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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1990

W. D. SHULTS
Director

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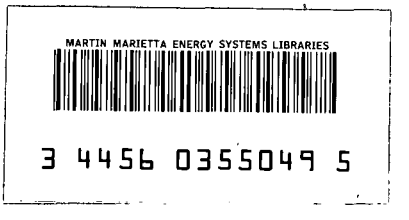

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INTRODUCTION

W. D. Shults
Director

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

1. **Analytical Research, Development, and Implementation.** The division maintains a program to conceptualize, investigate, develop, assess, improve, and implement advanced technology for chemical and physicochemical measurements. Emphasis is on problems and needs identified with ORNL and Department of Energy (DOE) programs; however, attention is also given to advancing the analytical sciences themselves. This program is composed of medium- to long-term projects and is supported primarily by the DOE.

2. **Programmatic Research, Development, and Utilization.** The division carries out a wide variety of chemical work that typically involves analytical research and/or development plus the utilization of analytical capabilities to expedite programmatic interests. The effort in this category comes from ORNL and DOE programs and from Work for Others agreements. Emphasis here is on "applied" chemistry.

3. **Technical Support.** The division performs chemical and physicochemical analyses of virtually

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

The Analytical Chemistry Division is organized into four major sections, each of which may carry out any of the three types of work mentioned above. Chapters 1 through 4 of this report highlight progress within these four sections during the period January 1 to December 31, 1990. Chapter 5 contains information about the division's quality assurance/quality control, safety and training programs. Chapter 6 summarizes the education programs, which have grown in both magnitude and importance. Supplementary professional activities, publications, and presentations are given in Chapters 7 and 8.

During 1990, the division continued to publish and present its work: 34 reports; 67 proceedings and/or book chapters; 73 journal articles; 152 presentations. Some 279,438 analytical determinations were performed.

HIGHLIGHTS

The following excerpts highlight some of the technical activities carried out during 1990. They illustrate the diversity of programs within the Analytical Chemistry Division.

Persistent spectral hole burning is a laser processing technique in which a normally broad, smooth optical absorption band is modified to produce sharp, narrow dips at certain wavelengths. If the dips are sufficiently narrow and persist for long times, the technique can have potential applications in the area of high density information storage. The main difficulty in finding a practical system to make use of this effect is that the systems studied all require the hole burning to be done at very low temperatures, ~1 K. We have recently shown that dye molecules can be coupled to an ensemble of spherical microparticles to form a system with a homogeneous linewidth determined by the optical Q of the particles and the inhomogeneous broadening determined by the variation in their diameter. A permanent spectral hole can be created at a particular wavelength at room temperature by photolyzing the dye molecules coupled to those spheres that are optically resonant. We are exploring potential applications of this phenomenon.

In the course of studying the mass spectra resulting from the interaction of slow positrons with large organic molecules, a time-of-flight mass spectrometer that has the capability of sampling large source volumes was developed. Our positron ionization studies require that the positrons and the ions they produce be contained in a Penning trap of 10 cm length for long periods of time (ca. 100 milliseconds). When the ions are accelerated out of the trap for mass measurements, their starting positions with respect to the

detector may vary by as much as 15%. This problem is overcome by using an accelerating field whose strength increases linearly with distance from the detector. When this condition prevails, ions whose starting positions are farther away from the detector receive more acceleration than those that are closer. If the initial velocities of the ions are negligible before the accelerating field is applied, all ions will arrive at the detector at exactly the same time. We have found this "quadratic potential spectrometer" to have great sensitivity due primarily to the long collision path and large volume of the source. This device should have utility for conventional mass spectrometry as well as positron ionization mass spectrometry.

A study has been performed with our VG-9000 glow discharge mass spectrometer in the dc discharge mode which demonstrates some unique capabilities of this instrument. One important finding was that the precision of isotopic ratio measurements was less than 0.05% RSD for the major isotopes. Accordingly, this approach can be competitive with conventional thermal ionization methods. We have also made considerable progress in interfacing an rf source to the VG-9000 spectrometer through a collaboration with Professor R. K. Marcus and D. C. Duckworth of Clemson University. A new electrical biasing scheme has been designed and installed to isolate the rf generator from the spectrometer accelerating voltage (8 kV). This eliminates problems with arcing and ill-defined ion energies associated with the previous design. Mass spectra have been acquired with the new biasing scheme and a modified discharge cell design. Problems with rf noise affecting the Faraday detector have been eliminated, and we are able to use all aspects of the VG software. Work is under way to characterize the sensitivity of the rf discharge ion source for both conducting and nonconducting samples.

We initiated studies into the possibility of using an electrodynamic trap for characterizing microparticles by laser ablation mass spectroscopy this year. A charged particle, from hundreds of microns in diameter to as small as a single electron, can be confined in the small volume of the trap. Because the trap can also be used for mass spectrometric analysis, there is the

exciting possibility of trapping a particle, ablating the ions from the particle with a laser, and then generating a mass spectrum of the ions left in the trap. It was decided to first evaluate the laser ablation mass spectroscopy technique on particles as they fall through the trap. A Nd:YAG laser is used to ablate ions from the falling particles. The trigger pulse for firing the Nd:YAG laser is generated with a HeNe laser beam which also intercepts the falling particle. We have demonstrated that all of the hardware components function properly when the particles fall through the trap and have begun to determine the conditions required for trapping and analyzing the ions ablated from the particles.

We are developing and will apply several spectroscopic and materials characterization techniques to foster a fundamental understanding of film growth by chemical vapor deposition (CVD) processes. Although many technologically-important materials are synthesized by this general family of processes, little is known about the details of the chemical and physical mechanisms involved in film growth. We have elected to examine first the growth of diamond films. This material was chosen because of its importance and experimental practicality. Diamond films have unique properties (high thermal conductivity, hardness, and resistivity) that make them attractive for a number of applications. This project is a collaborative effort with staff from the Metals and Ceramics and Fusion Energy Divisions and is funded by the ORNL Exploratory Studies program.

A method has been developed to determine the hyperfine splittings of two-photon excited atomic levels using two-color resonance ionization mass spectrometry (RIMS). These states are inaccessible from the ground state by one-photon processes. The method involves pumping individual hyperfine levels of an intermediate state with a high-resolution diode laser and then further promoting the atom to the two-photon level with a tunable, pulsed dye laser. An intracavity etalon is required in the dye laser in order to narrow its spectral bandwidth to approximately 0.03 cm^{-1}. Ionization results from

nonresonant absorption of an additional dye laser photon. The overall two-photon state splitting pattern is assembled by piecing together the individual spectra from the intermediate hyperfine levels. This method was applied to the 30354 cm^{-1} level of lanthanium 138 and 139.

We have demonstrated for the first time the coupling of matrix-assisted laser desorption (MALD) and Fourier transform mass spectrometry (FTMS) as a technique for obtaining structural information on compounds of very high mass. By using a nicotinic acid matrix we obtained peptide spectra with 266 nm laser desorption (single shot or signal averaged) that revealed reduced fragmentation as well as an increased abundance of ions related to the molecular weight; i.e., $(M+H)^+$, $(M+K)^+$, and $(M+Na)^+$. Peptides up to Gramicidin D (mw 1882) could be ionized "softly" with MALD. Examination of several different wavelength-matrix combinations indicated that pyrazinecarboxylic acid with 266 nm laser desorption and sinapinic acid with 355 nm also provided strong enhancement for the MALD FTMS experiments. Larger proteins such as bovine insulin (mw 5734) did not reveal molecular ions with any matrix-wavelength combination. Because these compounds have been observed in MALD TOF experiments, it appears that these $(M+H)^+$ ions for these higher molecular weight compounds are being generated, but are not detected in the FTMS. This may be due to poor ion trapping and/or ion detection factors. These limitations are presently under investigation. Initial investigations indicated that the MALD FTMS technique is also well-suited for the characterization of low picomole quantities of normal and modified oligonucleotides and provides a means of probing the structures of ions in remarkable detail. Both sequence and isomeric information can be readily obtained.

Gel electrophoresis is the most commonly used separation technique for biomolecules such as peptides and oligonucleotides, but a direct laser desorption from gels has been limited by poor detection limits and interferences from the gel matrix. We have developed a method for extracting large

oligonucleotides from agarose gels which promises to resolve these difficulties. This method, called "freeze-squeeze" extraction, involves freezing the analyte-doped gel with liquid nitrogen and manually squeezing the gel to extrude the interstitial liquid containing the analyte. This method was used to extract picomole quantities of small peptides and oligonucleotides from the gels for subsequent characterization by MALD FTMS. Radiotracers were employed to quantitate sample loading and recovery from the gel and indicated total efficiencies of about 50%. Methods have also been developed for the isolation of biomolecules from polyacrylamide gels using electroelution techniques.

As part of an ongoing project for the National Cancer Institute to investigate the effects of environmental tobacco smoke and passive smoking, a method for the rapid detection of markers of exposure to tobacco smoke was developed using the ion trap mass spectrometer (ITMS). In this method, 1-μL aliquots of untreated urine are thermally desorbed directly into the ITMS. Isobutane is used to selectively ionize nicotine and cotinine, a metabolite of nicotine, and fragments from collision-induced dissociation of the $(M+H)^+$ ions of each compound quantitatively monitored. Detection limits of approximately 10 pg for each of these semi-volatile compounds are obtained, with a linear dynamic range of two to three orders of magnitude. These detection limits are more than sufficient for the study of urine from smokers with no sample concentration. Analysis time is less than four minutes per sample. To improve quantitative measurements, deuterated nicotine and cotinine are used as internal standards. Analysis of an EPA/NIST Reference Material, 8444, demonstrated that the direct sampling method has excellent accuracy and precision. Additional pilot studies were also conducted on the rapid detection of other nicotine metabolites, including nicotine-N-oxide and 3-hydroxycotinine. These studies indicated that this technique has promise for more polar and less volatile compounds. A similar sampling approach has been used to detect a variety of drugs in urine, including cocaine, codeine, phenobarbital, tetrahydrocannabinol, amphetamine, and methamphetamine. The detection limits

for these drugs are at or below levels required for drug screening purposes. Additional work is being conducted with other drugs and other matrices at present.

Electrospray ionization was investigated for its utility for analysis of porphyrins. A number of different types of porphyrins including free-base and metal porphyrins containing alkyl, acid, ester, and/or hydroxyl functionalities were studied. For all the porphyrins investigated, hematoporphyrin IX and hematin being exceptions, only the molecular species were observed when using the appropriate focusing and ion injection parameters. We found that the solvent system from which the porphyrins are sprayed plays a role in determining the molecular species observed for some porphyrins. The molecular species observed from the vanadyl porphyrins, for example, was either M^+, $(M+H)^+$ or $(M+Na)^+$ depending on the solvent system. In the case of free-base alkylporphyrins such as etioporphyrin-III, the protonated molecule was observed regardless of the solvents used. To our knowledge, this is the first report of radical cation formation using electrospray ionization. The quantity of material necessary for detection of a porphyrin in a single scan ("figure of merit") was in the low femtomole range for all porphyrins studied indicating the potential utility of the ES/ITMS combination in analytical studies of porphyrins.

Last year we reported the development of a mixed mode reverse phase/anion exchange high performance liquid chromatography (HPLC) method for the determination of explosive compounds and trinitrotoluene (TNT) metabolites. This method has been extensively applied this year. Our analytical procedure for aqueous leachates and soils or composts was subjected to the U. S. Army Toxic and Hazardous Materials Agency Level IA Certification. It now is being applied to the analysis of explosives processing wastes composts and their EPA Synthetic Precipitation Leach Test leachates. The composts are from a field composting experiment designed to decontaminate lagoon sediments at the Umatilla Army Depot. Considerable biotransformation of the TNT to monoamino derivatives is being observed. The leachates and also

organic solvent extracts are being tested for bacterial mutagenicity and aquatic toxicity by collaborators in the Health and Safety Research and Environmental Sciences Divisions. The HPLC analytical method also has been applied to 168 samples of deer, quail and rabbit tissues extracted by other collaborators in the Environmental Sciences Division. No explosives or TNT metabolites were found in any tissues within a detection limit of 0.1 mg/kg. Surrogate standards, matrix spikes, and blanks were extensively used for quality assurance.

Field analytical methods are becoming an increasingly important component of environmental restoration activities. Work on fieldable instrumentation has centered on the development of solid sorbent sampling for use with the ion trap mass spectrometer. When the ITMS is used in the direct sampling mode, the majority of the sampled stream is vented to atmosphere. We are examining the possibility of collecting the vented material to allow for repeated or confirmatory analysis following field screening. We chose to evaluate a resin combination for this work, thus adopting the same philosophy as we previously used for collection of air samples with the "original" triple sorbent trap (TST). The sorbent combination evaluated was Carbotrap C, Carbotrap, and Carbosieve S-III. The first two resins are classified as graphitized carbon black and the third resin is classified as a carbon molecular sieve. The combination of all carbon-based resins allows for heating of the trap during thermal desorption to 350° C. This permits a faster and more complete desorption. For this evaluation we chose parameters, where applicable, which are used during actual ITMS water sample analyses. Analyte recoveries from spiked water samples analyzed originally on the ITMS and reanalyzed from the sorbent trap on the GC/FID system averaged 77% for a five-minute sample purge and 110% for a ten-minute sample purge for the 34 EPA target compound list (TCL) volatile organic compounds. The results of this preliminary study are very encouraging, and suggest that such a trap could be used to effectively collect and stabilize volatiles purged from soil and/or water samples in the field; then only these small traps need be returned to the laboratory for analysis.

During the past year a major effort was expended to develop a new set of procedures to better measure radionuclides in soil samples. A pressure monitor was installed on our microwave digestion system so that the pressure within the vessels could be controlled accurately. With the monitor in place, we are able to vary the number of samples that can be digested, the sample size, and acid volumes without losing any sample due to excess pressure within the vessel. We can totally dissolve up to 5 grams of soil with a mixture of hydrochloric, nitric, and hydrofluoric acids. Because of the complexity of the soil matrix, we sought to improve our separation scheme for radionuclides and ^{90}Sr, plutonium, uranihum, thorium, americium, and curium. We found that the ion-exchanger TRU-Spec is very selective for the actinides and nonselective for almost all other elements. We also investigated another material, Sr-Spec, which is selective for strontium. A soil dissolution adjusted to approximately 3M in nitric acid can be put directly through a column packed with this material with almost unbelievable results. Virtually all ions except strontium and the actinides pass through the columns and 99+ percent of the actinides can then be eluted with very weak nitric acid. The strontium resin retains strontium and only a small amount of barium from a solution adjusted to approximately 3M in nitric acid. The strontium can be eluted with warm water. These new-generation materials promise to improve both the speed and efficiency of our procedures.

A most important event in the analytical support area this year has been implementation of the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311). This procedure is to be applied to waste samples for the determination of "hazards" based on toxicity. The test replaces, in large measure, the dilution/extraction methods used in the past, and greatly expands the number of waste types which require testing. The test is complex, expensive, and labor intensive. The product of the test is an extract, which is an aqueous medium. The extract is analyzed for volatile organics, semivolatile organics, pesticides, herbicides and the eight RCRA metals. Implementation of the TCLP required much alteration of

facilities and operations, plus the acquisition of much new instrumentation. Since there are types of wastes to which the TCLP cannot be applied, including oils, waste solvents, and large metal pieces, we retain our dilution/extraction systems for use where applicable.

The High Flux Isotope Reactor (HFIR), which was shut down in November 1986, began operating at low power at the end of January 1990 and began routine operations at 85 MW in May 1990. Considerable effort was expended in getting our new neutron activation analysis (NAA) facility at HFIR into operation. Both pneumatic tubes were brought into compliance and the gamma spectrometry instrumentation was upgraded. Much effort was put on writing/translating a FORTRAN code for NAA such that it can run on a PC-based analyzer system.

A new inductively coupled plasma/mass spectrometer (ICP/MS) was received in December 1989 and made operative in February 1990. An electrothermal vaporization system was acquired somewhat later in the year. "Clean" facilities were developed for the ICP/MS because of its extreme sensitivity and broad applicability. The instrument has proved to be extremely useful as a supplement to and/or substitute for ICP/optical emission and graphite furnace spectrometers. We are evaluating the use of ICP/MS for the determination of uranium isotopes at the part-per-trillion level in urine.

The installation of a modern state-of-the-art ion microprobe/microscope (CAMECA Instruments) during 1990 has provided the Analytical Chemistry Division with significant new capabilities for research and analysis. The specific attributes of this instrument that will open new areas for us are: 1) advanced imaging capability in microscope mode with $< 1\ \mu m$ lateral surface resolution; 2) high mass resolution ($\geq$ 35,000 $M/\Delta M$); 3) an on-axis electron gun that will allow analysis of insulator materials; 4) secondary electron imaging of rastered areas; 5) a 250 nm spot size cesium ion gun for probe mode analysis; and 6) ultra-high vacuum in the sputtering chamber that allows ppm or lower analytical capability for the elements C, H, O, and N. Acquisition of this instrument has led to a new collaborative program with Chemistry

Division personnel, measuring isotopic ratios and rare earth elements in geological samples.

Considerable progress has been made toward the preparation of a monograph on the chemistry of environmental tobacco smoke (ETS) for the Center for Indoor Air Research (CIAR). Special attention is being given to respirable particulate matter, nicotine, carbon monoxide, volatile organic chemicals, trace organics (primarily polycyclic aromatic hydrocarbons and N-nitrosamines), oxides of nitrogen, and formaldehyde. The principle objective is to provide a comprehensive tabulation and review of data generated in studies of ETS exposure. A secondary objective is to provide background information on smoke chemistry, sampling and analysis methods and non-ETS sources of indoor air contaminants as an aid for future research.

