt and
recrystallize during the deformation. In cases where hydrogenated and deuterated blends of a polymer are known to have some segregation of the components, small angle neutron scattering (SANS) has shown that deformation reduces the segregation. A similar effect occurs when the samples are melted and subjected to a fast quench. The similarity between the two processes suggests that deformation involves melting and recrystallization. SANS data collection has been completed, and analysis of the results is in progress.

A new modulated scanning calorimeter was acquired with the help of TA Instruments, Inc., and the rather interesting ability to separate reversible and irreversible phenomena was investigated. The method to measure heat capacities was extended to nonisothermal measurements, and the theory of differential thermal analysis was extended to cover the case of the glass transition. It is expected that a major advance in analyzing irreversible polymer properties will be made in the next few years. Solid state NMR was used to analyze the mobility of several polymers to establish the changes in physical properties as they are linked to molecular structure. This NMR technique has developed into the most definitive tool for the distinction between various polymer mesophases.

Polymer fibers are typically partially crystalline, however, attempts to correlate mechanical properties on the basis of a simple model of crystalline and amorphous fractions have proven to be inadequate. We have developed a systematic approach for analyzing x-ray diffraction data from polymer fibers by accounting for all intensity over two dimensional reciprocal space (full pattern two dimensional Rietveld analysis). This much more extensive analysis has resulted in the identification of three distinct structural domains in typical polymer fibers: crystalline, "oriented intermediate," and isotropic amorphous. In the "oriented intermediate" domain, the polymer chains are still parallel to the fiber axis but do not have long range crystalline order. It has been found that a number of thermal and mechanical properties of the fibers such as modulus and shrinkage are mainly determined by the amount and state of the oriented intermediate domain. The technique has been applied to PET, PPTA (Kevlar-49), and various types of PE. Complementary information is provided by small angle x-ray scattering (SAXS), calorimetry, atomic force microscopy, and solid state NMR. SAXS is also being used as a diagnostic tool for assessing the effects of variation in spinning rate and annealing procedures on morphology in the production of PET fibers.

Computational synthesis, a method for predicting the properties or for designing materials that have desired properties, was developed and tested. This method entails a novel computational paradigm for making rapid and accurate estimations of physical properties for molecular based systems. Results have been obtained for up to 16 properties of 357 different polymers, for making accurate predictions on the detonation velocity and sensitivity of energetic materials, for estimating protein degradabilities, and for predicting properties of a series of isomeric forms of saturated hydrocarbons and fluororganic compounds. In addition, the method can also be operated in the reverse direction: designing chemical structures that meet specified performance criteria. This is accomplished by using genetic algorithms to determine possible candidates based on the optimization of the trained neural network predictions. The overall abilities of the computational synthesis method provide new and far-reaching capabilities in materials design and analysis, an area which up to now has been to a large extent an empirical science.

We have also investigated the use of computational neural networks to learn the overall dynamics of a particular system in a MD simulation, and then predicting the effects of changing the size of the
system or the simulation time. This approach has been very successful and represents a major advancement in computer simulation of macromolecular systems.

We have developed computer codes that permit us to routinely run MD simulations on polymethylene crystals of size over 227 nm$^3$ with both united atom and full atom models. All modes of motion are allowed in these simulations; such a system is sufficiently large to serve as a model of a macroscopic polyethylene crystal. Reasonable agreements with experimental data on density, defect concentration and motion, diffusion, lamellar thickening, heat capacity, melting temperature, and the speed of sound in a polymer crystal have been reached. The large volume of detailed information of the structure and motion permits a new level of understanding of these systems.

A molecular dynamics based method was developed to compute the vibrational spectra and dispersion curves for linear macromolecules. The results are compared and contrasted with those of normal mode calculations, demonstrating the validity of the approach and providing fundamental insight into a number of dynamical processes. The strength of the method is its computational efficiency, and that it represents an exact classical dynamics approach to calculating vibrational spectra, thereby eliminating many of the weaknesses of normal mode calculations (i.e., the harmonic approximation).

Finally, we have investigated an innovative numerical integration algorithm for MD simulations which can greatly reduce the time for advancing a trajectory by a given time step. These methods, called symplectic integrators (SI), were compared with several nonsymplectic integrators which were found to lead to more significant energy drifts than the SIs.