1. ANALYTICAL SPECTROSCOPY

J. A. Carter

The Analytical Spectroscopy Section is composed of four groups: Optical Spectroscopy, Inorganic Mass Spectrometry, Organic Mass Spectrometry, and Secondary Ion Mass Spectrometry. The R&D efforts in each group are directed toward enhancing analytical capabilities through new discoveries and developing a clearer understanding of fundamental physical processes that can be exploited into new instruments or analytical approaches for solving energy-related problems. Two significant accomplishments in laser research involved (a) detection of a single molecule by laser-induced fluorescence (as few as twelve molecules are suspended in a solvent drop in an electric field), and (b) laser ablation mass spectrometry of particles suspended in an ion trap. In mass spectrometry R&D advances in the development of the utility of electrospray ionization with ion trap mass spectrometry have led to better techniques for studying high molecular weight compounds. The technique has also been used for inorganic analysis and liquid chromatography coupled with electrospray. A CAMECA-4f instrument was acquired to increase capabilities in materials and geological studies. A quadratic potential time-of-flight mass spectrometer was designed and demonstrated for positron ionization studies. The VG-9000 DC glow discharge mass spectrometer was used to obtain very precise palladium isotopic ratios (±0.05%).

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

is about equally distributed among the DOE Offices of Safeguards and Security, Arms Control, and Industrial Processes (OIP). In-line Sensors for an Electrolytic Magnesium Cell is a new project for OIP and Dow Chemical Co. The balance of our effort is funded by Laboratory divisions and programs, the Y-12 and K-25 plants, various interagency agreements (FAA, ISPO/State, and IAEA), and other work-for-others contracts.

INORGANIC MASS SPECTROMETRY

D. H. Smith

This group carries out both research and support activities. This past year saw a substantial turnover in personnel as veterans retired and funding changes caused other shifts. Research continued in analytical applications of positrons, HIXSE, and inorganic mass spectrometry. Support work continued in various areas of inorganic mass spectrometry; gas analysis and isotope ratio work were chief among them.

This year saw the move of two instruments from Y-12 to space in Building 5505. Funds are being sought to renovate enough space in this building to accommodate all our isotope ratio operations.

Development of an rf probe for use in trace analysis with our glow discharge mass spectrometer made good strides. It is clear that the project will be successful and provide a highly useful tool for trace analysis of nonconducting samples. An evaluation of this instrument's ability to measure isotope ratios was highly encouraging and has stimulated us to consider a more thorough investigation.

Interest in using positrons as an ionization technique for mass spectrometry led to development of a novel mass spectrometer, dubbed a quadratic potential time-of-flight instrument. The source of this instrument focuses ions from relatively large volumes; normal mass spectrometers focus ions from only very small volumes. It has been used to continue our studies of positron ionization phenomena.

HIXSE research continued to advance. It was found to be sensitive to small changes in the subsurface environment difficult or impossible to detect via other means. There is evidence to suggest that HIXSE can detect any impurity ion in any matrix. Due to reductions in funding, the HIXSE project was terminated at the end of the fiscal year.

Glow Disscharge Mass Spectrometry

Considerable progress has been made in interfacing an rf glow discharge source to the VG-9000 mass spectrometer through a collaboration with Professor R. K. Marcus and D. C. Duckworth of Clemson University. The mass spectrometer was successfully moved to Building 5505 at ORNL, thus allowing more ready access by uncleared personnel; Duckworth is now working full time on this project. A new electrical biasing scheme has been designed and installed to isolate the rf generator from the mass spectrometer accelerating voltage (8 kV). This eliminates problems with arcing and ill-defined ion energies associated with the previous design. Mass spectra have been acquired with the new biasing scheme and a modified discharge cell design. Problems with rf noise affecting the Faraday detector have been eliminated, and we are able to use all aspects of the VG software. Work is under way to characterize the sensitivity of the rf discharge ion source for both conducting and nonconducting samples such as NIST Multicomponent Glass.

A study has been performed with the VG-9000 in the dc glow discharge mode which demonstrates the unique capabilities of this instrument. The samples were Pd metal rods which had been electrolytically charged with hydrogen and deuterium. A sample which had undergone a prolonged electrolysis and had exhibited both excess heat generation and neutron production was studied first to see if the isotopic composition of Pd had changed compared to the starting material. Significant isotopic differences were seen which subsequently were found to be a result of palladium hydride and palladium deuteride ion interferences. Heating of

the sample in air to 800° C removed the entrained gases and restored the isotopic values to those of the starting material. The precision of isotopic ratio measurements in this study was less than 0.05% RSD for the major isotopes, thus making this method competitive with conventional thermal ionization methods, especially for elements which are not easily determined by thermal ionization mass spectrometry. In addition to the high precision isotopic measurements, the high mass resolution capabilities of the instrument were utilized to study the effect of hydride and deuteride interferences on the Pd isotope peaks.

D. L. Donohue

A Quadratic Potential Time-of-Flight Mass Spectrometer (QP-TOF)

In the course of studying the ion spectra resulting from the interaction of slow positrons with large organic molecules, it has become necessary to devise a time-of-flight mass spectrometer that has the capability of sampling large source volumes. The nature of the positron ionization studies requires that the positrons and the ions they produce be contained in a Penning trap of 10 cm length for long periods of time. When the ions are accelerated out of the trap for mass measurements, their starting positions with respect to the detector vary by as much as 15%. This problem has been overcome, and the effort has resulted in a highly sensitive instrument, of good resolution, that has utility for conventional mass spectrometry as well as the special application to positron spectroscopy.

The times of flight of ions can be made insensitive to source volume size by using an accelerating field whose strength increases linearly with distance from the detector. When this condition prevails, ions whose starting positions are farther away from the detector receive more acceleration than those that are closer. If the initial velocities of the ions are negligible before the accelerating field is applied, all ions will arrive at the detector at exactly the same time. For discussion purposes in the next section, as well as this one, we will review the equations of motion of the ions. In order for the acceleration field to vary

linearly with distance from the detector, the potential must vary quadratically:

$$V = A*z^2 \qquad (1)$$

where z = distance of ion from detector, A = constant.

The acceleration of an ion is proportional to the gradient of the potential:

$$d^2z/dt^2 = -(2Ae/m)*z = -g^2*z \qquad (2)$$

Where e/m is the charge-mass ratio of the ion, the g-quantity is defined in terms of A, e, and m. The solution of the equation of motion and the TOF for an ion having zero initial velocity is:

$$(z/Z_o) = \mathrm{Cos}(gt) \qquad \mathrm{TOF} = \pi/2g \qquad (3)$$

The TOF is proportional to the square root of the ion mass, as for conventional TOF spectrometry, and that it is independent of the Z_o starting position.

Experimentally the quadratic potential spectrometer (QP-TOF) has been found to be very sensitive. At a vacuum pressure of 7 E-6 Pa, using a limited supply of positrons as ionization particles, the instrument served as an excellent residual gas analyzer. Water and oxygen were the main background components of the vacuum; their peak-to-background signals were over 50:1. Miscellaneous hydrocarbons were also detected in the vacuum background; their peak intensities indicated their partial pressures to be less than 7 E-7 Pa.

As will be described below, the main application of this instrument has been in the study of mechanisms by which positrons ionize large organic molecules. This has required that pulses of positrons be held in the Penning trap source volume for extended periods of time. In the work reported below, contact times as long as 100 milliseconds have been used. Effective collision path lengths were more than 50 kilometers for these experiments. The long collision path, plus the ability to extract ions from a large source volume, are the main contributors to the high sensitivity of instrument.

Mass resolution is limited by the thermal velocities of the ions. Because of heating by the Penning trap coils, the positron experiments were done at temperatures above 100° C. Intrinsic

resolution for this condition was estimated to be one dalton for a mass of 135. Experimentally, the resolution was found to be less than this, presumably due to geometric aberrations in the accelerating lenses.

Other possible applications of the QP-TOF instrument include negative ion spectroscopy (electron attachment), and applications that require large source volumes such as photon ionization and ion production by electrospray.

L. D. Hulett, D. L. Donohue,
*T. A. Lewis**

*Instrumentation and Controls Division

A Practical Theorem for the Bunching of Charged Particles

In the manipulation of charged particles, and in mass spectrometry, the ability to spatially bunch the particles is often desirable. From the above discussion on the QP-TOF spectrometer, it is seen how a quadratically varying acceleration potential can be used for such a purpose. This method is commonly used in the brightness enhancement of positrons. In the designing of a bunching device the experimenter often invests considerable effort and expense in either building or purchasing the pulser that applies the voltage to the electrostatic lenses that impose the acceleration field. The equations of motion, written above, for ion flights in the QP-TOF spectrometer imply that the accelerating potential must be applied instantaneously as a square wave. Perfect square waves are physically impossible to achieve, and 'clean' square waves with short rise times require expensive electronics. Thus, it is not only interesting but very good news when the experimenter learns that a perfect square wave pulser is not at all necessary.

Let us modify the acceleration potential equation (1) by inserting a time-dependent function f(t):

$$V = f(t)*A*z^2 \qquad (4)$$

where f(t) represents some arbitrary pulse function. It can be any of the types commonly put out by low-quality pulsers, such as overshoot or undershoot.

Taking the gradient of equation (4) with respect to z and substituting it into the equation of motion, we have:

$$d^2z/dt^2 = -g^2*f(t)*z \qquad (5)$$

Equation (5) can be solved as a Taylor series. Applying the condition of zero initial velocity, we have:

$$Z/Z_o = 1 - (g^2f_o)*t^2/2 - (g^2f_1)*t^3/3! + ...(6)$$

Where the f_n quantities represent the n^{th} derivatives of the pulse function, evaluated at t = 0. The initial starting position, Z_o, occurs to the first power in all terms of the Taylor series. Thus it can be completely factored out, such that the right hand side of the equation is a function of time only. This means that, even if the pulse function has a slow rise time, the time of arrival of all charged particles at z = 0 is the same.

The Taylor series solution to equation (5) is used for conceptual demonstration only. The use of a numerical integration algorithm, such as the Runge-Kutta technique, is a more practical method of treating equation (5). Cases for which the initial velocity is not equal to zero have been studied. It has been found that, even if the rise time of the pulse function is greater than the flight time of the particles, there is little aberration in the time required for the particles to bunch at z = 0.

Equation (2) and its solution are of identical form to equations for the pendulum and other simple harmonic oscillators. It is commonly known that the period of the pendulum is independent of its initial displacement. The QP-TOF spectrometer/buncher device is an electrostatic analog of the pendulum, and therefore its period should also be independent of the initial displacement of the charged particle. It does not appear to be commonly known, however, that if the force constant of the 'pendulum' has a time dependence it will still retain the property that flight times to the z = 0 position are the same, regardless of the initial displacement. No doubt this interesting bit of physics has been discovered by some earlier worker. We have searched the literature and have not yet found this person. Since the principle has high practical importance, we feel that it is worth pointing out to others. We are taking

advantage of the principle by economizing on the pulsers we use in our spectrometers and bunchers.

L. D. Hulett, D. L. Donohue,
*T. A. Lewis**

*Instrumentation and Controls Division

The Ionization of Large Molecules By Low Energy Positrons

The QP-TOF spectrometer described above has been used in conjunction with the ORELA slow positron facility to continue studies of the mechanisms by which molecules are ionized by positrons. Positrons of 3 keV energy are delivered to the entrance of the Penning trap, where they are intercepted and thermalized by a 100 nm single crystal tungsten foil. The thermal positrons diffuse from the interior of the foil to its surfaces where they are ejected with about 2.7 eV of energy. As the positrons escape from the surface facing the trap, the potential of the input grid is lowered to ground. After the positrons pass through the input grid its potential is restored, thus trapping the positrons. The exit grid is at a fixed positive potential. A magnetic field of about 1 kilogauss is imposed axially on the trap to prevent the lateral escape of the positrons.

After allowing the positrons to interact with gas molecules for the desired period of time, the input grid is lowered to ground potential again for about 5 microseconds to allow remaining positrons to escape. The thermal ions, moving much more slowly, do not escape to any large degree. It is necessary to purge the remaining positrons from the trap before the ions are accelerated out. Otherwise, the positrons ionize water and oxygen molecules in the rear of the spectrometer and the background is greatly increased.

The walls of the Penning trap consist of a string of cylindrical lens segments. During the period in which the positrons are interacting with the molecules, the potentials of all of the trap lenses are at ground. To accelerate the ions out of the trap the lenses are pulsed such that the entire spectrometer is put into the quadratic potential configuration. That is, the potentials of

all the lenses, inclusive of the trap, are set to be proportional to the square of their distances from the ion detector (microchannel plate). The ions in the trap are accelerated past the exit grid and into the fields of the rear lenses, where they continue to be accelerated to the detector.

Previous work, using the less sensitive spectrometer, showed that ionization by positronium formation is a universal mechanism for all molecules. This mode of ionization involves the ejection of an electron from the molecule, followed by combination of the positron with the electron to form a bound pair, having neutral charge. The positronium particle has many of the characteristics of an atom, including a binding energy of 6.8 eV, exactly 1/2 that of the hydrogen atom. The binding energy of the positronium atom provides part of the driving force for ionizing the molecule. Therefore this process exhibits a rapid increase in cross section when positrons are given energies above IP-6.8 eV, where IP denotes the ionization potential of the molecule. The ionization potentials for the molecules studied ranged from 9 to 14 eV; therefore, the positronium thresholds all occurred at energies less than 10 eV.

The greater sensitivity of the QP-TOF spectrometer, and its ability to retain positrons and reaction products in the Penning trap for long periods of time, have made it possible to study ionization events that occur below the positronium threshold. When the initial energies of the positrons injected in the Penning trap exceed the positronium threshold by only one or two eV, the mass spectra tend to have a high percentage of unfragmented ions of the parent molecule. When the initial energies of the positrons are less than the positronium threshold, the spectra have almost no parent molecule ions and only ion fragments are seen. The distributions of ion fragments in the spectra have a strong dependence on the residence time of the positrons in the Penning trap when the initial energies of the positrons exceed the positronium threshold. For long residence times the percentage of unfragmented parent ions decreased by factors of 5 or more, and the smaller fragments predominate.

Several molecules, decane, tetraethyl silane, tertiary butyl alcohol,

nitrobenzene, toluene, and bromobenzene, have been studied with the QP-TOF spectrometer, using positrons with energies both above and below the positronium threshold. For the non-aromatic compounds it appears that ionization processes occurring below the positronium threshold tend to induce molecular fragmentation. The time-dependence of the ion spectra suggests that positrons are being degraded in energy by collisions with the molecules, and that when the lower energy positrons ionize the molecules they induce fragmentation.

At present, two mechanisms are postulated by which ionization is believed to take place below the positronium threshold. One mechanism is referred to as "in-flight", or "pickoff" annihilation, in which the positron passes sufficiently close to the molecule for its wave function to acquire a high degree of overlap with one of the electron wave functions. The cross section for this process is believed to be rather low, however. The other mechanism is believed to involve attachment of the positron to the molecule, analogous to that of electron attachment. The attachment mechanism is believed to be sufficiently slow to allow changes in the atomic positions of the molecule to accommodate the positive charge of the positron. When annihilation finally occurs, the resulting ion should be in a lower energy state and fragmentation should be less likely to occur. The ionization events taking place below the positronium threshold appear to induce a high degree of molecular fragmentation, and they do so with rather high cross sections. It appears that one or both of the two postulated models, pickoff and attachment, will have to be modified to account for our experimental results.

There is evidence that positron-induced ion-molecule reactions occur in the Penning trap. Tertiary butyl alcohol, when ionized above the positronium threshold, loses a methyl group, producing predominantly the mass-59 ion. Toluene, when ionized either above or below the positronium threshold, always produces the parent ion. The phenyl ion, which would result from the loss of a methyl group by toluene, is never seen when only toluene is present in the Penning trap. But when a mixture of

tertiary butyl alcohol and toluene is present in the Penning trap, a significant amount of phenyl ion is generated. There is also a higher-mass species produced that appears to be a reaction product of the t-butanol with the mass-59 ion. We conclude that the phenyl ions are produced by a reaction of the mass-59 ion with toluene molecules to 'rob' a methyl group. At present, we are not able to explain how the higher-mass species is produced.

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High-Resolution HIXSE Studies of the Chemical Environment of Ions Implanted in Insulator Matrices

Advances in technology often require corresponding advances in materials fabrication and characterization. Perhaps the most publicized advance in materials fabrication has been the ability to engineer materials with improved or unique physical properties through surface or subsurface materials modifications: e.g., ion implantation and thin film formation. Future advances will, in part, depend upon analytical chemists to develop methods which can characterize not only the elemental composition of these novel materials but also the chemical nature or bonding of their constituents. An example of a difficult chemical measurement problem is the characterization of a small change in the concentration profile of a major species in a complex sample. Any analytical technique chosen requires high precision because the problem typically reduces to a comparison of two large numbers. If the small change in concentration is limited to a narrow spatial band below the surface of the sample (for example, an ion-implanted layer), new or alternative approaches to the analysis must be developed. One such alternative approach is to find a chemical difference induced by the localized change in concentration. If a chemical variation can be discerned, the technique must also be able to probe the narrow band without destroying that chemical information. This latter requirement eliminates techniques which

rely on destructive depth profiling to probe the subsurface variations in the analyte profile. Heavy-ion-induced X-ray satellite emission (HIXSE) spectroscopy, because it nondestructively probes the near surface region (5-1000 nm) and yields chemical information, is ideally suited for this task. HIXSE combines the advantages of particle-induced X-ray emission (PIXE), i.e., being able to detect an element in almost any matrix, with the ability to obtain chemical information similar to electron spectroscopy methods. As part of our continuing program to study the chemical environment of ion-implanted species, we have chosen to test HIXSE's ability to solve this difficult chemical measurement problem by observing changes in the high-resolution HIXSE measurements of implanted sulfur induced by co-implanted oxygen in an oxide substrate.

A series of optical-grade, quartz glass targets were implanted with 70 keV sulfur ions at 2.5 uA/cm^2 to doses ranging from 2 to 8 x 10^{16}/cm^2 and another series with 70 keV sulfur and 35 keV oxygen ions co-implanted to equal depths and dose at the Solid State Division's Surface Modification and Characterization (SMAC) Facility. Each sample was analyzed with 3 MeV He ion scattering at the SMAC facility to verify the sulfur dose, depth (90 nm) and implant uniformity. An estimate of the dose and depth of the implanted oxygen was obtained indirectly by SIMS oxygen depth profiles of silicon wafers implanted simultaneously with the quartz targets. A 24-MeV Si ion beam, extracted from the Oak Ridge EN tandem Van de Graaff accelerator, was used to excite the sulfur X-ray spectra. Using the Oak Ridge High-Performance X-ray Spectrometer (HI-PER-X 200), high-resolution sulfur KL^n X-ray measurements were obtained. A comparison of the sulfur HIXSE spectra of the sulfur and oxygen samples with the sulfur only targets reveals a clear shift in the satellite intensity distribution from higher-order to lower-order satellites. This trend was observed over the entire dose range. These results are consistent with oxygen increasing the valence electron density of the local sulfur environment. An increase in the valence electron density will increase the L-vacancy refilling which will be observed as a lower yield of the higher-order (e.g., KL^5) satellite lines.

These results not only demonstrate the sensitivity of HIXSE to small changes in the subsurface local chemical environment but they also suggest that, with an appropriate choice of an implanted probe ion, high-resolution HIXSE measurements may be capable of detecting not only atomic oxygen in an oxide matrix, but almost any impurity ion in any matrix, including matrices that normally mask the impurity.

The program to study the chemical environment of ions implanted in insulator matrices as a function of concentration, energy (depth), initial charge state, deposition rate, substrate matrix and spectator ions using heavy-ion-induced X-ray satellite emission (HIXSE) spectroscopy has been terminated.

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Safeguards-Related Projects

We participated in the CALDEX experiment at the behest of the International Atomic Energy Agency. The goal is to evaluate the lutetium double spike technique developed in this group some years ago for independent verification of the fissile content of tanks; the lutetium double spike procedure is a method for determining the amount of liquid actually in the tank at any given time. The CALDEX experiment was carried out at a German facility by German and British staff. Samples were sent to a number of laboratories for analysis.

Analysis of the samples is well under way; we are using our VG-354 mass spectrometer for this project so our results will be directly comparable to those of other laboratories. Problems were encountered due to introduction of NaCl to the solutions to simulate the density expected at reprocessing plants. Sodium is always bad news for the thermal ionization process; it so reduces ionization efficiency for the analyte element that analysis is virtually impossible. Another contaminant, as yet

unidentified, had a similar effect. It was necessary to develop a procedure for separating lutetium from the species inhibiting ionization. This has been accomplished, and mass spectrometric measurements are now progressing smoothly.

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Isotope Ratio Mass Spectrometry

Collaboration with Professor George Swihart of Memphis State University has continued this year. The goal is to make high precision isotopic ratio measurements of boron from geological samples. We are using a technique that generates $Cs_2BO_2^+$ on the filament surface. This ion has isotopic masses of 308 and 309 (corresponding to boron isotopes 10 and 11); use of such a high mass reduces problems of isotopic fractionation. Our goal has proven quite elusive. We can reliably analyze about half the boron samples loaded, an unacceptably low fraction. Temperature control appears to be a highly critical parameter, and we are presently looking into this aspect of the process.

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Mass Spectrometric Support Activities

Mass spectrometric support for various actinides activities has continued. The final fuel pin of the joint US-UK actinides program has been fully dissolved, and we are well along on the mass spectrometric analyses required. This pin is the most crucial in the series of three. It has undergone very high burn up (over 500 days at high neutron flux) and presents a unique opportunity as to the kind of information that can be obtained.

A 1983 study of the uranium content of pine needles from the area around the Portsmouth Gaseous Diffusion Plant was confined to one octant. This year we were directed to analyze the remaining seven octants. These samples had been gathered in 1984 and had since been

stored in a freezer.

About 130 samples were analyzed, all but two of them evergreen needles. No surprises were encountered; all samples were enriched in ^{235}U, and were most enriched at those sampling sites nearest the plant, declining with increasing distance from it. Isotopic results are consistent with the mixing of natural uranium (0.7% ^{235}U) with uranium enriched to over 90% ^{235}U. No sample had enough uranium in it to be considered an ecological or health hazard.

We have continued to provide support for the numerous programs that require mass spectrometric analysis of gases. These are mostly for trace constituents, but we have provided isotopic analyses when requested. We hope to obtain a new instrument to fulfill this function in the not-too-distant future. Our present mass spectrometer was down one-third of the time in 1990.

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OPTICAL SPECTROSCOPY

J. Michael Ramsey

Single Molecule Detection

We have been trying to detect single molecules of rhodamine-6G (R6G) dye in droplets of glycerine-water by laser-induced fluorescence. The charged droplets, about 10 μm in diameter, are suspended in an electrodynamic trap in the beam of an argon-ion laser. The dye molecules undergo from 10^5 to 10^6 excitation-emission cycles during their photochemical lifetime. A small fraction of the fluorescence is collected by a GRIN lens in the ring electrode of the trap and focused through appropriate filters onto a cooled photomultiplier. We collect and count 200-400 photons per dye molecule - more than enough for single molecule detection. Our actual sensitivity has been limited by impurities in the solvents.

We have achieved a considerable reduction in the size of our blank signal by switching to HPLC-grade water as the solvent with which the glycerol is diluted.

A recent series of measurements was made on droplets ranging from 13 to 28 μm diameter with a dye concentration of 17 pM in the sample droplets. The fluorescence was excited by a 514-nm laser beam with an intensity at beam center of 300 W/cm^2. At this intensity, the fluorescence was observed to decay due to photolysis of the sample with a time constant of a few seconds. The average number of photocounts per dye molecule over a 20-s interval was 290 counts/molecule. The blank droplets also showed an initial decaying fluorescence with an average of 210 counts/pL. This photolytic decay shows that the blank signal is not due to intrinsic emission from the solvent, Raman scattering or fluorescence, but rather from the presence of impurity molecules. An estimate of our detection limit is twice the variation of this blank signal, 150 counts/pL, corresponding to a signal-to-noise ratio of 4 for one R6G in a one pL droplet. We have experimentally observed as few as 12 molecules of R6G under these conditions. A detection limit in pure solvent can be estimated from the blank noise measured after the impurities have been photolyzed. Twice this noise for a one pL volume corresponds to less than 0.1 the counts detected from a single R6G molecule.

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Persistent Spectral Hole Burning at Room Temperature

Persistent spectral hole burning is a laser processing technique in which a normally broad, smooth optical absorption band is modified to produce sharp, narrow dips at certain wavelengths. If the dips are sufficiently narrow and persist for long times, there are potential applications in the area of high density information storage. For example, a semiconductor memory chip currently can have roughly 1000 by 1000 separate areas for electrical data storage, or 10^6 bits. The switch to optical storage with the same spatial resolution with an additional

resolution of 1000 units in the spectral dimension would increase the storage capability to 10^9 bits on a chip of the same size.

Most of the systems that have been studied to apply this phenomenon rely on atomic or molecular transitions of fundamentally narrow linewidth that have been inhomogeneously broadened by the environment in which the absorbing species are placed, an amorphous medium, for example. Thus, each of the absorbing molecules will have its absorption line at a somewhat different wavelength. If the sample is exposed to an intense laser beam with a narrow wavelength spread, and if there is a physical or chemical way that the molecules that absorb the laser light or their environment can be altered so that they no longer absorb, the remaining molecules will exhibit a spectrum with a hole burnt at the laser wavelength.

The main difficulty in finding a practical system to make use of this effect is that the systems studied all require the hole burning to be done at very low temperatures, ~1 K. We have recently shown that dye molecules can be coupled to an ensemble of spherical microparticles to form a system with a homogeneous linewidth determined by the optical Q of the particles and the inhomogeneous broadening determined by the variation in their diameter. A permanent spectral hole can be created at a particular wavelength at room temperature by photolyzing the dye molecules coupled to those spheres that are optically resonant. The room temperature width of the spectral hole is determined by the particle Q that can surpass 10^5 for a free particle.

Our experiments were performed on latex spheres, 24 μm in diameter, infused with Nile Red dye. The fluorescence excitation spectrum of a large number of these spheres (~2500) on a microscope cover glass exhibits a broad peak extending from 565 to 585 nm. If the ensemble is exposed to an intense laser beam (40 W/cm^2) at a fixed wavelength within this range for about 5 minutes, subsequent excitation spectra now show a sharp minimum at the wavelength of the intense beam. Minima as narrow as 0.1 nm have been obtained.

We are exploring other potential

applications such as determination of the size distribution of spherical particles produced on space flights.

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Advanced Techniques for the Chemical Characterization of Microparticles

The purpose of this study is to develop advanced methods for the chemical characterization of microparticles (particles less than about 100 um in diameter). The chemical nature of a microparticle or the species adsorbed on the particle can provide important information about the environment from which the particle was collected. The small size of the particles and the small amount of material required for analysis would also be conducive to the subtle collection of materials present in the environment.

We are currently investigating the possibility of using an electrodynamic trap for characterizing microparticles by laser ablation mass spectroscopy. The ultimate goal is to levitate a charged microparticle in an electrodynamic trap with subsequent characterization by mass spectrometric analysis. A charged particle, from hundreds of microns in diameter to as small as a single electron, can be confined in the small volume of the trap. Because the trap can also be used for mass spectrometric analysis, this leads to the exciting possibility of trapping a particle, ablating the ions from the particle with a laser, and then generating a mass spectrum of the ions left in the trap.

We have modified the ion trap electrodes of a commercial Finnigan MAT Ion Trap Detector (ITD) to allow for the introduction of particles and laser beams into the internal volume of the trap. The trap is a three-dimensional quadrupole made up of three electrodes with hyperbolic surfaces having rotational symmetry. The internal volume of the trap is about four cubic centimeters. The ITD electronic system is used to supply and control the rf scan voltage for mass analysis and to acquire the mass

analysis data. The original trap was removed from the ITD and the rf output was interfaced with the modified trap in a separate vacuum system. Tuning of the rf coil is very sensitive to the location and configuration of the trap. However, with some modification to the rf coil and shielding of the rf lead to the trap it was possible to tune the coil over the entire mass range covered by the ITD.

Although we have demonstrated that polystyrene particles can be levitated in the trap under vacuum, it was decided to first evaluate the laser ablation mass spectroscopy technique on particles as they fall through the trap. This eliminated the immediate need for circuitry to switch the trap from a particle levitation mode to an ion trapping mode.

An Nd:YAG laser is being used to ablate ions from the particles as they fall through the trap. In order to intercept the particles with the laser beam it is necessary to synchronize the firing of the laser with the arrival of the particle at the center of the trap. The trigger pulse for firing the Nd:YAG laser is generated with a HeNe laser beam which also intercepts the falling particle. The scattered HeNe radiation from the particle is detected with a photodiode and the output is converted to a TTL pulse. When this pulse is coincident with an ion trapping timing pulse from the ITD, a trigger pulse is generated from an AND gate which fires the Nd:YAG laser. This sequence of events insures that the mass scan of the ion trap does not begin until after the laser fires.

At the time of this report we had just started to check out the operation of the system. We have demonstrated that all of the hardware components function properly according to design when the particles fall through the trap. We will proceed to determine the conditions required for trapping and analyzing the ions ablated from the particles.

These experiments will be followed by development of a method for switching between particle levitation voltages and ion trapping voltages so that mass spectroscopy can be performed on a single levitated particle.

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

Resonance Ionization Mass Spectrometry

We are exploring the use of tunable diode lasers for analytical resonance ionization mass spectrometry (RIMS) to capitalize on their desirable properties: operational simplicity, low cost, and narrow spectral bandwidth. High resolution atomic spectra, isotopically-selective ionization, and spectral information concerning two-photon states (not directly accessible from the ground state) have resulted. In addition, an unbiased one-color RIMS isotope ratio measurement has been demonstrated using a copper vapor laser (CVL)-pumped dye laser.

A detailed évaluation of isotopic selectivity for diode laser-assisted RIMS of lanthanum (mass 138 and 139) has been conducted. The sample was enriched in mass 138 to approximately 14.3%. A 753.4 nm diode laser was used to pump the ground state to 13260 cm^{-1}, followed by 1 + 1 ionization at 584.8 nm using a CVL-pumped dye laser as described previously. Tuning the diode laser to a hyperfine line of 138, we measured an increase in the $^{138}La/^{139}La$ isotope ratio (i.e., a selectivity factor) of 200 over that found using thermal ionization mass spectrometry (TIMS); we found a selectivity for mass 139 of 60. With an intracavity etalon inserted into the dye laser to narrow its output bandwidth to 0.03 cm^{-1}, the mass 138 selectivity increased to 2000, and that for mass 139 to 200.

We found that there is weak ion formation near, but off-resonance of, the hyperfine structure of the isotopes; the isotope ratio of these ions appears to be similar to the thermal ionization ratio. This effect may be the result of absorption into wings extending from the hyperfine structure or, possibly, from broadband background emission of the laser. In any case, the count rate is very low, and it is not certain whether the ratio is wavelength-dependent. The background signal does statistically limit the apparent selectivity factor we measure and its precision.

A method has been developed to determine the hyperfine splittings of two-photon excited atomic levels using two-color RIMS. These states are

inaccessible from the ground state by one-photon processes. The method involves pumping individual hyperfine levels of an intermediate state with a high-resolution diode laser and then further promoting the atom to the two-photon level with a tunable, pulsed dye laser. An intracavity etalon is required in the dye laser in order to narrow its spectral bandwidth to approximately 0.03 cm^{-1}. Ionization results from nonresonant absorption of an additional dye laser photon. The overall two-photon state splitting pattern is assembled by piecing together the individual spectra from the intermediate hyperfine levels. This method has been applied to the 30354 cm^{-1} level of lanthanum 138 and 139 with the following results:

Isotope	A (MHz)	B (MHz)
^{138}La	405	317
^{139}La	502	-94

The linewidth and frequency scan precision of the dye laser limit the precision and accuracy of the measurement; the values for the electric quadrupole coefficients (B) are particularly uncertain, as they represent a second order term. Even with these shortcomings, this technique is of value for determining estimates of otherwise unknown coefficients and spectral isotope shifts of upper levels.

The initial reason for selecting a copper vapor laser pumped-dye laser for RIMS was that data could be collected at high pulse repetition rates for improved counting statistics. It was found that isotopic bias effects were severe using the CVL system (e.g., 30% for uranium) relative to those found using broader bandwidth, flashlamp-pumped dye lasers. However, a one-color RIMS study of the 1+1+1 CVL/dye laser ionization of lanthanum at 585.0 or 590.4 nm has indicated that the TIMS isotope ratio can be reproduced. The TIMS data required correction for the ^{138}Ba isobaric interference. The 139/138 ratio was 5.78 ± 0.06 by RIMS; the corrected TIMS ratio was 5.84 ± 0.10. This is an interesting result in that it is contrary to other evidence that RIMS ratios for odd-to-even mass isotopes usually exhibit bias. Lanthanum does represent a special case

in that both isotopes possess nonzero nuclear spin and that the spectral isotope shift is very small.

R. W. Shaw, J. P. Young

Resonance Ionization in an Ion Trap Detector

We reported on photoionization of nitric oxide and rubidium in an Ion Trap Detector in last year's annual report. The nitric oxide experiments demonstrated the ability to selectively ionize molecular species in given energy states with great sensitivity (≈ 50 molecules) in the ion trap. During the past year we continued experiments with rubidium vapor. Previous experiments introduce Rb atoms by evaporation from a heated filament. To provide a more stable supply of atoms, a Knudsen cell containing Rb replaced the electron gun and was used to provide Rb atoms for these experiments. Laser light was produced by a Quanta-Ray pulsed dye laser. The fundamental of the dye laser was used directly to excite the 5s to ns or nd two-photon transitions, and was frequency doubled to excite the 5s to np single-photon transitions.

Resonance ionization spectra recorded using the dye laser fundamental show photoionization from the ns and nd levels. The spectra included Rydberg states of nd = 19 up to approximately n - 73, and peaks were discernible to approximately n - 40. Ionization of the ns levels (not normally observed) is believed to be caused by electric field state mixing and partial saturation of the nd photoionization. Spectra obtained using both the fundamental and frequency-doubled laser light include both the np and the nd resonances. The principal ionization mechanism from low energy p and d Rydbergs is believed to be photoionization with the fundamental frequency photons. The s transitions were observed to a much lesser degree than in the previous experiment, probably due to the diminished intensity of the fundamental light. It was also apparent that the higher energy Rydberg states were being ionized by some other mechanisms, possibly by collisions with photoelectrons produced by the UV laser light. A binary encounter model was used to calculate the electron ionization

probability under the operating conditions of the trap. The model is in good agreement with the data acquired during the laser experiments for the n - 30 to 70 Rydberg states.