A program on polymer blends, in collaboration with Sandia National Laboratory and the University of Illinois, aims to provide a scientific basis for the molecular design and characterization of multicomponent polymer blends. The primary objective is to provide a foundation for multiphase materials development similar to the knowledge base in small molecule chemistry that underlies single phase polymers. Our approach involves polymer theory (PRISM, molecular dynamics, Monte Carlo), synthesis, and characterization (wide and small angle x-ray and neutron scattering). Some recent activity is given below.

SANS experiments are in progress on a blend with structural and energetic differences between the components. The system chosen was polystyrene/poly(p-methylstyrene) (PS/PPMS), because of the interesting observation that the FH interaction parameter ($\chi$) appeared to exhibit a significant molecular weight dependence. The first SANS measurements have confirmed that $\chi = \chi(MW, \phi)$ is a function of both molecular weight and concentration, and further experiments to quantify the phase diagram are in progress.

The phase separation mechanisms in binary alkane mixtures have been investigated via SANS and SAXS. A 50/50 blend of $n$-C$_{30}$H$_{62}$/n-C$_{30}$D$_{44}$ showed a layered structure of single periodicity within 15 minutes of quenching from the melt, and subtle changes indicative of a superlattice occur within 30 hours. The SAXS/SANS results were in qualitative agreement with model calculations for an alternating layer structure, composed of ~80/20 mixtures.
Blends of linear and branched polymers are widely used commercially, though there is no consensus on the state of mixing of such materials. For mixtures of linear high density (HD) and long chain branched low density (LD) polyethylenes, widely different views continue to be expressed in the literature ranging from complete compatibility to phase separation in the melt. SANS and SAXS have been used to investigate the solid state morphology in linear/branched mixtures (HDPE/LDPE) and blends of HDPE with short branched linear low density polyethylene (LLDPE). The aim is to understand the influence of branching type and frequency, molecular weight, and polydispersity on melt compatibility.

The first systematic study of the influence of chain branching and backbone stiffness on the equilibrium properties of dense polymer melts has been carried out. Calculations at the atomistic, semiflexible chain, and Gaussian levels reveal the connection between polymer structure, packing, and thermodynamic properties. Theoretical predictions based on computationally convenient "intelligently" coarse grained models (in which the monomer unit is represented as a single site) were found to be in good agreement with the atomistic level results. Calculated melt solubility parameters of complicated polyolefin chains were found to be in good accord with recent PVT and neutron scattering observations.

Molecular dynamics and Monte Carlo simulations and PRISM calculations were performed for athermal polymer blends (i.e., with no heat of mixing) composed of short, freely jointed chains with different monomer size. Excellent agreement between the simulations and the PRISM predictions were found for interchain packing correlations, the excess free energy of mixing, and the effective $\chi$-parameters. These comparisons between PRISM theory and simulations of systems of modest chain lengths ($N < 100$ segments) provide benchmark tests of the ability of PRISM to correctly predict the intermolecular packing in conformationally asymmetric athermal polymer blends.

Based on the success in describing packing correlations in athermal mixtures, thermodynamic perturbation theory was employed to compute the enthalpy of mixing effective $\chi$-parameters and phase diagrams of various polyolefin and related blends, using a chemically realistic (atomic) single chain model of polyethylene (PE) and isotactic polypropylene (i-PP). In accord with experiment, the theory finds that this blend is much more incompatible than predicted by FH theory. Moreover, similar large enthalpic $\chi$-parameters were found using "intelligently" coarse grained semiflexible chain models, which mimic the conformational asymmetry associated with chain branching in polyolefin mixtures. These findings provide a theoretical basis for the use of solubility parameter approaches to polyolefin phase stability and have stimulated the development of a simple analytic solubility parameter theory of polymer alloy miscibility. Moreover, the theoretical ideas suggest new alloying and synthetic strategies based on controlled manipulation of molecular features such as chain branching and chemical microstructure to either promote or hinder phase separation.