Experiments were repeated with only the frequency-doubled photons entering the trap. Under these conditions relatively little photoionization occurred in the trap because of the low photon flux and the reduced photoionization cross section from the excited state. Carbon tetrachloride was then introduced into the trap as an electron scavenger. These data demonstrated that a restoration of the ionization from the Rydberg p states had occurred in the presence of CCl_4, supporting an electron attachment model. It also showed a decrease in the ionization thought to be caused by collisions with free electrons. The CCl_4 apparently either scavenges electrons before they are accelerated by the fields present in the trap or reduces photoelectron production.

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*UT Postgraduate Research Program

Fundamental Studies of Chemical Vapor Deposition Materials Growth Processes

We are developing and will apply several spectroscopic and materials characterization techniques to foster a fundamental understanding of film growth by chemical vapor deposition (CVD) processes. Although many technologically-important materials are synthesized by this general family of techniques, little is known about the details of the chemical and physical mechanisms involved in the film growth process. We have elected to examine the growth of diamond films initially. This material was chosen because of its importance, experimental practicality, and local expertise. Diamond films have unique properties (high thermal conductivity, hardness, and resistivity) that make them attractive for a number of applications. This project is a collaborative effort with staff from the Metals and Ceramics and Fusion Energy Divisions and is funded by ORNL Exploratory Studies.

Hot filament decomposition of methane in hydrogen at 5.3 kPa leads to

diamond films on various 1000° C substrates. By use of several spectroscopic techniques, intermediate species present in the bulk reactor volume, the thin active volume immediately above the growing film, and the actual growing surface will be identified. Such a comprehensive examination of the overall deposition process is necessary because a combination of gas phase and surface chemistry is probably operating. Ionization-detected absorption spectroscopy and nonlinear optical surface spectroscopy is being emphasized.

A diamond film growth reactor has been assembled. An O-ring sealed quartz cylinder serves as the replaceable reactor vessel. An alumina heater has been fabricated for substrate temperature control, independent of the hot filament. Flow and pressure control equipment has been installed to provide metered inlet gas flow rates and closed-loop reactor vessel pressure control. Safety features have also been implemented using this hardware; e.g., the hydrogen flow to the reactor is terminated if either the reactor pressure exceeds 13 kPa or ac power is interrupted. All of the flow and pressure control equipment is computer compatible for future automation.

Diamond films on single crystal silicon have been grown by decomposing 1% methane in hydrogen on a tungsten carbide filament heated to about 1900° C. The growth process occurred over a 16-hour period. The films were examined using SEM. Reasonable growth rates have been found, but sparse nucleation leading to discontinuous films has been a problem. The art of substrate surface preparation (i.e., creation of a dense pattern of nucleation sites) has not been mastered as yet.

Atomic hydrogen was detected using resonance enhanced multiphoton ionization (REMPI) in the reactor under diamond growth operating conditions. Hydrogen dissociation is known to occur at the hot tungsten carbide filament yielding atomic hydrogen, an important species for diamond film growth processes because it preferentially etches graphitic carbon from the film as it grows. A 3 + 1 ionization scheme at 365 nm was used to ionize the hydrogen atoms present, and the electrons created were collected using a platinum wire near the substrate. The ionization signal

strength was recorded as a function of filament temperature and found to approximately double between 1860 and 1990° C. Detection of other species (e.g., CH, CH_3, etc.) should be possible using REMPI.

The reactor was designed to serve as the molecular beam source for a crossed time-of-flight mass spectrometer; there is a 0.5 mm diameter sampling orifice through the substrate, heater, and quartz vessel wall. REMPI mass spectrometry of species sampled from the boundary layer above the growing film will be performed. The signature of the ionization spectrum of any molecular species will provide insight into its internal energy distribution. A quartz nozzle protruding through the substrate connects the reactor with a differentially pumped region (1 to 10 micron pressure); the resulting gas expansion is skimmed with a 0.5 mm orifice to enter the mass spectrometer. In the source region, both electron impact (EI) ionization and REMPI are possible. For room temperature testing of REMPI, a surrogate mixture of 0.7% nitric oxide in argon was employed. An Nd:YAG-pumped tunable dye laser at 430 nm was used to effect the 2 + 2 ionization of NO. The optical spectra recorded by scanning the dye laser indicated that no cooling of the NO occurred in the expansion process. Electron impact ionization was conducted with both the NO/Ar and CH_4/H_2 gas mixtures. For the latter case, extensive fragmentation of the methane was observed for 70 V electrons; this would be a problem for gas analysis performed under deposition conditions because it would be unknown whether the fragments were present in the initial hot gas mixture or were created during EI. For REMPI experiments this will not be a problem, as the spectral signature of an intermediate must be observed when the laser is scanned to qualify it as a bona fide component of the reactor gas mixture.

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

Fluorescence Studies of f-transition Elements

The study of two-photon excitation of Cm(III) fluorescence has continued this year. We have observed such fluorescence from CmF_3, $CmCl_3$, $CmBr_3$, and CmI_3. In the case of $CmBr_3$, sequential absorption of two 16,605 cm^{-1} photons excites an available level in Cm(III) near 33,200. Fluorescence is then observed from all six of the lower lying manifolds. It is noteworthy that four of those manifolds of energy greater than 22,000 cm^{-1} have not previously been detected by fluorescence spectroscopy. The ability to observe these transitions is believed to be related to the low background emission resulting from the two-photon absorption process. If this is true, the technique may be of value in determining or verifying excited states of other amenable actinides that have heretofore only been seen in absorption.

We have also observed terbium (III) and curium (III) fluorescence from single resin beads. The terbium bead was excited with photons at a wavelength of 488 nm. Fluorescence was seen in transitions from three levels to the ground state. The fluorescence was relatively independent of temperature over the range of 77 to 300 K. The Cm(III) bead was excited at a wavelength of 458 nm. Only one fluorescence peak was seen, at 16,700 cm^{-1}, and it sharpened considerably on cooling the bead to 77 K. Cation beads were used in this study; it is not known why there is a difference in the temperature behavior of the two elements. The bead preparation presently used for mass spectrometry was used to prepare the samples for the present study. For screening tests these two techniques could be quite symbiotic; sample beads could first be analyzed for metal ion fluorescence. If any were found, a mass analysis of the bead could be performed if one wished isotopic information.

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In-Line Sensors for Electrolytic Magnesium Cells

We have received funding this year from Dow Chemical Company and DOE Office of Industrial Processes, Conservation and Renewable Energy, for a three-year project to develop analytical sensors to reduce the energy required to produce magnesium by electrolytic reduction of Mg^{++} in an NaCl-KCl-$CaCl_2$-$MgCl_2$ melt. The proposal is based on the premise that continuous control of Mg ion concentration will save at least 5% of the energy costs. Such control is not currently used; we plan to develop a Raman-type monitor to make this determination. There is a need for an F^- monitor as well; this may be of an electrochemical type. Fluoride ion is an additive in the melt.

A bibliography has been prepared of previous work in the fields of purification of $MgCl_2$, spectral and electrochemical studies of $MgCl_2$ molten salts, and application of fiber optics to possible analytical techniques of interest. Initial Raman spectral studies of the magnesium ionic species have been carried out in both molten and solid $MgCl_2$ and NaCl-KCl-$CaCl_2$-$MgCl_2$. The spectral results differ from some of those reported by earlier workers, but the differences can be explained by errors in the former studies. The preparation of pure $MgCl_2$ by the stepwise thermal decomposition of $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$ is being studied. It appears that the final product, $MgCl_2$, may not need to be distilled, but this point is still under study. The chemical composition and impurities such as $O^=$ or OH^- will be followed to determine the quality of the $MgCl_2$. Solid state reflectance spectral analysis by either infra-red (IR) or near IR instrumentation has been found to be useful for identifying OH^- in prepared samples similar to the unknown samples. A sealed IR reflectance cell has been developed to carry out this task.

The final sensor will have to be compatible with the industrial electrolytic melt. Preliminary results suggest that pure molten $MgCl_2$ at temperatures near 800° C is noncorrosive to SiO_2; however, the molten salt mixture does etch SiO_2 at temperatures of 720° C, the temperature of the industrial melt process. Further

compatibility tests of various possible transparent optical windows are planned.

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Adversarial Analysis of Counterfeit Currency Deterrent Concepts

The U.S. Department of Treasury, Bureau of Engraving and Printing (BEP) is planning to make subtle changes in U.S. currency to improve their ability to detect and deter counterfeiting. BEP is currently investigating the possibility of introducing taggants into the inks for U.S. currency as a Covert Counterfeit Deterrent System (CCDS). Part of the evaluation of the CCDS involves adversarial analyses to assess the degree of difficulty for detecting the taggants, reproducing the taggants, and simulating the authentication scheme without reproducing the taggants.

We entered into a contract with BEP to perform analyses on two types of tagged Federal Reserve notes and to provide the above described assessment of the CCDS. We were successful in distinguishing the two types of tagged Federal Reserve notes from one another and from normal currency. The work for this project was completed and a report was submitted to BEP.

J. M. Dale, L. N. Klatt

ORGANIC MASS SPECTROMETRY

G. L. Glish

The past year has been a very active one for the Organic Mass Spectrometry Group with significant research results obtained in a number of areas. The most significant of these has been the continued development of the utility and demonstration of the versatility of the combination of electrospray ionization with a quadrupole ion trap. A number of projects have been initiated, both in

fundamental and applied areas, with a number of papers already published or in press.

In parallel with the electrospray work, we have continued our work in the development of the quadrupole ion trap as an analytical and research mass spectrometer. Several aspects involved in ion formation, ion manipulation within the ion trap, and instrumental and physico-chemical considerations for MS/MS and MS^n experiments in the ion trap have been studied.

Another major area of continued interest for us is in instrument construction and modification. There have been major initiatives in construction of instrumentation. In addition, two new mass spectrometers were installed, one for support of current projects and the other which is to be modified for a new project.

Specifics related to these three areas are discussed below. It is probably worth noting that all the data this year have been acquired with quadrupole ion traps or quadrupole mass filters. The old sector instruments have proven to be very difficult to get back into operation following the move from Y-12 to ORNL. An ion beam has been obtained on the ZAB but shortly after that a failure of the vacuum protect system combined with electrical problems caused a catastrophic failure of the analyzer diffusion pumps. The MS50 is slowly being coaxed into working condition.

Electrospray Ionization/ITMS

Improvements in the performance of the electrospray/ion trap mass spectrometer (ES/ITMS) combination are continuing along with our understanding of the behavior of multiply charged ions. Mass accuracy has been improved through the use of fixed rf/swept frequency axial modulation for mass analysis and the use of a rapid axial modulation "pre-ramp" has been shown to be useful in desolvating ions in the ion trap.

Electrospray ionization was investigated for its utility for analysis of porphyrins. A number of different types of porphyrins including free-base and metal porphyrins containing alkyl, acid,

ester, and/or hydroxyl functionalities were studied. For all the porphyrins investigated, hematoporphyrin IX and hematin being exceptions, only the molecular species were observed when using the appropriate focusing and ion injection parameters (see below). We found that the solvent system from which the porphyrins are sprayed plays a role in determining the molecular species observed for some porphyrins. The molecular species observed from the vanadyl porphyrins, for example, was either $M^{+\cdot}$, $(M+H)^+$ or $(M+Na)^+$ depending on the solvent system. In the case of free-base alkylporphyrins such as etioporphyrin-III, the protonated molecule was observed regardless of the solvents used. To our knowledge, this is the first report of radical cation formation using ES ionization and the phenomena responsible for this observation are under investigation. The quantity of material necessary for detection of a porphyrin in a single scan ("figure of merit") was in the low femtomole range for all porphyrins studied indicating the potential utility of the ES/ITMS combination in analytical studies of porphyrins.

A collaborative project with J. D. Henion and E. C. Huang from Cornell was completed in which a liquid chromatograph coupled with ion spray, a variation of electrospray, was interfaced with our ion injection/ion trap mass spectrometer. The potential this combination holds for biochemical applications was demonstrated with synthetic mixtures of peptides and proteins and a protein tryptic digest. High quality HPLC/MS/MS spectra, and HPLC/MS data were acquired with injection levels as low as a few pmol with the tryptic digest mixture. Mass spectra of the proteins could be acquired with high fmol injections. Despite the fact that little or no optimization for coupling ion spray, which uses much higher flow rates than normal electrospray (40 μL/min vs. 1 μL/min), with the ITMS was attempted, sample quantities 10-20 times lower than normally required with a triple quadrupole system optimized for ion spray were required for analysis.

Studies of the ion/molecule reactions of multiply protonated peptides and proteins with strong gas-phase bases have

been initiated. These reactions promise to reveal fundamental information regarding the preferred sites of protonation and the relative strengths of binding sites in the presence of the Coulombic field created by the multiple charges. These studies are not restricted, however, to deriving strictly fundamental information. Ion/molecule reactions of multiply charged ions may also find important practical applications in analytical electrospray mass spectrometry. The use of proton transfer as part of an MS/MS/MS experiment to determine the mass of collision-induced dissociation products of several multiply protonated parent ions was demonstrated. Some product ions tend to form adducts with the base, which also allows charge state determination.

A study exploring the utility of the ion trap mass spectrometer for the structural analysis of small peptides using the MS/MS and MS^n capabilities of the ion trap was initiated. Most of the experiments have been done with leucine enkephalin. The MS/MS efficiency for the protonated molecule is 100%. A variety of structure-specific product ions are formed (i.e., the so-called A, B, Y, and internal fragment ions are all present in this spectrum). Even though the initial parent ion current is distributed over a number of product ions, the sensitivity of the ion trap for MS/MS allows a wide variety of MS^n experiments to be performed. Another species that was studied was Na cationized leucine enkephalin. In contrast to the MS/MS spectra of the protonated peptides, only one type of fragmentation is observed. That is the well-known rearrangement ion that nominally loses the C-terminal residue to give $(B+Na+OH)^+$. This is a very efficient dissociation pathway; thus, MS^n experiments are readily performed. The MS^3 experiment shows the same reaction occurring again, i.e., $(B_4+Na+OH)^+ \rightarrow (B_3+Na+OH)^+$, as essentially the only dissociation pathway. The MS^4 experiment with this latter ion is less efficient and a number of product ions are formed, including the ion analogous to the first and second generation product ions.

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

Quadrupole Ion Trap Development

Development and better understanding of ionization techniques have been major areas of interest for us over the years. In keeping with this theme we have extended our investigations into ionization processes as they are related and applied to the quadrupole ion trap.

Substantial work has been done applying fixed wavelength resonant enhanced multi-photon ionization (REMPI) to analysis using the quadrupole ion trap. The quadrupole ion trap, because of its pulsed nature of operation, is an ideal analyzer to be used with REMPI. It has been shown that REMPI provides good sensitivity and selectivity, and this combined with the MS/MS and MS^n capabilities and sensitivity of the ion trap is a powerful means for mixture analysis. One very promising area is the analysis of organics in ambient air. REMPI preferentially ionizes the organics and thus reduces the potential for the analyte ions being space-charged out of the ion trap by the orders of magnitude more abundant matrix species.

We have also done a comparison of the sensitivity and detection limits of electron ionization (EI) and chemical ionization (CI) in the ion trap. While these are well-known standard ionization techniques, because of the pulsed nature of the ion trap there are some differences from conventional sources of this type that are used with beam instruments. While CI is generally more sensitive and provides better detection limits on beam instruments, this was not expected to be the case for an ion trap. The study showed that this expectation was correct with EI being more sensitive and having better detection limits. It was also shown that, while longer EI ionization times provide better sensitivity and detection limits at a given point in CI, sensitivity actually starts to decrease at longer ionization times.

In a related investigation, we are working on understanding the effects of the rf and dc fields on ion yield during electron ionization. Both axial and radial "effective path lengths" have been calculated using the SIMION software (ion trajectory simulation software). These values represent the range of starting positions (such as during the

ionization process when an ion is formed by EI) for an ion that is fully stable within the ion trap. Results thus far indicate that the axial effective path length decreases 56% from an rf level of 30 to an rf level of 110. Experimentally, ion abundances decrease about 90% when ionizing over the same rf level range. Thus, there appears to be more than one process responsible for the loss in signal. Radial effective path lengths decrease by only 17% over this rf level range. It has also been observed that application of positive dc to the ion trap endcaps (within the bounds of the stability diagram) increases ion abundance for a given rf level. Axial and radial effective path lengths increase with increasing the "a" parameter (the dc level) in the SIMION simulations. Average electron energy and the shape of the electron beam also change with rf level in these simulations. We are currently assessing how these changes may affect ion yield.

In addition to studies related to ionization in the ion trap we have been working on ion manipulation methods. Techniques for selective ion storage or rejection over a wide mass range have been demonstrated. These techniques involve resonant ejection along with the conventional mass-selective instability ejection of ions from the ion trap. These techniques were shown to work for cases in which the ions are already resident in the ion trap or during ion injection into the ion trap. The latter ability allows increased dynamic range for ion injection experiments by eliminating background matrix ions which can space-charge out analyte ions. It is pertinent for applications such as explosives detection.

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Instrumentation

There has been much progress in the area of instrument development in the past year. The hardware for a translational spectrometer has been put together and development of the software and electronics is in progress.

Work has also continued on the redesign of the front end of the QEB to incorporate a high mass quadrupole and interface an electrospray ion source. This work has been slowed by a multitude of problems with the MS50 which are probably mostly the result of moving such an old instrument from Y-12 to ORNL.

An ASGDI/ITMS has been constructed and shipped to Professor J. F. J. Todd at Kent University in the U.K. Significant improvements in design from our prototype were made and these will be used as the basis for the two ASGDI/ITMS systems we are assembling for our DOE projects.

A Finnigan ITS40 GC/MS based on a quadrupole ion trap was installed this year. This instrument will be used to support several of our projects involving ion traps and organic analysis. At the end of the year a Finnigan TSQ 700 triple quadrupole system was installed. This system will be modified by incorporation of an ASGDI source for use as an explosives detector in a project for the FAA.

We also received and installed an ion mobility spectrometer (IMS). Some initial work has been done using electrospray ionization. Plans are to investigate ways to control the ion chemistry and improve resolution and specificity of IMS.

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SECONDARY ION MASS SPECTROMETRY

W. H. Christie

This group conducts research in both organic and inorganic secondary ion mass spectrometry (SIMS) and provides specialized analyses that require the unique capabilities of the SIMS technique. During this reporting period a CAMECA IMS-4f ion microscope/microprobe was acquired and installed. This instrument is being used mainly in our inorganic SIMS program but will also be used to investigate imaging capability for biological matrices.

Inorganic SIMS

The installation of a modern state-of-the-art ion microprobe/microscope (CAMECA Instruments) provides the Analytical Chemistry Division with significant new research and analytical capability. The specific attributes of this instrument that will open new areas for us are: 1) advanced imaging capability in microscope mode with < 1 μm lateral surface resolution; 2) high mass resolution (≥ 35,000 M/ΔM); 3) an on-axis electron gun that will allow analysis of insulator materials; 4) secondary electron imaging of rastered areas; 5) a 250 nm spot size cesium ion gun for probe mode analysis; and 6) ultra-high vacuum in the sputtering chamber that allows ppm or lower analytical capability for the elements C, H, O, and N.

As the CAMECA was purchased to replace the 16-year-old IMMA ion probe, it was of some interest to make comparisons of our new capability with the old. One of our first comparisons was to depth profile hydrogen that had been ion implanted into single crystal silicon. This standard had been distributed by the ASTM Committee E-42 on Surface Analysis to be used in inter-laboratory comparisons. The silicon had been implanted at 30 keV to a total dose of 1 x 10^{15} hydrogen atoms. Using the old IMMA microprobe, we could only measure a back-side dynamic range (peak signal to background) of about 50. This was done using an O_2^+ primary beam and detected H^+ ions. With the

CAMECA we were able to optimize conditions to take advantage of chemical factors in the sputtering region. We used a Cs^+ primary beam and detected H^- ions. Even with our inexperience in operating the CAMECA probe, we were able to produce a depth profile of H in Si with a back-side dynamic range of over 1000. These results were achieved because of the above-mentioned chemical factors, as well as the low pressure in the sputtering chamber (13 x 10^{-8} Pa) that essentially eliminates spurious H background.

The cesium ion source combined with high mass resolution was used to demonstrate another new capability. With our old equipment we were unable to analyze for S because of the lack of sensitivity as well as the inability to resolve the S signal from that of O_2. For a number of years our group has provided analytical assistance in the certification of Ir alloys that are used to clad radioactive heat sources. We had prepared ion implanted S in Ir to use as standards in this work but had no success analyzing them with the old IMMA. Again we used a Cs^+ primary beam and detected S^- ions. Using 100 nA of Cs^+ to sputter a 100 x 100 μm area we were able to measure a Gaussian distribution for S that was peaked near the surface. The back-side dynamic range approached four orders of magnitude. A surprising feature was noted in this depth profile. We were able to show that the background impurity S contained in the Ir alloy was inhomogeneously distributed. This S showed up as a series of randomly distributed peaks below the ion implantation peak. This new information was conveyed to the Ir project engineer.

We have developed a collaborative program with the Chemistry Division and the University of Tennessee. The major thrust of this effort will be in the development of techniques using the CAMECA to measure isotopic ratios and rare earth elements (REE) in geological samples. Initial work has focused on quantitative analysis of REE's in glasses and silicate minerals. Attempts by other workers to develop REE analytical routines have employed techniques using energy filtering to eliminate cluster ions and linear deconvolution of the resulting mass spectrum to eliminate oxide

interferences. We are taking a different approach, analyzing doubly charged ions of odd isotopic species. This technique virtually eliminates all interferences, yields a much simpler analytical routine and removes the need for peak stripping, at the expense of a relatively minor loss in total peak intensities for some species. Using National Institute for Standards and Technology (NIST) glass standards, we have demonstrated linear response patterns for all analyzed REE's (La, Nd, Sm, Eu, Gd, Dy, Yb, and Lu) over 2.5 orders of magnitude in concentration (2 to 500 ppm). Reproducibility on a particular day is better than ± 5%, and we have found that the intensity/concentration slope remains constant from day to day, although a small offset in the slope lines is observed. Absolute precision over a two-week period was ± 10% without drift correction.

Our intent is to use the methodology developed in REE analysis to provide a base from which we can move on to the more exacting requirements of isotopic analyses in silicate and carbonate minerals. The CAMECA easily provides the mass resolution needed to avoid hydride interference, and our initial REE results indicate that we can attain the instrumental stability required for precision isotopic measurements. One major obstacle that will have to be overcome is compensating for charge buildup on the sample surface from the Cs^+ beam when measuring elements such as C, O, and S, a problem that is not encountered when using an O^- beam for REE analysis. This problem, which has prevented successful analysis of C, O, and S in other labs, will hopefully be overcome by the recently developed normal incidence electron gun with which the CAMECA is equipped.

In collaboration with workers in the Metals and Ceramics Division, SIMS was used to investigate the cause of a casting crack in a nickel aluminide alloy. The wt. % composition of this alloy is: 80.4 Ni, 8.0 Al, 7.7 Cr, 3.0 Mo, 0.85 Zr, with 50 ppm B. Optical microscopy showed that the crack formed along a line composed of material segregated from the alloy. This line is made up of long, narrow streamers ranging in length from 20 to 300 μm. As the casting

cooled, internal stresses were generated which were sufficient to cause cracking along the line of segregation. SIMS analysis showed these segregations to be enriched in Zr and B and depleted in Ni, Al, Cr, and Mo relative to the base alloy. Boron and Zr were not as uniformly distributed as the other alloy elements in regions away from the crack. It is felt that, as grain growth occurred during cooling, the B and Zr segregated along dendron cell boundaries within a grain. If these segregations were large enough and in close proximity, a crack could form.

In this work, both the IMMA and the CAMECA were used to make scanning ion images of an area containing the crack. An image was made for each element in the crack region. In this comparison, it was seen that the CAMECA has much improved lateral surface resolution and its gray scale for photographic ion images covers about five times the concentration range of that of the IMMA. Because of this, additional information can be gleaned from the CAMECA ion images. A poster showing the results of this comparison is on display in the CAMECA lab.

It would seem that these comparisons seal the fate of the IMMA instrument. However, a few last gasps still seem possible for IMMA. Some years ago we reported on the isotopic ratio measurement capability of the SIMS technique. We plan to keep this instrument running in support of the Laboratory's stable isotope program for the short term. This program generates separated stable isotopes that are usually very pure chemically. High chemical purity eliminates the major problem (polyatomic ion formation and subsequent mass interference) that prevents the low mass resolution IMMA instrument from having general applicability as an isotopic analysis technique. Thus, we plan to use IMMA to service the needs of the stable isotopes program until other arrangements can be made.

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Organic SIMS

Secondary ion emission is but one of several methods that can be used to generate ions from involatile organic compounds. Unlike the other techniques, SIMS, in principle, can be used to determine the spatial distribution of organic compounds in various samples. This feature of SIMS has long been used to obtain inorganic ion micrographs, but imaging of organic samples cannot make use of techniques developed for inorganic samples. Organic compounds and samples suffer from ion damage, analytes of interest often exist at concentration levels of only a few parts per million, and for many samples there is a very large number of other organic compounds present.

We have chosen to approach these barriers to organic ion imaging directly with the aim of finding instrumental and chemical remedies for these problems. For example, to deal with the problem of low concentrations, we have chosen a sample size of about 2 cm in diameter, which is large. We have been investigating tandem mass spectrometry to reduce the chemical noise caused by primary ion damage and isobaric and isomeric interference. We have also been investigating the chemical nature of primary ion-induced damage.

Some of the remedies listed mandate instrumental development. For example, a wide angle secondary ion source had to be developed and tested to deal with the large sample size. The source required a departure from traditional ion optics because of the sample size, and because the secondary ion mass analyzer had to be based on quadrupole technology. The design that was chosen features computer control of the ion optical electrode potentials, which are optimized for each of 10-20,000 points on the sample. A data acquisition and control system based on a PC/AT was developed to tune the instrument, control it during data acquisition, and store and display the data.

Such systems are fine in theory. Testing them is a wholly different matter. For example, no device existed to evaluate a low energy (5-50 eV) ion beam, such as would be generated by the secondary ion source. To solve this

problem, we invented a low energy ion beam projector. We used this to test both the wide angle secondary ion source, and later the ion beam profile at the exit of a quadrupole mass filter. We found that by tightly focusing the ion beam at the entrance of the quadrupole, we could transform a cloverleaf-shaped beam shape into a more desirable circular-shaped cross section.

The microprobe has been used to investigate emission of various substances dissolved in, and deposited on, glycerol droplets. For a solution, a uniform emission of secondary ions would be expected since a solution is by definition homogeneous. By focusing a primary ion beam of 100 pA onto a single spot of glycerol solution for up to 15 seconds, we have been able to produce a region on the sample where the damage limit has been exceeded. When a secondary ion image of the sample is obtained, the region of damaged area shows a different level of emission. We have also found, however, that damage is not apparent for some glycerol solutions. For example, solutions of arginine do not show evidence of damage, whereas solutions of methylphenyl peridinium bromide (MPP) do. While these results are in conflict with some reported SIMS studies, they are consistent with the general observation that emission from some glycerol solutions is different from that of other samples. The current microprobe system is the only apparatus at the present time which provides secondary ion imaging capabilities for large (up to 1.5 cm diameter) samples, and thus provides a unique opportunity for further investigations of sample damage and solution chemistry in secondary ion emission.

Investigations are also under way to determine the most efficient method of tandem mass spectrometry (MS/MS) for the microprobe. Surface induced dissociation (SID) using a microchannel plate (MCP) to fragment parent secondary ions is being studied. While W. H. Aberth (University of California, San Francisco) has demonstrated that reasonably high fragmentation efficiency can be achieved with this technique, it is not clear that the method is directly applicable to the microprobe. Consequently, characterization of

daughter ion production is currently being studied. In particular such parameters as daughter ion production efficiency, and kinetic energy and angular distributions of parent and daughter ions are measured.

Computer control of the microprobe parameters and data acquisition is essential for the success of the microprobe. The programs for these processes - which include control of primary ion gun deflectors, secondary ion source deflectors and lens elements, quadrupole parameters, self-tuning of dynamic emittance matching, data acquisition, averaging, and real-time image displays - are all in-house written in assembly language. These programs have been continually developed and updated in parallel with the microprobe development. An added benefit from this work is that related programs can be used with other types of mass spectrometers.

P. J. Todd, C. C. Grimm, R. T. Short**

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*UT Postgraduate Research Program

2. RADIOACTIVE MATERIALS ANALYSIS

J. R. Stokely

The Radioactive Materials Analysis Section performs radiochemical and neutron activation analysis, chemical and instrumental analysis of radioactive materials, and special development projects for a large number of Laboratory and DOE programs and a few non-DOE governmental agencies and private corporations. The section provides major support to Laboratory environmental monitoring, waste operation, waste and environmental remediation efforts, and the transuranium element production program. The section consists of three separate groups: Low-Level Radiochemical Analysis, Transuranium Analytical Laboratory, and Inorganic and Physical Analysis.

Start up of the High Flux Isotope Reactor (HFIR) during the Spring of 1990 has had a positive impact on work activities in neutron activation analysis (NAA) and at the Transuranium Analytical Laboratory (TAL). We have regained our capability for NAA and are utilizing a new pneumatic system which was installed in 1986. A new PC-based gamma spectrometry system was recently placed in operation at the HFIR NAA facility. Irradiation of curium targets is currently under way at HFIR for production of transuranium isotopes, and a processing campaign is anticipated within the next few months. The TAL supports the processing activities to separate and purify transuranium elements from the target material and byproducts.

Work has continued over the past year in characterization of radioactive mixed waste from ORNL storage tanks. Two reports on this work were published. Staff of the section along with members of the Organic Chemistry Section have been involved in implementation of the new EPA Toxicity Characteristic Leveling Procedure (TCLP) for radioactive material. Efforts are being made to develop capabilities for regulatory analysis of radioactive waste that can be of general use for DOE. Instrumentation was acquired

and put into operation this year to perform ion chromatography, inductively coupled plasma spectrometry, and TCLP extractions on highly radioactive samples. We are also in the process of obtaining funding for a gas chromatograph/mass spectrometer system for analysis of volatile organics in radioactive materials by the purge and trap method.

LOW-LEVEL RADIOCHEMICAL ANALYSIS

J. W. Wade

The Low-Level Radiochemical Analysis Group provides analytical support and development for several environmental monitoring programs at ORNL. Both the air and groundwater monitoring programs were stepped up during the past year to provide a more comprehensive sampling and analysis scheme. Many new groundwater wells were brought on line and new sampling stations were added to the ORNL stack monitors. All groundwater wells were sampled quarterly and analyzed for gross alpha and beta, gamma emitters, ^{90}Sr, and tritium. We received stack charcoal and filters weekly for gamma-ray spectrometry and gross alpha and beta determinations. The filters are composited for a quarter and then analyzed for specific actinides by radiochemical separations and alpha spectroscopy. Thirty residential wells in the vicinity of the Oak Ridge Reservation were sampled twice during the year. This program was begun during 1989 and will continue until enough information has been compiled to ensure the homeowners that no contamination is present in their well water.

A project to characterize the sediment from two former waste ponds at K-25, consisting of over three hundred samples for the determination of uranium, plutonium, technetium, strontium, neptunium, and gamma emitters, consumed a large block of our time during the past year. These two ponds were used in the past as evaporators of low-level waste. Both were drained and the bottoms of each were scraped with a dozer in an attempt

to remove the contamination. The samples sent to us were three segments of core drillings taken from the remaining sediment. The data that we provided are being interpreted by risk analysis personnel to determine if further cleanup work should be done on the pond sediments. Work is expected to be completed on this project sometime during the first quarter of 1991.

This past Fall, we were again asked to provide assistance in sample collection and analysis for a survey of the deer herd at the Paducah Gaseous Diffusion Plant (PGDP). The PGDP was opened to hunters in 1989 and the potential exists for the transport of radiological and chemical contaminants. Three members of our group travelled to Paducah the day of the harvest and prepared samples as each deer was brought into a special preparation area. In addition to these deer, two animals were taken from the Land Between the Lakes Recreational Area to provide control information. Bone, tissue, liver, thyroid, and tail hair samples were taken from each deer. We were asked to measure radionuclides in all of the samples and PCBs in fatty tissue. We did not find elevated levels of either PCBs or radionuclides in any of the deer this year.

Several instruments were procured or upgraded during the past year. We purchased two microprocessor controlled muffle furnaces to replace our old furnaces. The new units fit into a standard hood, have multi-stage program capabilities and automatic shutoff after ashing is complete. Samples are placed in the furnace, the ashing program initiated, and the system will automatically do the rest. We upgraded our LB-5100 proportional counting system this past year to operate with an MS-DOS based computer. A surplus IBM XT was obtained and successfully interfaced to the system after the upgrade. The new operating system allows us to easily produce custom reports, generate backups of counting parameters, and save counting data to the PC's hard disk. A package of programs was developed on the ND-9900 MicroVAX-based system to process alpha spectra. Command procedures were written for the ND-9900 that transfer the

channel by channel counts of each spectra to disk files. The software package interrogates the user and obtains standard spike information, aliquot size, and reporting units. An area of channels is displayed corresponding to where each peak of interest should be located, and the user is asked to select for the computer the appropriate peak areas to integrate. Manual intervention is required because low count rates and poor energy resolution are encountered with environmental spectra. Using the software package, we are able to process 16 alpha detectors in approximately 30 minutes, and the data reported are ready to be transferred to AnaLIS. Before the software was written, it could take as long as two hours to process 16 spectra. Our next goal is to transfer the data included in the reports directly to ACD's VAX for inclusion into the division's data management system.

During the past year, a major effort was expended to develop a new set of procedures to better measure radionuclides in soil samples. A pressure monitor was installed on our microwave digestion system so that the pressure within the vessels could be controlled more accurately. With the monitor in place, we are able to vary the number of samples that can be digested, sample size, and acid volumes without losing any sample due to excess pressure within the vessel. We were able to totally dissolve up to 5 grams of soil with a mixture of hydrochloric, nitric, and hydrofluoric acids. Because of the complexity of the soil matrix, we sought to improve our separation scheme for such radionuclides as ^{90}Sr, plutonium, uranium, thorium, americium, and curium. We procured some ion-exchange material from Eichrom Industries. The material, named TRU-Spec, is very selective for the actinides and nonselective for almost all other elements. We also investigated another of their products, Sr-Spec, which is selective for strontium. These materials hold promise for our applications. A soil dissolution adjusted to approximately 3M in nitric acid can be put directly through a column packed with this material with almost unbelievable results. Virtually all ions besides those of interest go right through the columns and 99+ percent of the

actinides are eluted with very weak nitric acid. The strontium material retains (besides strontium) only a small amount of barium when a solution adjusted to approximately 3M in nitric acid is passed through. The strontium is eluted with warm water. These new-generation materials promise to improve both the speed and efficiency of our procedures.