A numerical study of structurally symmetric ("isotope-like") blends has been carried out, based on PRISM theory which uses the recently developed "molecular closures" and self consistently determines the chain conformation. Distinctive intrinsic and finite size fluctuation effects, including nonideal conformational changes for the minority component near the phase boundary are found. These non-FH effects depend on variables such as the density ($\rho$), concentration ($\phi$), chain length and the spatial range of the van der Waals forces. Detailed comparisons with benchmark Monte Carlo simulations of Binder and coworkers show very good agreement, thereby verifying the accuracy of
self-consistent PRISM for describing density and concentration fluctuation phenomena in polymer alloys. These findings reproduce the functional dependence of \( \chi \) on \( \phi \) found via SANS in isotopic polymer mixtures at ORNL for PE, polyethylethylene, polyvinylethylene, etc. Simulation of \( \chi(\phi) \) for polystyrene, which shows a qualitatively different shape of \( \chi(\phi) \), is in progress.

Research Staff: B. K. Annis, A. Habenschuss, B. G. Sumpter, D. W. Noid, G. D. Wignall (Solid State Division), B. Wunderlich; Postdoctoral Fellows: J. Cheng, Y. Fu, A. A. Gakh, C. Getino, Y. Jin, G. Liang, J. D. Londono, J. Mueller, M. Pyda, M. Ralle, R. E. Tuzun, M. Varma-Nair, C. E. Wozny, A. Xenopoulous; Guests: E. G. Gakh (Moskow, Russia), R. A. Guenther (University of Nebraska), S. N. Kreitmeier (University of Regensburg, Germany), S. A. Meyer (The Colorado College), M. A. Morgenstern (The Colorado College), I. Okazaki (Toray Industries, Inc., Japan), R. Triolo (University of Palermo, Italy), Q. Wang (Lanzhou University, China); Student Guests: A. Boller (UT Knoxville), W. Chen (UT Knoxville), S. V. Gerdes (UT Knoxville), M. T. Spining (UT Knoxville), G. Zhang (UT Knoxville); Collaborators: F. S. Bates (University of Minnesota), J. G. Curro (Sandia National Laboratory), K. S. Schweizer (University of Illinois), S. Z. D. Cheng (University of Akron), L. Mandelkern (Florida State University), R. Snyder (University of California)
5. OFFICE OF ESH&Q PERFORMANCE AND FACILITY MANAGEMENT
F. J. Smith, Manager

It is the policy of the Chemical and Analytical Sciences Division (CASD) to conduct all work in a manner commensurate with maximum personal safety and health and to ensure minimal environmental impact. During 1994, CASD consolidated all Environmental, Safety, Health and Quality (ESH&Q) activities into a single office, the Office of Environmental, Safety, Health, and Quality Performance and Facility Management. This office, managed by F. J. Smith, provides leadership for division ESH&Q matters with special emphasis on maintaining safe and healthy working conditions and complying with federal and state laws, DOE orders, and LMES and ORNL policies and procedures pertaining to safety, conduct of operations, and environmental protection. S. D. Wright, Division Safety Officer, K. B. Thomas, Environmental Protection and Non-Nuclear Training Officer, J. L. Wagner, Quality Assurance Specialist, and R. F. Peacher, Nuclear Training Officer, provide guidance and one-on-one assistance to the research staff. The current ESH&Q and facility management "level of effort" in CASD is approximately five person years.

This year the division was the recipient of approximately 15 reviews, appraisals, and audits by external evaluators. All corrective actions are tracked on the MMES ESAMS with none overdue. Only three occurrence reports were filed with DOE for calendar year 1994 with most of those being related to contamination incidents.

1994 HIGHLIGHTS

1. The integration of individual ESH&Q activities of the predecessor divisions into a single Environmental, Safety, Health & Quality (ESH&Q) program. A single set of ESH&Q documentation was implemented.

2. Chemical and Analytical Sciences Division ESH&Q Self Assessment Program

Independent Appraisal of CASD Self Assessment Program

An ORNL ESH&Q Management Appraisal of the ORNL Chemical and Analytical Sciences Division was conducted in August 1994. Assessment of the structure, implementation, and effectiveness of the division's self assessment program identified no findings. A number of positive observations and proficiencies were noted. Among those were the use of Project ES&H Evaluation and Summary forms, the use of Management by Walking Around, and a divisional deficiency tracking database.