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Radiological Surveys for DOE-TWRA Deer Hunts

The division continued its cooperative program to monitor deer harvested during the annual DOE-Tennessee Wildlife Resources Agency managed hunts. These hunts were conducted on the Oak Ridge reservation on the weekends of 20 October, 10 November, and 8 December during the calendar year 1990. The first weekend was limited to archery permits; remaining hunts were open to shotguns and muzzleloaders. The goal of this program is to survey harvested animals for radioactive contamination to ensure that appropriate regulatory guidelines concerning radiation exposure are being met.

Radionuclide contamination of soft tissue is estimated by performing a quantitative gamma-ray spectroscopic measurement, with particular emphasis on the assay of ^{137}Cs. The primary organ used for this test is the liver. If a hunter returns to the checking station without the liver, a sample of muscle tissue is removed for testing. Simultaneous with the soft tissue assay, a beta particle screening measurement is made on a sample of bone from each deer. This test is used to evaluate possible contamination by ^{90}Sr. When the result of either measurement exceeds predetermined levels, the animal is confiscated and disposed of appropriately.

The final deer hunt weekend coincided with the goose hunting season. TWRA requested that we make our checking facilities available to evaluate

potentially contaminated birds that might be brought to the checking station. This was done with virtually no significant change in our checking procedures.

The deer harvest for 1990 was 442 animals collected over the six separate hunts. Six animals were retained (1.4%); all of these were the result of excessive ^{90}Sr concentrations in the bone tissue samples. The "hot-test" deer was estimated to contain a total of 6.3 E4 Bq of ^{90}Sr. Although trace amounts of ^{137}Cs were found in a number of the harvested deer, none exceeded our confiscation limit of 0.2 Bq/g and only two (0.45%) were above the 0.04 Bq/g level. None of the limited number of geese brought to the checking station on the final weekend exhibited excessive radionuclide levels.

After the first two hunting days, we carried out a series of laboratory tests to validate our ^{90}Sr field operations. The tests consisted of selecting 30 samples of bone from the first two days of hunting. Fifteen samples were selected (out of 151 total) at random. Fifteen more that exhibited slightly elevated beta counts were also chosen. The samples were assayed in the laboratory via Cerenkov counting techniques. The results showed that bones exhibiting elevated field counts also gave statistically higher laboratory results compared to the bones picked at random. This information confirms the validity of our field screening procedure at levels well below our confiscation limit.

Radiological survey procedures for these hunts were unchanged from those of previous years. These are detailed in a "Hunt Survey Procedures" document prepared by J. S. Eldridge dated 1 October 1987. This memo describes in detail the equipment used, the measurements made, and the data collection and processing techniques that are employed. Also, as in past hunts, the division mobile van was used as an operational base for both equipment and supplies.

H. H. Ross, N. A. Teasley, Jr.,
C. C. Grainger

TRANSURANIUM ANALYTICAL LABORATORY

J. M. Keller

The Transuranium Analytical Laboratory (TAL) has continued to provide analytical support to the Radiochemical Engineering Development Center (REDC) of the Chemical Technology Division (CTD) and to the monitoring of radioactive waste effluent for Waste Operations (WO) of the Environmental and Health Protection Division (EHPD). In addition, the group has provided analytical support to the Remedial Action Program (RAP) within EHPD and the Waste Tank Characterization Program within CTD. Almost 16,500 samples were received by the TAL with approximately 41,000 analytical determinations completed during 1990. This sample load was an increase of 50% over 1989 and the total analytical measurements completed were up by a factor of 20%. In addition to an increase in work for WO, we provided support for the contamination survey at the Laboratory; this involved qualitative identification of nuclides on numerous contaminated objects found by the health physics teams. The analytical support work for REDC operations has continued to increase throughout the year. The increase in work load from REDC operations was predominately related to the process flow-sheet development for the recovery of ^{243}Am from the Mark-42 fuel assemblies from the Savannah River site. There has also been an increase in other REDC activities involving routine operations, inventory of radioactive sources, hazardous material inventories, and contamination surveys.

The TAL had numerous audits during this year which included standard analytical method (SAM) surveillance by QA personnel on various procedures; review of ACD radioactive/hazardous materials operations; audit of ACD nonreactor nuclear training programs; ORNL Functional Appraisal by DOE-Oak Ridge Operations; and DOE Headquarters environment, health and safety quality verification inspection. In addition, there was an extensive health physics surveillance of the TAL operation during May and June.

Work in support of the CTD Waste Characterization Task and the Remedial Action Program for EHPD continued during the past year. Most of this work involved radiochemical characterization of both liquid and solid waste from active and inactive storage tanks. Reports on both of these projects were published this year.

A DOE review of the Laboratory identified REDC as one of the two ORNL facilities that will be required to have a Training Accreditation Program (TAP) which follows DOE specifications. Since the TAL group operates within the REDC Facility, we must also structure our training to meet the DOE requirements. A review team appointed by the Training Accreditation Steering Committee (TASC) conducted a self-evaluation of the REDC Training Program (which includes the TAL Training Program) in mid-November 1989. The team assessed the training program status by interviewing facility training and line management personnel and prepared an Initial Self-Evaluation Report (ISER). After a review of the ISER prepared by TASC, REDC management decided the document was not acceptable and another consultant was brought in for the self-evaluation. The second ISER was completed for the TAL group in May 1990. A Training Program Accreditation Plan (TPAP) was prepared and submitted to DOE for approval.

Although we had expected the current TAL Training Program to satisfy some of the new requirements, a complete restructuring of the program will be required. The DOE TAP requirements include a highly structured and formalized training plan with extensive documentation that covers job descriptions, job entry requirements, lesson objectives, lesson plans, and testing. In addition, the training instructors must be DOE certified. Based upon current information, we will have 3-4 years to implement the new training program. The review team estimated a cost of about $600K to meet the requirements of DOE Order 5480.18.

R. F. Peacher, R. D. Johnson, R. T. Pack, C. S. White, R. A. Jones, D. A. Caquelin, B. K. Larkins, J. E. Sutherland

Instrumentation Upgrades at the Transuranium Analytical Laboratory

An ongoing effort by the TAL group is to upgrade computer software and counting instrumentation to meet customer needs. The low level alpha-beta counting system was upgraded with the addition of a Tennelec low-background LB-4000 proportional counter. The LB-4000 four detector system, which can be expanded to sixteen detectors, has increased sample throughput fourfold. The computer operation of the LB-4000 has improved data accountability and QA for Waste Operation samples. An Aptec high purity germanium X-ray detector was placed into service this year. The X-ray detector will be useful in both qualitative and quantitative determinations of certain transuranic elements. In particular, the X-ray detector will be an important tool in characterizing the separated americium from the Mark-42 Assembly. Also a series of Tennelec TC-256 alpha spectrometers was added to the counting room. The alpha spectrometers are interfaced to the ND-9900 for control and processing of sample data.

The TAL group is the emergency response laboratory during off-hours for ORNL; this dictates that we have reliable backups for all our counting systems. Our two gamma spectrometers are normally controlled via the ND-9900 data acquisition system; however, if the ND-9900 goes out of service, gamma spectroscopy can still be achieved using a personal computer (PC). Multi-channel analyzer (MCA) and gamma data reduction software (commercially available from various vendors) in conjunction with a specialized MCA card allows reliable operation of a gamma spectrometer through a PC. The existing software on the PC was cumbersome for technicians and required too much interaction. In light of this problem, the TAL upgraded the MCA and gamma data reduction software on the PC. The new software has batch processing capability that allows us to write in-house, user-friendly programs that will reduce processing errors and save time.

The TAL group plans to develop software to link the three computer systems in the counting room. Data from the LB-4000 computer and ND-9900 computer will be transferred to

the IBM PC-AT that is linked via broadband to the division computer. Transfers by computer should increase data accountability and reduce manual transcription errors.

J. M. Keller, K. O. Jeter

Special Projects

The TAL group has provided analytical support for the Mark-42 Assembly Process flow sheet development during the past year. The development of a flow sheet to ultimately obtain pure ^{243}Am from the Mark-42 assemblies from the Savannah River Site is a major project for REDC. The TAL group will provide most of the analytical support for this project. Several other groups within ACD will also be involved with this project. Over the past year, TAL has analyzed numerous samples for ^{241}Am and ^{244}Cm from a series of ion exchange column separations that were made in the hot cells at REDC. In addition to the Am-Cm separation studies, the TAL group has also provided analytical support for plutonium extraction studies, which is a different aspect of Mark-42 flow sheet development project. TAL sample load should increase dramatically with the continued flow sheet development followed by actual processing of the Mark-42 assemblies. The high activity level of the samples from this project will be similar to samples from a HFIR target campaign. Current plans indicate that REDC will alternate between the Mark-42 Assembly Process and the TRU Processing Program to increase the overall productivity of the operation.

The TAL has continued to provide analytical support for the testing of coating materials. The objective of this support is to determine the decontamination efficiency of various coating materials, usually paint, to be employed at nuclear reactor facilities. Prepared specimens, either steel panels or concrete blocks, were received from prospective vendors of these coating materials. These specimens were contaminated with a tracer solution of near equal amounts of ^{137}Cs and ^{60}Co. The initial contamination was measured

by gamma spectroscopy. The relative gamma activity was then measured after various decontamination steps.

We have also been involved with several high priority projects during the past year. Sludge and liquid samples from the leaking Graphite Reactor canal were characterized to determine environmental impact. The total gross alpha levels ranged from 10^4 to 10^5 Bq; ^{60}Co and ^{90}Sr contamination was also observed. Another high priority project involved samples of pipe scale from an assembly at Y-12 that was scheduled to be dismantled by an outside contractor. An assay of the radioactive material in the sample was requested. It was suspected that any activity present in the sample would be ^{232}Th and daughters. The concentration of ^{232}U and ^{233}U was also of special interest. The gross alpha activity was slightly more than 10^4 Bq/g and the alpha pulse height analysis (PHA) identified all the alpha activity to be Th daughters. The total thorium content was determined colorimetrically by the Thoron method and found to be 520 mg/g. The uranium activity was determined by the hexone extraction method and found to be < 200 Bq/g of both ^{232}U and ^{233}U. The results verified that essentially all the activity was derived from ^{232}Th and its daughters.

The TAL provided analytical support to a joint research program between the U. S. and U. K. in which the higher actinides were incorporated into fuel pins for irradiation in the Dounreay Prototype Fast Reactor (PFR) in Scotland. A major part of this effort is to determine the cross sections of a wide variety of actinides in this type of reactor. The TAL prepared special sources for the Physics Division and analyzed numerous samples for the project. The fuel pins were dissolved in the hot cell at Building 2026 and a small portion of the sample was sent to TAL for actinide and other radiochemical measurements. In addition to the radiochemical measurements, about 30 mass spectrographic preparations on resin beads were completed for Pu, Am, and Cm isotopic determination. The beta gamma radiation from these samples measured up to 2 R/h at contact and approximately 180 mR/h at 6 inches. Because of the high level of activity and the precision

required for this project, this was a difficult and time-consuming task.

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C. S. White

Status of the HFIR Neutron Activation Laboratory

Neutron activation analysis (NAA) at ORNL is beginning to be viable again following restart of the HFIR. The reactor, which was shut down in November 1986, began operating at low power at the end of January 1990 and started routine operation at full power (85 MW) in May 1990. The NAA laboratory now has both pneumatic tubes, PN-1 and PN-2, in operation and a new gamma-ray spectroscopy system based on a personal computer. Thus far about 75 samples of ^{129}I have been measured by NAA. Fairly extensive neutron flux measurements have been made since the reactor resumed operation.

Considerable effort has been taken to satisfy both old and new requirements governing the operation of the NAA laboratory. These requirements include pressure testing at 4.82 MPa of certain critical regions of both pneumatic tubes, low pressure testing of all regions of both systems, and testing of check valves and water monitors of both systems. Both pneumatic tube systems have now passed all necessary tests. Initial test of the water monitors on PN-2 failed to detect demineralized water, and the electronic controllers, which were different than the controller used on PN-1, had to be replaced with more sensitive instruments. The new controllers, Beckman Conductivity Controller Model RA-6, function as required.

Because of extensive deterioration of a Nuclear Data multi-channel analyzer, Model 6620, we have made efforts to get our gamma spectroscopy capability back to one of efficiency and accuracy. To that end, a 33 MHz Northgate PC and a Canberra Accuspec B MCA board were purchased to form the basis of a multichannel analyzer. A Canberra

Analog Multiplexer, Model 589, was added to the system to allow acquisition of up to four gamma spectra of 4096 channels each. A board was also added to the PC that permits each of the spectra to be acquired with independent timing. Software for basic spectroscopy and nuclide identification was also purchased for this system. The software closely resembles in both form and function the software used with the ND-6620 system. Although the multiplexed system will permit four gamma spectra to be acquired simultaneously, limitation on count rates for the system as a whole or on individual detector systems has not been investigated. As far as we have been able to determine, we are the first to acquire large-channel gamma spectra with an analog multiplexing system. The system appears to function well, but we are continuing to test it in several ways.

Although nuclide identification software was purchased for the PC-based MCA system, no software was available for neutron activation analysis. An extensive effort has been made to write and/or translate a FORTRAN code that will perform NAA. This effort is nearing a stage where it can be used.

F. F. Dyer, L. Robinson

Neutron Flux Measurements at the HFIR

After the HFIR began operating at 8-10 MW, neutron flux measurements were made in the old pneumatic tube system, PN-1, where the flux was lower than expected. Staff of the Research Reactors Division suggested that ^{3}He formed by the decay of tritium in the permanent beryllium reflector during the 3-plus years of downtime was absorbing some of the thermal neutrons thus lowering the flux. Tritium is formed during operation by a series of nuclear reactions involving ^{9}Be.

As the reactor operated, first at reduced power and then at 85 MW, the neutron flux gradually increased indicating that the ^{3}He was being "burned up". (^{3}He absorbs thermal neutrons to form tritium by a neutron-proton reaction.)

The measured thermal flux in PN-1 soon converged to about 2.3×10^{14} n cm^{-2} s^{-1}. Measurements made over many years with a reactor power of 100 MW indicate that the measured thermal flux in PN-1 with a power of 85 MW should be in the range of $3.5\text{-}4.0 \times 10^{14}$ n cm^{-2} s^{-1}. Thus the measured thermal flux is only slightly more than half of its expected value. Attempts have been made to determine if the rabbit is perhaps failing to reach the mid-plane irradiation position during irradiation, but these tests are not presently conclusive. Further tests to explain why the measured thermal neutron flux is apparently low in PN-1 are planned.

F. F. Dyer, L. Robinson

Removal of Europium from Surfaces of Stainless Steel Contaminated by ^{152}Eu and ^{154}Eu in the HFIR Pool

A few years ago it was found that certain regions of the HFIR control plate that contained europium oxide were, after use, rich sources of ^{152}Gd. These regions would be cut from spent plates in the HFIR pool and used for recovery of the ^{152}Gd. The ^{152}Gd was used to produce ^{153}Gd by neutron capture. During one cutting operation, a small misplaced cut eventually resulted in minute quantities of the Eu_2O_3 containing the long-lived activities ^{152}Eu and ^{153}Eu being released to the pool water. The low-level contamination was not removed efficiently by the ion exchange resins through which the water is circulated. A brief study was made to determine if dilute nitric acid can be used to remove the europium from stainless steel surfaces.

A small piece of stainless steel rod having a measured amount of radio europium contaminant on its surface was suspended on a platinum wire in a glass jar. A few hundred ml of water were added and acidified to pH 4, and the water was stirred and heated to about 32° C for about a week. A similar system was run at pH 5. The specimen was removed periodically and its ^{154}Eu was measured.

With the pH set to 4, it was found that most of the europium was removed from the steel over a period of a day. The remainder of the europium continued to gradually come off the steel. A similar, but much slower, behavior of the deposited europium was observed at pH 5. The europium in the water, including the part that was there originally, was then nearly completely removed by a single passage through a column of the ion exchange resin IR-120, the cation resin in the reactor's cleanup resins.

F. F. Dyer, L. Robinson

Proposed Analytical Chemistry Facilities for the Advanced Neutron Source

As a result of meetings held in San Francisco, Ann Arbor, and Nashville during 1989 and 1990, and in addition to some reevaluations locally, considerable revisions have occurred in the Analytical Chemistry Division facilities proposed for the Advanced Neutron Source (ANS). The revised Neutron Activation Analysis Facility (NAAF) will consist of two parts, NAAF-1 and NAAF-2. NAAF-1 will be located inside containment, and NAAF-2 will exist as a separate building outside the reactor containment dome. NAAF-1 will consist of a small counting room and an Irradiation Control Room (ICR). Sample irradiations will be initiated from this facility and it will contain counting equipment to measure short-lived radionuclides. The ICR will house a shielded cell containing the loading station for five pneumatic tubes. The loading station of two additional pneumatic tubes will be located in a fume hood inside NAAF-1. Two additional pneumatic tubes that originate in the shielded cell in NAAF-1 will terminate in a similar, but smaller, cell in NAAF-2. These two pneumatic tubes will be used to transfer samples which contain radionuclides with moderate to long half-lives from NAAF-1 to NAAF-2; however, due to security concerns, transfer from NAAF-2 to NAAF-1 will not be allowed.

The NAAF-2 facility will be a self-sustaining structure with a size of about 600 m^2. Some of the building's major

components include sample preparation rooms, counting rooms, radiochemistry laboratories, a clean room, and office space to accommodate approximately 12 people. This concept is being proposed as a means of avoiding a situation in which analytical chemistry facilities are located throughout the ANS in little or no functional order.