CASD Self Assessment Program Plan

In 1994, the CASD completed the first pass through a three year self assessment cycle. The rolling three year cycle of twelve elements covered principal ESH&Q functional areas in CASD and promoted comprehensive coverage. The elements receiving focus in 1994 were radiation protection, division-specific training, quality assurance, and division management and oversight.
Special Assessment Activities Arising from External (to ORNL) Drivers included Plutonium Vulnerability Assessment; 10CFR830.120 Price Anderson Amendments Act Compliance Assessment; Compliance Assessment for DOE Order 5480.20 Personnel Selection, Qualification, Training and Staffing Requirements for DOE Reactor and Nonreactor Nuclear Facilities; and Compliance Assessments for Compliance with Nuclear Facility Safety Documentation.

3. CASD had no lost time occupational injures last year (only one first aid case).

4. Facility restart was achieved for the RMAL, Building 2026.

5. Radiation doses were maintained substantially below ALARA goals for the electrical upgrade of hot cells in building 2026 and for analytical support activities during the transuranium production campaign, Building 7920.

6. CASD operated over 75 RCRA waste accumulation sites last year with no significant "environmental noncompliances."

7. CASD personnel received over 3500 hours of required training during calendar year 1994. This office provided new employee orientation/training, including site-specific training, to all new employees and long-term guests of CASD.
6. OFFICE OF ADMINISTRATIVE SERVICES
S. D. Wright, Manager

The Office of Administrative Services (OAS) was formed during the merger of the Analytical Chemistry Division and the Chemistry Division. It was created in order to consolidate, where possible, the administrative functions of the two divisions. This office performs all administrative duties necessary to support a research organization of approximately 140 full-time staff members.

Those duties and the personnel responsible for them are listed below:

- Resources Coordinator, J. P. Hall
- Clerical Support, M. H. Limburg
- Finance Officer, M. Pasupathi
- Support Services Coordinator, L. K. Plemons
- Procurement, L. K. Woods
- Personal Computing and Network Consultation, S. D. Wright
- Manager, S. D. Wright

The Current OAS “level of effort” is 5.5 person years.

1994 Highlights

1. The integration of separate administrative organizations from the two divisions has gone smoothly. Personnel were assigned responsibilities in accordance with their personal strengths and attributes.

2. Our procurement function has constantly changed and adapted in order to meet the ever increasing requirements of MMES’ ESH&Q procedures. The level of orders in this office has increased from approximately 1200 to 2400. Though it has not been without its growing pains, it continues to perform at an extremely high level of efficiency.

3. CASD began implementing a strategy to convert from the existing DCA computing network to the 10Mb/s ethernet network currently being installed at ORNL. Approximately 65% of CASD now has access to the internet through this effort. Efforts included installation of approximately 70 ethernet drops in Buildings 4500N and 4500S, as well as initiation of a project which will bring fiber optic ethernet service to four facilities (5505, 5507, 5510, and 5510A) which previously had no link to the ethernet.

4. This office coordinated the 35th Annual DOE/ORNL Conference on Analytical Chemistry in Energy Technology. There were over 400 attendees and 32 exhibitors, which made this our most successful conference ever in terms of participation.

\[1\] Finance and Business Management Division
## APPENDIX A. SOURCES OF FUNDING

### FUNDING SOURCES (FY 1994)

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<thead>
<tr>
<th>Source</th>
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<td>Department of Energy</td>
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<td>Other</td>
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<td>Special Analytical Projects**</td>
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<td>Laboratory-Directed R&amp;D**</td>
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<td><strong>TOTAL</strong></td>
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*Chemical Sciences, 6.64; Materials Sciences, 2.33; Geosciences, 1.03.