Two of the seven pneumatic tubes used for irradiation of samples will terminate in the light water pool outside of the deuterium oxide reflector tank. One of the tubes will be used to irradiate samples in a cylindrical rabbit with a volume of 40 cm^3. The second pneumatic tube will be rectangular and will accommodate a circular box or "hockey puck" rabbit. Both the cylindrical and circular box rabbits will hold multiple samples.

As opposed to the major revisions made in the neutron activation analysis facilities, neutron beam facilities remained essentially unchanged.

L. Robinson, F. F. Dyer, J. F. Emery

INORGANIC AND PHYSICAL ANALYSIS

J. L. Botts

The Inorganic and Physical Analysis (IPA) Group performs analyses on intermediate and high-level radioactive materials that require the use of gloveboxes, c-zone hoods, and hot cells in the High Radiation Level Analytical Laboratory (HRLAL). The level of samples processed and analyses performed remains about the same as during the previous 2-3 years: approximately 2000 samples and 5000 determinations per year. In December, the activities of the Radiochemical and Activation Analysis Group were consolidated into the IPA group.

The characterization of mixed radioactive/hazardous chemical waste continues to be the principal activity within the group. To evaluate methods for treatment and disposal of this waste, the group characterizes the waste for radionuclide and chemical constituents and determines some physical properties. These data are essential to meet both

regulatory and engineering treatability requirements.

The analysis of radioactive liquid waste and sludges from the Melton Valley Storage Tanks (MVST) was completed, and the data reported in an ORNL report (ORNL/TM-11652). Aqueous and composite sludge samples from these tanks were analyzed for major constituents, radionuclides, total organic carbon and RCRA metals. In addition, some physical properties were measured. When they applied, EPA-approved analytical procedures were followed. Modification of procedures from the EPA guide SW-846 were used. Modifications were necessary because of high radiation levels, high salt content, and complex matrices in the samples. In addition, ACD procedures and other analytical chemistry methods were used for some analyses. The radiation level of the samples ranged from 0.1 to 2.8 R/h. In general, the waste was found to be 3-5 M in nitrate salts with a pH of from 11-13 with the major radionuclides being ^{90}Sr and ^{137}Cs. These characterizations included radiochemical and physical measurements, anion analyses by ion chromatography, and metal analysis by ICP/AA.

C. Cook, Jr., M. T. Davis, H. J. Hall, L. R. Hall, M. G. McClung, L. C. Tabor, M. E. Peters, R. N. Ceo

Analytical Capability Upgrade

Since the various waste programs at the Laboratory continue to be the major source of work for the IPA group, the upgrade of its capability to meet the analytical requirements of these programs is continuing. A Dionex 4500I ion chromatograph has been acquired and configured to quantify the common anions, weak acid anions, and Group I and II cations in radioactive samples. This instrument is a modular chromatograph with a liquid chromatograph module and a pulsed electrochemical detector (PED). The PED is microprocessor-controlled with the data being transferred to a Dell system 310 microcomputer by an advanced computer interface.

The Perkin-Elmer Model 6500 inductively coupled plasma spectrometer presently in use by the group for elemental determination on radioactive samples is being replaced. A new Spectro-ICP has been purchased and is presently being installed to replace the Perkin-Elmer unit. The Spectro-ICP uses fiber optics to transmit the optical emissions from the plasma torch to the optical dispersion and measurement devices. This feature allows the unit to handle up to three polychromators and one monochromator which will give up to 64 simultaneous analysis channels. This feature also allows both simultaneous and sequential operation, greatly decreasing sample analysis time.

The Ethernet II communications network has been installed in the HRLAL facility. This physical network links some 15 computers together, in which a Dell System 310 computer is used as a dedicated file server connected to the PC-compatible workstations using interface cards and coaxial cable. Banyan VINES/386 is being used as the network software. The HRLAL network service includes password control, shared files, shared programs (WordPerfect 5.1, and dBase IV), on-line message system, and shared LaserJet printer access. The network is being configured to couple with the ACD VAX as well as to integrate into the Laboratory's 2000 microcomputers in a Lab-wide network as other local area networks become established.

M. T. Davis, R. N. Ceo, M. E. Peters, L. C. Tabor, C. Cook, Jr., L. R. Hall

Cleanup of Hot Cell Facilities

For the first time in more than five years, the high radiation level storage cell at Building 2026 is empty of radioactive waste. Due to changes in waste disposal guidelines, no waste had been removed from the facility for several years, resulting in a significant housekeeping and contamination hazard. More than 2.5 m^3 of contaminated waste were transferred to a permanent disposal site, requiring about four months of effort.

Phase I of the cleanup and decontamination of the Building 3019B

hot cells was completed in February 1990. This project consisted of removal of all contaminated waste from the cells. Approximately 1.7 m^3 of waste were removed and sent to a solid waste burial ground. During this operation, a number of large pieces of equipment were dismantled using electric saws and plasma welding torches. Phase II of this work is being planned which will include further decontamination of the interior of the cells. This work is supported by the Remedial Action Program at ORNL.

C. Cook, Jr., J. L. Botts

Support to the Consolidated Fuel Recycle Program

The satellite laboratory located in Building 7602 continues to provide analytical service for the 7600 Fuel Recycle Facility. This process and engineering R&D work is part of the Consolidated Fuel Recycle Program (CFRP). Processing campaigns to develop technology for reprocessing breeder fuel are part of the program. Chemical analysis and physical measurements are performed during these campaigns to provide data for evaluation of processing operations.

M. T. Davis, M. G. McClung

3. INORGANIC CHEMISTRY

W. R. Laing

The Inorganic Chemistry Section provides analytical support and methods development in areas of classical and instrumental analyses and in physical measurements to ORNL, DOE, DOD, NRC and outside contractor programs. Effluent monitoring programs to ensure compliance with state, DOE, and EPA discharge regulations continued to provide the largest single segment of support for the section. The monitoring and analysis of well and surface waters, fish tissue, soils, sediments and air filters for mercury, toxic metals by ICP, cyanide, sulfide, asbestos, and measurement of a wide range of other potentially hazardous materials have been accomplished in a timely fashion by a smaller staff.

A significant support effort was required during startup of the new nonradiological wastewater treatment plant, to the Industrial Hygiene groups at ORNL and K-25, and to the Environmental Sciences Division study of nitrate deposition to foliar surfaces.

An inductively coupled plasma-mass spectrometer facility was prepared, the instrument purchased and installed, and the facility was placed in routine operation. Other new equipment included an electrothermal vaporization accessory for the ICP/MS to permit simultaneous measurement of femtogram concentrations of elements and their isotopes.

Emphasis on quality assurance continued with the preparation of additional standard operating procedures, training procedures, increased training workshop attendance, group-level quality assurance programs, formalized compilation of reference data on asbestos and ceramic fibers, and responses to a series of external audits.

CHEMICAL AND PHYSICAL ANALYSIS

N. M. Ferguson

The Chemical and Physical Analysis (CAPA) group provides technical support to ORNL programs, to other Martin Marietta facilities (Y-12, K-25, Paducah), and to external organizations including the Nuclear Regulatory Commission, the Strategic Petroleum Reserve, and the DOE Environmental Survey Program. New methods and modifications of existing procedures were needed to meet the requirements for these programs. Significant efforts were also necessary to meet the stringent time limitations for completion of the analyses. Approximately 75,000 analytical results were reported during this period. The Environmental and Health Protection Division continued to generate the largest number of samples.

CAPA provided technical support for new and continuing programs. Groundwater and effluent samples were received for the National Pollution and Discharge Elimination System (NPDES), Resource Conservation and Recovery Act (RCRA), and special programs of the Environmental and Health Protection Division. The Remedial Feasibility Investigation (RFI) of the Clinch River by the Environmental Sciences Division (ESD) produced more than 300 fish samples for PCB, lipid, and metal analyses. Work for the Industrial Hygiene group was heavy; blood, urine, air filters, and waters were analyzed. Numerous wastes (solids, oils, and aqueous) were characterized for ORNL groups, K-25, Y-12, and Paducah. Asbestos was measured in water, air, surface, and bulk samples for ORNL and Y-12 Industrial Hygiene groups.

The ICP/OES laboratory experienced minimal instrument problems this year. The minor problems (faulty connection in the rf cable, instability of intensities, loose connections and dirty capacitors in the generator, etc.) encountered with the JY48 polychromator were short-lived with little downtime. All the required discharge permit analyses were met in a timely manner and all deadlines for the quarterly EPA Contract Laboratory Program Performance Evaluation samples were met. We modified the ICP/OES method to measure nine elements

(Ag, Cd, Cr, Cu, Ni, Pb, Sb, Se, Zn) in fish tissue. Zinc was measured at approximately ten μg/g and all other elements were measured at concentrations below one μg/g. Graphite furnace methods were used previously for the analysis of Zn. The ICP/OES method provided a more rapid and inexpensive method of analysis.

Support of the DOE Environmental Survey Program (DOEES) was completed this year. The Analytical Chemistry Division was responsible for compiling closeout packages for 13 sites. These DOE Environmental Survey sites included Argonne National Laboratory, Idaho National Engineering Laboratory (INEL), Los Alamos National Laboratory, Lawrence Livermore, Sandia National Laboratory, Morgantown Energy Technology Center, Paducah, Pantex, Pittsburgh Energy Technology Center, Brookhaven National Laboratory, Mound, Nevada Test Site, and Rocky Flats. The packages included survey-related records from the Analytical Chemistry Division, ORNL Sampling Team, Data Management Group, the ORNL DOEES program manager, and other laboratories (e.g., K-25 and Battelle). More than 43 containers of documentation were shipped to the archive at INEL for the 13 sites.

CAPA measured polychlorinated biphenyls (PCB) for several groups in the Environmental Sciences Division. Lipids and 1254 and 1260 PCB isomers were measured in fish and clams. Blanks, spiked samples, and International Atomic Energy Agency (IAEA) samples of fish homogenates were extracted and analyzed with each batch of samples to determine analytical quality levels. Spike recoveries ranged from 90-110%. For two years CAPA has participated in a Tennessee Valley Authority (TVA) Interlaboratory QC Program for measuring lipids and PCB in fish. Four laboratories (ORNL, Tennessee State Environmental Laboratory, TVA, EPA Region IV) were involved with the second QC program. Two types of samples (homogenized tissue samples and homogenized-Na_2SO_4-pooled controls) were analyzed for this work. There was excellent agreement in the results and a third program is planned for next year.

The new ICP/MS analyzer was received in December 1989 and the first samples were analyzed in February 1990.

The instrument has been used to supplement our ICP/OES work where it offers improved sensitivity and to measure elements that cannot be determined by the emission instrument. The ICP/MS has also been used to perform work previously done by the graphite furnace since it can simultaneously measure multiple elements at part-per-billion concentrations.

The first samples analyzed were waste samples for the new Toxic Substance Control Act (TSCA) waste incinerator facility at K-25. Be and Th were measured down to 0.3 ng/ml. Over 300 fish tissues were analyzed for As, Tl, Be, and U for the ESD with lower reporting limits of less than 0.05 μg/g for As, less than 0.1 μg/g for Tl, less than 0.003 μg/g for Be and U. We measured lead in blood and urine for K-25 and ORNL Industrial Hygiene (IH) groups and analyzed hundreds of air filters for eight elements (Ag, As, Be, Cd, Cr, Ni, P, V) at the parts-per-billion concentrations for the ORNL IH group. We measured uranium in sediments, vegetation, and waters at the parts-per-billion concentration for several programs.

CAPA obtained a VG Micro Therm Electrothermal Vaporization System (ETV) for the ICP/MS. It is being evaluated as a method to measure low concentrations (parts-per-trillion) of uranium in urine. Preliminary work with pure uranium standards is encouraging. We obtained detection limits of 6 parts-per-trillion for ^{234}U, ^{235}U, and ^{238}U isotopes.

The ICP/MS analyzer has performed well this year with very little downtime.

The Physics Methods lab continued to provide technical and service support in the fields of transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), optical microscopy (OM) and electron-excited X-ray analysis (EDX). We maintain a full service asbestos-analysis capability and routinely analyze air (clearance), water, surface, and bulk samples for a variety of customers including ORNL Industrial Hygiene, K-25, Y-12, and Portsmouth. We procured and installed a TEM double-gap condenser pole piece and a double-tilt Gatan sample holder, which improved the specificity of analyses for individual fibers. All of the appropriate quality

assurance documents were written and placed in routine operation. These included 16 standard operating procedures, a training program, and a quality assurance program. In addition, two "standards" books were compiled. These included photographs showing typical morphology, X-ray spectra, and electron diffraction zone axis patterns for asbestos fibers, asbestos "look-alikes", and ceramic or man-made fibers.

We have enrolled in the inaugural AIHA-TEM-PAT program, and have provided TEM backup for the polarized light microscopy "PAT" program.

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ENVIRONMENTAL ANALYTICAL LABORATORY

N. M. Ferguson, T. B. Shope

The Environmental Analytical Laboratory (EAL) provides analytical support for the Environmental Sciences Division (ESD) and other ORNL divisions. Approximately 9,000 analytical results were reported during this period.

The Environmental and Health Protection Division continued to generate a substantial portion of our workload. Weekly, biweekly, and monthly effluent samples were analyzed to demonstrate compliance with National Pollution and Discharge Elimination System (NPDES) permits. Groundwater samples were analyzed quarterly to meet Resource Conservation and Recovery Act (RCRA) requirements.

The Industrial Hygiene Department continued to supply EAL with biological fluid, air filter, and charcoal filter samples which require rapid turnaround time due to possible health-related consequences of human exposure. The Industrial Hygiene group at K-25

submitted air filter samples for As, Pb, and V analyses. The required turnaround time for these samples was less than one week.

EAL provided start-up analysis for the Nonradiological Wastewater Treatment Plant (NRWTP). Initially, daily samples were taken on the influent and effluent streams of the NRWTP. Mercury and total organic carbon were measured in each sample. A turnaround time of approximately two days was maintained during the initial phase of the start-up program.

We continued to provide support for the ESD study of nitrate deposition to foliar surfaces work. ESD performed experiments on seedlings of several forest tree species to determine the fate of dry deposited nitric acid vapor within forest canopies. Seedlings were exposed to ^{15}N-labelled HNO_3 for several hours in a controlled exposure facility. Surface deposition experiments were done in a dark facility while combined surface and internal deposition studies were done in a lighted facility. The HNO_3 concentrations were checked by pulling air from the system through an NYLABSORB filter, which collects HNO_3. The nitrate was extracted from the filter, and determined by ion-chromatography.

EAL continued to analyze quarterly performance evaluation samples from EPA to maintain active Contract Laboratory Program (CLP) qualification. Instrumentation detection limits were determined for As, Ag, Hg, K, Na, Pb, Se, and Tl on a quarterly basis.

Graphite furnace work was extremely heavy this year. Considerable time, including much overtime work, was spent measuring metals (As, Se, Sb, Tl, Cr, Ag, Cd, Pb) for NPDES and RCRA programs. Such programs require extensive quality assurance measures, which greatly increase analysis time. In cooperation with the Bechtel characterization effort, the graphite furnace laboratory measured Sb, As, Se, and Tl for Waste Area Group (WAG) wells sampled in September. The turnaround time for WAG-1 results was 30 days, with complete CLP packages to be finished later. Two graphite furnaces (Perkin-Elmer Zeeman 5000 and 5100) were used for this work.

Data processing programs for the Perkin-Elmer 5100 AA Spectrometer were installed this year. One program performs essentially the same function as the programs FIS-PARSE and MERCURY do for their respective jobs: to parse the data in a file in order to recover pertinent information, to review the data for quality, and to prepare a file for incorporation into AnaLIS. The "program" consists of three programs, each of which can call the other two as needed. The first program is a menu driven and file listing program. The second reads the data file, provides for search and browse as well as parsing features, and enables the third or processing (review) program to be called.

All sample preparation for EAL was done in the "clean room facility" at Building 2026. This included the preparation of samples (NPDES, RCRA) for metal determinations using a flame AA or graphite furnace and for mercury determination by cold vapor atomic absorption.

The mercury laboratory provided results for a variety of samples of unusual matrices including oil samples from the Exxon Valdez oil spill, various insects, fish, and grasses submitted by the Environmental Sciences Division, and metal and concrete samples submitted as special project samples. We continued to provide Hg results for ongoing projects such as Remedial Feasibility Investigation (RFI) of the Clinch River.

For several years, EAL has been using two Dionex Ion Chromatography systems for anion analyses. A single anion scan can include results for fluoride, chloride, bromide, nitrate, phosphate, and sulfate, but the majority of our work is targeted for chloride, nitrate, and sulfate. This year we provided IC scans for work submitted under the Environmental Sciences Division's Forest Service Project. Under this program, rain and throughfall samples are collected at the Smoky Mountain field sites. Also, the Industrial Hygiene Department submitted several requests for sulfate and sulfite analyses on air filters.

L. S. Barringer, L. A. Greenman,
S. A. MacIntyre, T. L. Mims,
M. L. Moore, T. R. Mueller, J. Summers,
C. L. Watson

SPECIAL PROJECTS

J. H. Stewart, Jr.

The Special Projects group is responsible for coordinating interactions between the Analytical Chemistry Division and requesters of nonroutine analytical services for ORNL programs and by Work for Others external programs. The group performs analytical development and nonroutine specimen analyses until the methods are evaluated, laboratory procedures are written, and technicians are trained. Another group responsibility has been the preparation of purchase specifications, technical testing procedures, and installation of new major equipment items. During this reporting period specifications were written for an inductively coupled plasma-mass spectrometer, an electrothermal vaporization ICP/MS accessory, and a combined simultaneous-sequential inductively coupled plasma optical spectrometer.