**Adjusted for overhead exemption.
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<th>Inorganic Mass Spectrometry</th>
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<td>N. Zul4</td>
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## Organic Chemistry Section

**M. R. Guerin, Head**

**P. M. Tretham**

**K. L. Hagerman**

**E. T. Maestas**

### Analytical Methods

- W. H. Grist, Leader
- S. A. Barzick
- J. E. Cotten
- S. H. Harvion
- C. H. Ho
- C. L. Ma
- M. P. Maskarinec
- R. L. Schenley
- G. A. Sega
- S. M. Smith
- B. A. Tomkins
- P. F. Wolfe
- J. N. Weaver
- J. T. Skenen

### Instrumentation

- W. B. Wise, Leader
- K. J. Bart
- S. A. Lassawert
- R. Merriweather
- C. V. Thompson

### Physical Organic Chemistry

- A. C. Buchanan, Leader
- P. F. Britt
- R. T. Dabestani
- R. M. Bagianen
- R. H. Sigman
- T. R. Reckaw
- A. A. Gak
- S. W. Lee
- Z. Shi
- S. A. Vierkotter
- J. A. Straw

### Environmental Monitoring

- R. A. Jenkins, Leader
- A. L. Cowper
- A. B. Dindal
- W. L. Griffith
- R. H. Ligner
- M. A. Palauny
- R. B. Smith
- L. C. Waters
- J. T. Skenen

### OREM/UPE Research Program

- G. A. Gilovich
- H. Qwu

## Physical and Materials Chemistry Section

**R. E. Mesner, Head**

**R. G. Violet**

**D. L. Greene**

**J. D. Patterson**

### Chemical Separations

- B. A. Motzer, Leader
- F. V. Bovenese
- G. M. Brown
- J. C. Bryan
- T. J. Haverlock
- R. A. Sachlennan
- F. V. Sloop
- Y. Ding
- S. Kilmah
- W. K. Kor
- F. J. Moeha
- Y. Sun
- L. M. Bates
- D. J. Frechley

### Geochemistry

- D. J. Wesolonski, Leader
- J. G. Blencoe
- D. R. Cole
- L. M. Anwitz
- P. Benezech
- T. H. Burch
- S. M. Porlier
- J. Horita
- M. K. Ridler
- J. C. Selz

### High Temperature Aqueous Chemistry

- R. E. Mesner, Acting Leader
- M. S. Grusskiewicz
- P. C. Ho
- D. A. Palmer
- J. M. Slawson
- P. Benezech
- D. B. Joyce
- C. Nguyen-Trung
- G. H. Zimmerman

### Inorganic Materials

- D. B. Beach, Leader
- C. E. Basberger
- L. Mays
- M. Paranthaman
- C. E. Vallet
- D. E. Heatherly

### Polymer Science

- A. Harrischern, Leader
- B. K. Annis
- D. W. Mold
- B. G. Swompton
- B. Wunderlich
- A. Boller
- Y. Fu
- C. Getino
- J. D. London
- I. Okazaki
- M. Kalle
- R. E. Tiran

---
APPENDIX C. PUBLICATIONS, PRESENTATIONS, AND REPORTS

ANALYTICAL SPECTROSCOPY SECTION

INORGANIC MASS SPECTROMETRY GROUP

Books/Book Chapters


Journal Articles


**Presentations/Conference Proceedings**


Reports


OPTICAL SPECTROSCOPY GROUP

Books/Book Chapters


Journal Articles


**Presentations/Conference Proceedings**


particles in an Ion Trap," IV Laser Applications to Chemical Analysis Meeting, Jackson Hole, WY, 

Ramsey, J. M. "Miniature Chemical Instrumentation: The Next Generation?" Abbott Laboratories, 
Chicago, IL, Aug. 11, 1994.

Devices," 6th International Symposium on High Performance Capillary Electrophoresis, San Diego, 

9, 1994.

Ramsey, J. M. "Ongoing Activities in Micromachining at ORNL," Micromanufacturing Technology 

Ramsey, J. M. "Miniaturization of the CE Process," Advanced Lab Exposition and Conference 

Ramsey, J. M. "Miniature Instruments for Liquid Phase Analysis," Federation of Analytical Chemis-

Ramsey, J. M. "Miniature Chemical Instrumentation: The Next Generation?" Stanford University, 

Ramsey, J. M. "Micromachined Devices for Performing Chemical Reactions and Separations," 
National Institute of Standards and Technology, Gaithersburg, MD, Nov. 15, 1994.

Ramsey, J. M. "Microfabricated Chemical Instrumentation for Chemical Sensing," Section Meeting 

Ramsey, J. M. "Microfabricated Chemical Instruments," Gordon Conference on Bioanalytical 

Ramsey, J. M. "Microfabrication of Chemical Instruments," Fourth International Workshop on Bio-

Ramsey, J. M. "Counting Molecules: The Ultimate Approach to Chemical Analysis," Society of 
Applied Spectroscopy Speakers Tour, Detroit Section, Dearborn, MI, April 11, 1994.

Ramsey, J. M. "Analysis of Ultradilute Solutions Based on Single Molecule Detection in Micro-


Reports


ORGANIC MASS SPECTROMETRY GROUP

Books/Book Chapters


Journal Articles


**Presentations/Conference Proceedings**


Buchanan, M. V. Graduate Lecture on FTICR, Department of Chemistry, University of Tennessee, Nov. 1, 1993.


SECONDARY ION MASS SPECTROMETRY GROUP

Journal Articles


**Presentations/Conference Proceedings**


**Other**

SURFACE CHEMISTRY AND HETEROGENEOUS CATALYSIS GROUP

Journal Articles


Overbury, S. H. and van den Oetelaar, R. J. A. "Structure of the p(2x1)-O/Mo$_{0.75}$Re$_{0.25}$(001) Surface Studied by Low Energy Li$^+$ Ion Scattering," Surf. Sci. (1994) 301, 313-325.


**Presentations/Conference Proceedings**


Reports


NUCLEAR AND RADIOCHEMISTRY SECTION

NEUTRON ACTIVATION ANALYSIS GROUP

Journal Articles


Presentations/Conference Proceedings


Reports


RADIOACTIVE MATERIALS ANALYSIS GROUP

Journal Articles

Presentations/Conference Proceedings


Reports


Thesis


TRANSURANIUM ELEMENT CHEMISTRY GROUP

Books/Book Chapters

Journal Articles


**Presentations/Conference Proceedings**


Peterson, J. R. "Introduction to the Symposium Comparative Aspects (Similarities and Differences) of Lanthanide and Actinide Behavior," 20th Rare Earth Research Conference, Monterey, CA, Sept. 12-17, 1993.


Peterson, J. R. "Bulk Phase Chemical Studies on the Edge of Matter: Lessons Learned About the Consequences of α and β Decay," San Jose State University, San Jose, CA, July 2, 1993.


Peterson, J. R. "Bulk Phase Chemical Studies on the Edge of Matter: Lessons Learned About the Consequences of $\alpha$ and $\beta$ Decay," San Jose State University, San Jose, CA, June 29, 1994.


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Reports

Agouridis, D. C., Gayle, T. M. and Griest, W. H. Development of the Prototype Munitions Case Moisture Meter Model ORNL-1, ORNL/TM-12334 (February 24, 1993).


Griest, W. H. [Characterization Team Leader and Section Editor for] Oak Ridge National Laboratory Technology Logic Diagram, Volumes 1 and 2, ORNL/M-2751 (September 1993).


Other


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Thesis


HIGH TEMPERATURE AQUEOUS CHEMISTRY GROUP

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Journal Articles


**Presentations/Conference Proceedings**


Mesmer, R. E. "Research in High Temperature Aqueous Chemistry at ORNL," Bristol University, United Kingdom, August 13, 1993.


Nguyen-Trung, C. and Palmer, D. A. "Hydrolysis of the Uranyl(VI) Ion in Aqueous Solutions up to 100°C, 0.1 MPa," 49th Calorimetry Conference, Santa Fe, New Mexico, July 1994.


Wesolowski, D. J. and Palmer, D. A. "The Hydrolysis of Mg$^{2+}$ in 0.5 Molal NaCl Brines from 0 to 250°C by Potentiometric Titration," American Geophysical Union Annual Meeting, Baltimore, MD, May 23-27, 1993.

Reports


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Paranthaman, M., Sun, Y. R. and Thompson, J. R. "Synthesis and Magnetic Characterization of Bulk HgBa$_2$CuO$_{4+y}$, HgBa$_2$CaCu$_2$O$_{8+y}$ and HgBa$_2$Ca$_2$Cu$_3$O$_{8+y}$ Superconductors," American Physical Society Meeting, Pittsburgh, PA, Mar. 21-25, 1994.

Paranthaman, M. "Thallium Based High-Tc Superconducting Oxides -- An Overview," Midwest Superconductivity Consortium Workshop, Purdue University, West Lafayette, IN, Aug. 11-12, 1994.


**POLYMER SCIENCE GROUP**

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**Journal Articles**


Schweizer, K. S. and Yethiraj, A. "Polymer RISM Theory: New Molecular Closures for Phase

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Wozny, C. E., Sumpter, B. G. and Noid, D. W. "Calculating the Vibrational Spectra of Linear Polymers


**Presentations/Conference Proceedings**


Boller, A. and Wunderlich, B. "Temperature-modulated DSC," Colloquium at the Sektion fuer Kalorimetrie, Department of Physics, University of Ulm, Ulm, Germany, June 20, 1994.

Boller, A. and Wunderlich, B. "Temperature-modulated DSC," Department of Physics, University of Rostock, Rostock, Germany, June 10, 1994.


Schweizer, K. S. "Integral Equation Theories of Polymer Alloys," Physics Department, University of Mainz, Germany, March 1993.


Sumpter, B. G. "Applications of Computational Neural Networks in Materials Science: An Introduction," Artificial Neural Networks in Engineering, St. Louis, MO, November 1994.


Wunderlich, B. "Thermodynamische Charakterisierung von Mesophasen," Awards Lecture, Joint German Society for Thermal Analysis (GEFTA) and the Swiss Society for Thermoanalytic and Calorimetry (STK), Munich, Germany, September 13-15, 1993.


Wunderlich, B. "Thermal Properties and Motion in C60, C70, and C70 C6H5CH3- Complex as Analyzed by DSC and NMR," Poster, Material Research Society Fall Meeting, Boston, MA, November 28-December 3, 1993.


Wunderlich, B. "The Rigid Amorphous Fraction of Crystalline Polymers," Two Lecture Series and Discussion at the Research Laboratory of the Toray Research Center, Otsu, Japan, June 7, 1993.


Wunderlich, B. "Computer Simulation of Macromolecular Crystals and Their Defects," Osaka University International Macromolecular Symposium on Ordering in Macromolecular Systems (to recognize the 30 Year Anniversary of the Department of Macromolecular Science of the University of Osaka), Osaka, Japan, June 3-6, 1993.


Wunderlich, B. "Large-Amplitude Motion in Polymer Crystals and Mesophases," University of Hiroshima, Higashi-Hiroshima, Japan, October 26, 1994.

Wunderlich, B. "Large-Amplitude Motion in Polymer Crystals and Mesophases," in Proc., International Symposium on Polymer Crystallization, Gakunan, Okayama, Japan, October 28-29, 1994.


Wunderlich, B. "Modulated DSC - Capabilities and Limits," III Laehnwitz Seminar on Calorimetry (Bestimmung von Umwandlungsenthalpien), Serrahn, Germany, June 2-4, 1994.


Xenopoulos, A., Roles, K. and Wunderlich, B. "A Possible Glass Transition for Poly(L-methionine) and Poly(L-serine)," American Physical Society Meeting, Seattle, WA, March 22-26, 1993.


**Other**

APPENDIX D: HONORS, AWARDS, AND PROFESSIONAL ACTIVITIES

M. D. Barnes
Martin Marietta Energy Systems Publication Award (with J. M. Ramsey and W. B. Whitten), 1994

C. M. Barshick

P. V. Bonnesen
Martin Marietta Energy Systems Technology Transfer Award (with B. A. Moyer and R. A. Sachleben), 1994

A. C. Buchanan
DOE/BES Program Review on Coal Chemistry at Pacific Northwest Laboratory, 1994

R. A. Glenn Award (with P. F. Britt), Division of Fuel Chemistry, American Chemical Society, 1994

A. L. Compere
R&D-100 Award for development of the CI\textsuperscript{2}EANOUT process (with W. L. Griffith, W. P. Huxtable, J. M. Googin, B. G. Davis, and R&D Solutions), 1993

D. C. Duckworth
Chairman-elect, American Society for Mass Spectrometry Elemental Interest Group, 1995-1996

Chairman-elect, North American Glow Discharge User Group, 1995-1996

W. H. Griest
Technical Communication Award, East Tennessee Chapter of the Society for Technical Communication, 1994

W. L. Griffith
R&D-100 Award for development of the CI\textsuperscript{2}EANOUT process (with A. L. Compere, W. P. Huxtable, J. M. Googin, B. G. Davis, and R&D Solutions), 1993

G. A. Guiochon
Alexander von Humboldt Foundation Research Award for Senior American Scientists, 1994

R. L. Hettich
Martin Marietta Energy Systems R&D Accomplishment Award, 1994
B. A. Moyer
Secretary/Treasurer of the Separation Science and Technology Subdivision, Industrial and Engineering Division, American Chemical Society, 1991-1993

Associate Editor, Solvent Extraction and Ion Exchange, 1993-present

Vice Chairman elect, Separation Science and Technology Subdivision, Industrial and Engineering Division, American Chemical Society, 1994

Lind Lecture Committee, East Tennessee Section, American Chemical Society, 1994

Martin Marietta Energy Systems Technology Transfer Award (with P. V. Bonnesen and R. A. Sachleben), 1994

Editorial Board, Hydrometallurgy, 1994-present

D. R. Mullins
Newsletter Editor, Tennessee Valley Chapter, American Vacuum Society, 1994

J. R. Peterson
Member, Program Advisory Council, The Glenn T. Seaborg Institute for Transactinium Science, Lawrence Livermore National Laboratory, 1992-present

Councilor, Division of Nuclear Chemistry and Technology, American Chemical Society, 1993-1995

International Advisory Board, 2nd International Conference on f Elements, Helsinki, Finland, 1993-1994

Vice Chairman, Committee on Nuclear and Radiochemistry, Board on Chemical Sciences and Technology, National Academy of Sciences - National Research Council, 1992-1993

Alternate Councilor, East Tennessee Section, American Chemical Society, 1991-1993

M. L. Poutsma
Elected Fellow, American Association for the Advancement of Science, 1994

Editorial Advisory Board, Energy and Fuels, 1993-present

Board of Visitors, Chemistry Department, The University of Tennessee/Knoxville, 1994-present

J. M. Ramsey
Editorial Advisory Board, Analytical Chemistry, 1995-present

Martin Marietta Energy Systems Publication Award (with M. D. Barnes and W. B. Whitten), 1994

L. Robinson
Chairman-elect, Board of Directors, Oak Ridge Housing Development Corporation, 1995

Member, Martin Marietta Energy Systems Honors and Awards Committee, 1993-presents

Martin Marietta Energy Systems Outstanding Community Service Award, 1994

R. A. Sachleben
Martin Marietta Energy Systems Technology Transfer Award (with P. V. Bonnesen and B. A. Moyer), 1994

R. L. Schenley
Technical Publications and Art Competition Award for Mechanical Illustration and Tone Distinction, Local East Tennessee Chapter of the Society for Technical Communication (with D. G. Cottrell), 1994

R. W. Shaw
Chairman, Chemical and Analytical Sciences Division Improvement Council, 1994-1995

J. M. Simonson
Sunner Memorial Award of The Calorimetry Conference, 1993


ORNL Exploratory Studies Review Committee Chairman, 1992-1993

D. H. Smith
Martin Marietta Energy Systems R&D Accomplishment Award, 1994

F. J. Smith
ORNL Operations Support Award, 1994

Staff of Bldg. 2026
ORNL ALARA Award for dose reduction efforts during electrical upgrade of hot cells, 1994

P. J. Todd
Chairman-elect, East Tennessee Mass Spectrometry Discussion Group, 1994

D. J. Wesolowski
Associate Editor, *Geochimica et Cosmochimica Acta*, 1992-present
Adjunct Associate Professor, Department of Geological Sciences, The University of Tennessee at Knoxville, 1990-present

W. B. Whitten
Martin Marietta Energy Systems Publication Award (with M. D. Barnes and J. M. Ramsey), 1994

M. C. Woody
ORNL Most Valuable Player Award, 1993

J. P. Young
American Chemical Society representative to WATTEC Sponsors Committee, 1993-1995

Chairman, East Tennessee Section, American Chemical Society, 1993
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