Detailed procurement specifications for the replacement inductively coupled plasma-optical emission spectrometer system were completed, the bids evaluated, and a contract for the Thermo Jarrell Ash Model 61E combined simultaneous-sequential spectrometer was completed.

The Portsmouth facility has requested and obtained information on ICP/MS facility site preparation, to utilize the ORNL experience and expedite their new ICP/MS facility renovation.

One goal of the group is to encourage software standardization through use of vendor software programs that allow end users to supply data to their runtime programs and to specify that ASCII files be available for producing customized output data. Two major instrument manufacturers have responded favorably and will provide these programs. The long term goal is to develop a software specification similar to ASTM and ANSI standards which can be referenced, and be assured that the software package will perform the intended tasks.

Several short range development projects were successfully completed, including accurate and precise determination of U(IV) and U(VI) in

chloride media by $(NH_4)_4$ $Ce(SO_4)_4$ redox titration, the measurement of europium in reactor coolant water at the 0.5 part-per-billion concentration level using chemical preconcentration followed by inductively coupled plasma-optical emission analysis, and the electronic transfer of the Los Alamos quality assurance standard reference library to ORNL.

D. A. Bostick, C. Feldman, T. R. Mueller, N. A. Teasley, Jr., J. H. Stewart, Jr.

Preliminary Evaluation of Laser Ablation ICP/MS for Analysis of Tree Growth Rings

For several years, the ORNL Environmental Sciences Division has requested the ACD to develop a technique for the simultaneous determination of trace-to-ultratrace concentrations of metallic elements within individual growth rings of cores removed from trees in several geographic locations within the U.S. These include the New England states, the Smoky Mountains, and the Rocky Mountains. Rapid, progressive tree death has been noted at the 1524 meter elevation in the last five years in the Tennessee-North Carolina mountains.

The ACD inductively coupled plasma (ICP) spectrometer has been successfully used to demonstrate the capability of ICP for measuring trace metals in digestates of small segments of tree core material. The preparation is very slow and costly, and the ultimate detection limits are not as sensitive as needed.

The laser ablation source presently being used for refractory metals and minerals analysis was tested for measurement of elements of environmental concern in specific tree ring specimens in September. The results were highly encouraging, and indicate that ORNL should aggressively investigate the potential for combining the laser ablation-ICP/MS analyzer system to support these studies. This recent work strongly supports initial studies in 1988-1989 which indicated that the technology could be developed.

Data obtained in the recent tests illustrate the large increase in Al, Cu,

Hg, Ni, P, Pb, Rb, Ti, Tl, W, and Zn from 1850 to 1980, while the ratios (1850/1980) for Ba, Ca, and Sr are similar. These simple ratios illustrate the potential for ORNL to become a leading facility for this type of environmental analysis. Serious effort will be required to quantitate the ratios if absolute values are needed, but the trend-analysis of element ratio versus geologic time may be of immediate value to the investigation of the causes of tree death.

A computer controlled, automated laser ablation-ICP/MS system to perform low- cost, high-throughput measurements of trace elements within individual annual growth rings is now a distinct possibility.

J. H. Stewart, Jr., S. B. McLaughlin, Jr., T. Rettberg***

*Environmental Sciences Division

**VG Elemental Corporation

4. ORGANIC CHEMISTRY

M. R. Guerin

This section is responsible for a diverse program of research, methods development and analytical services. Research is directed toward separations and spectroscopic techniques that can yield faster and more accurate methods for identifying and quantitating trace organics in complex media. Fourier transform mass spectrometry and ion trap mass spectrometry are being studied for this purpose both alone and in combination with separations techniques. High performance liquid chromatography with fluorescence detection, capillary zone electrophoresis and supercritical fluid chromatography are the principle separations methods under development. Research continues to emphasize environmental media and has expanded to include physiological media. Field sampling and direct-sampling mass spectrometry methods are being developed for the rapid determination of organic pollutants in water, soil, wastes and air. Thermal desorption ion trap mass spectrometry has been shown to be very promising for determining constituents of physiological media. Progress has also been made in applying our unique analytical capabilities to physical and materials sciences problems. Examples include the use of laser ablation Fourier transform mass spectrometry for the generation and analysis of carbon cluster ions and the use of reverse chromatography to characterize the surface properties of ceramic powders. New or expanded activities are under way in the areas of field analytical methods and radioactive mixed waste characterization. Our analytical services operation has continued to expand in size and capability. Environmental compliance and survey services are being routinely provided for both ORNL and other DOE installations. Specialty services involving various chromatographic and mass spectrometric techniques as well as infra-red and nuclear magnetic resonance spectrometry are carried out in support of life sciences and physical sciences research at ORNL.

ORGANIC SPECTROSCOPY

M. V. Buchanan

The goal of this group is to develop spectroscopic techniques for the unambiguous identification and quantitation of trace organics in environmental and biological matrices. The primary tools in our research are trapped ion mass spectrometric techniques, including Fourier transform mass spectrometry (FTMS) and ion trap mass spectrometry (ITMS). Other organic spectroscopic tools are also employed. These include conventional gas chromatography/mass spectrometry (GC/MS), with either electron impact or chemical ionization, Fourier transform nuclear magnetic resonance (FTNMR) spectrometry, and Fourier transform infrared (FTIR) spectroscopy.

Previous work in our group has demonstrated the unique capabilities of FTMS for obtaining detailed information on the structure of modified nucleotides and nucleosides using ultra-high resolution mass measurements, collision-induced dissociation processes, and gas phase ion-molecule reactions. This has allowed detailed information concerning the identity of the adduct and the site of adduct substitution on a nucleoside to be established. This year, substantial effort was directed to the generation of higher mass ions to allow extension of previously developed ion structural methods to modified oligonucleotides and to the interfacing of separation methods with the FTMS to allow complex biological samples to be analyzed. Especially noteworthy was the fact that we were the first to report successful coupling of matrix-assisted laser desorption techniques with FTMS. This technique has tremendous potential for extending the upper mass limit of compounds which can be studied with the FTMS. Techniques have also been developed for analyzing compounds isolated on slab gel electrophoresis plates by FTMS, thus allowing the most commonly used biochemical separation techniques to be coupled with the structural characterization powers of FTMS. In addition, an electrospray source for potential coupling of on-line separation techniques with the FTMS was designed and constructed.

Work has also continued on the development of rapid methods for the detection of trace organics in a wide variety of matrices by direct sample introduction into an ITMS. This work has been focussed in two areas: detection of toxic compounds in environmental samples and detection of drugs and metabolites in physiological media. Extensive experience has been obtained on rapid detection of chemical agent simulants and volatile compounds from the EPA Target Compound List. Additional work has been conducted with a variety of drugs, metabolites and other semi-volatile compounds. Matrices studied to date have been diverse and include air, water, soil, surfaces, urine, oil, prepared food, milk, plant tissue and meat. The direct sampling method has also been used to monitor gases evolving from bacterial action. In general, direct sampling ITMS has proven to be a highly successful approach for rapid, confident detection of trace organics, and potential applications for this type of methodology, for either laboratory- or field-based use, seem to be limitless.

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

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

Recent developments with time of flight (TOF) analyzers have shown that matrix-assisted laser desorption (MALD) may be used for the generation of very high mass ($m/z > 400{,}000$) ions from large proteins. Coupling this ionization method with FTMS should provide extensive ion manipulation capabilities not available with TOF instruments for obtaining structural information on these large ions. While both TOF and FTMS are pulsed techniques which can be used with pulsed laser desorption, there are substantial instrumental differences between the two techniques in terms of ion lifetimes, dynamic range and ion detection. Although several research groups have been examining experimental

parameters for interfacing MALD with FTMS, we were the first to demonstrate MALD with FTMS and have used this technique to characterize peptides and oligonucleotides. By using a nicotinic acid matrix we obtained peptide spectra with 266 nm laser desorption (single shot or signal averaged) that revealed reduced fragmentation as well as an increased abundance of ions related to the molecular weight; i.e., $(M + H)^+$, $(M + K)^+$, and $(M + Na)^+$. Peptides up to Gramicidin D (mw 1882) could be ionized "softly" with MALD. Examination of several different wavelength-matrix combinations indicated that pyrazinecarboxylic acid with 266 nm laser desorption and sinapinic acid with 355 nm also provided strong enhancement for the MALD FTMS experiments. Larger proteins such as bovine insulin (mw 5734) did not reveal molecular ions with any matrix-wavelength combination. Because these compounds have been observed in MALD TOF experiments, it appears that these $(M + H)^+$ ions for these higher molecular weight compounds are being generated, but are not detected in the FTMS. This may be due to poor ion trapping and/or ion detection factors. These limitations are presently under investigation.

Initial investigations indicated that the MALD FTMS technique is well-suited for the characterization of low picomole quantities of normal and modified oligonucleotides and provides a means of probing the structures of ions in remarkable detail. For example, spectra of d(AG) (deoxy-adenosine-guanosine) revealed an $(M - H)^-$ ion at m/z 579, along with fragment ions at m/z 428 (cleavage of the glycosidic bond to eliminate a nucleic base) and 346 (cleavage of the phosphate ester bond). The latter fragmentation not only provides sequence information, but also indicates specific elimination of the 5' nucleoside, giving isomeric information; that is, d(5'-AG-3') can be differentiated from d(5'-GA-3'). This observation was verified using several isomeric dimers, trimers and tetramers. It was determined that sequence information and the location of adducts can be readily obtained from the observed fragmentation, which arises primarily from phosphate ester cleavage from the 3' end of the oligomers. Without the

addition of the nicotinic acid matrix, however, all molecular and larger fragment ions were lost, verifying the enhancement effects of the matrix. A number of modified nucleic acid constituents have also been successfully characterized with this technique, including the modified nucleotide benzo(a)pyrene tetrol-deoxyguanosine-5'-monophosphate (using 10 pmoles of sample applied to the probe) which was obtained from collaborators at the American Health Foundation. This result was especially encouraging due to the fact that many other research groups had previously been unable to generate a mass spectrum of this compound. Our success in using the MALD FTMS technique for the characterization of modified oligonucleotides has been well-received by the biochemical community and has resulted in a number of collaborative research efforts.

R. L. Hettich

Isolation and Introduction Technology for the Determination of Biochemicals by FTMS

Based on previous success of direct laser desorption for FTMS analysis of biological compounds on thin layer chromatograms, we have examined the extension of this technique to slab gel electrophoresis. Gel electrophoresis is the most commonly used separation technique for biomolecules such as peptides and oligonucleotides, but a direct laser desorption from gels has been limited by poor detection limits and interferences from the gel matrix. We have developed a method for extracting large oligonucleotides from agarose gels which promises to resolve these difficulties. This method, called "freeze-squeeze" extraction, involves freezing the analyte-doped gel with liquid nitrogen and manually squeezing the gel to extrude the interstitial liquid containing the analyte. This method was used to extract picomole quantities of small peptides and oligonucleotides from the gels for subsequent characterization by MALD FTMS. Radiotracers were

employed to quantitate sample loading and recovery from the gel and indicated total efficiencies of about 50%. Methods have also been developed for the isolation of biomolecules from polyacrylamide gels using electroelution techniques.

Work has continued on the development of an electrospray ionization source for the FTMS. The purpose of this work is to ionize large biomolecules and to interface separation methods with the structural characterization capabilities of the FTMS. The electrospray source is external to the magnetic field of the FTMS and generates ions at atmospheric pressure followed by differential vacuum pumping and passage through ion optics necessary for coupling to the FTMS. SIMION calculations were used to model low energy ion injection into the fringing magnetic fields of the FTMS. The source is currently being tested on a quadrupole instrument and, after examination of experimental parameters, will be interfaced to the FTMS. Other researchers have generated multiply-charged ions from very large peptides and oligonucleotides using electrospray. Although this source shows some promise for the investigation of large compounds, additional research will be required to ascertain whether this source will be truly analytically useful for the characterization of unknown compounds due to the complexity of the resulting spectra. Investigations are currently under way to more fully probe and control the chemistry occurring in the electrospray process so as to allow the spectra to be more easily interpreted.

J. C. Dunphy, R. L. Hettich,*
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*ORAU Graduate Research Program
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Characterization of Laser Desorption and Laser Ablation Processes

In order to understand and optimize laser desorption for biological compounds, we have begun an investigation of the fundamental nature of laser effects on substrate surfaces. The objective of this work is to examine the effect of matrix enhancement by

compounds such as nicotinic acid as well as to probe the nature of laser ablation on substrate surfaces. We have noted the ease of generating cluster ions from various surfaces by laser ablation and have begun to examine in detail the structures, energetics, and ion-molecule reactions of these cluster ions. For example, carbon cluster ions containing as many as 150 carbon atoms per cluster can be easily generated by laser ablation of graphite targets. The structures and properties of these clusters are currently under examination in a number of research groups, due to the importance of these species in areas such as catalysis and combustion processes. We are particularly interested in the application of laser ablation FTMS for the generation and structural characterization of species which are important in the materials science field.

Carbon clusters C^{n-} where n = 2-10 were generated and examined by LD FTMS. The fragmentation of these cluster ions by collision-induced dissociation indicated predominant loss of C_3, which agreed well with results obtained by other researchers. These cluster ions were trapped in the FTMS cell and allowed to react with oxygenated compounds such as oxygen, water and carbon dioxide. While these clusters have high electron affinities and are completely unreactive with most small compounds, they do react readily with water, forming C_nOH^- and $C_nH_2O^-$ as the ionic products. The formation of C_nOH^- dominates when n is an odd number whereas $C_nH_2O^-$ is observed when n is an even number. Collision-induced dissociation of these product ions indicated facile losses of CO and (C_2OH), although loss of OH or H_2O was never observed. C_3^- is the only cluster ion that will react with CO_2, and yields C_3O^- as the product ion. Collisional dissociation of this ion gave C_2^- as the only fragment ion, once again suggesting that CO loss from oxygenated clusters is a favorable pathway.

We have extended these studies to examine a variety of substrates in collaboration with other researchers. Work is in progress with R. N. Compton of the Health and Safety Research Division to examine larger carbon clusters such as buckminsterfullerene, C_{60}, with particular emphasis on the detection of multiply-charged cluster ions.

Other investigations include examination of meteorite samples with Bishun Khare and Carl Sagan (Cornell) to identify the higher molecular weight organic polymers present.

R. L. Hettich

Development of Methods for Detection of Chemical Agents in Air, on Surfaces, and in Physiological Media

The last annual report described our development of instrumentation for the rapid, confident detection of trace levels of chemical agents in air as part of a U. S. Army project. This equipment consisted of a commercial ion trap mass spectrometer (ITMS) and an automated thermal desorption (ATD) unit which was specially designed and constructed here. After the entire system was tested for about a year at Tooele Army Depot, the ATD was returned for some minor improvements, including circuitry for enhanced temperature control, error checking and more versatile communication with external devices. The ATD is now back at Tooele running routinely with either a GC with a flame ionization detector or with the ITMS.

Based on the success of the Tooele project, we were asked to develop methods for the rapid trace detection of agents on surfaces and in agricultural media as part of the overall issue of personnel re-entry after environmental exposure to chemical agents. Building materials, such as brick, concrete block, gypsum wall board and wood need to be tested to determine how much contamination is present and how complete decontamination processes are. In addition, we are also measuring rates of diffusion of chemical agent simulants into these various building materials to determine how effective simple surface measurements with a special surface sampling probe with the ITMS will be. Agricultural products such as meat, milk, wheat and forage crops also need to be tested to determine if they are fit for use after exposure to chemical agents. Rapid methods of sample isolation for subsequent thermal desorption into an ITMS are being developed. In one approach, countercurrent dialysis is being evaluated to strip the lower molecular weight agent from the complex sample

matrix and concentrate it on a sorbent trap. The development of this isolation method is described in detail elsewhere in this report. The overall goal of this activity is to develop methods which could be used in the field to test buildings and agricultural products in an emergency situation so as to assure the safety of human health and the environment.

M. V. Buchanan, R. H. Ilgner, J. E. Caton, M. B. Wise

Rapid Detection of Organics in the Environment: Water, Soil and Air

Work has continued on the development of rapid methods of detecting and quantitating trace organics in environmental samples, including air, water and soil. Previously, we had demonstrated that volatile organics in water and soil samples may be determined in as little as three minutes by purging a 25 mL water sample or a 5 g soil sample slurried in water with a stream of helium (150 mL/min). The effluent is introduced directly either into an ITMS or a quadrupole instrument outfitted with a glow discharge ionization source. Recent work has centered on establishing and verifying standard analytical conditions. A series of twenty-five EPA Target Compound List volatile compounds were examined to determine the time required to purge the materials from water. Spectral interferences from these compounds were also examined. Extensive tests with benzene, trichloroethylene and tetrachloroethylene in water demonstrated good linearity for tetrachloroethylene from 1 to 1000 ppb (by volume) and 1 to 100 ppb for benzene and trichloroethylene. The effect of sample matrix on the analysis of organics in soil and water was also studied. For example, changes in pH (pH = 2, 10 and neutral) had little effect on the purgability of the compounds from water. Different soil types (high or low clay content, sandy, etc.) did exhibit differences in recovery, ranging from 17 to 90%. This range of recoveries is due in part to irreversible adsorption of the volatiles to soil particles as well as losses during sample preparation. With work on volatile compounds nearing completion, studies have begun with the

rapid analysis of semi-volatile environmental compounds.

A new inlet system has been designed which allows direct, real-time sampling of air into the ITMS and analysis with conventional electron impact or chemical ionization. This inlet includes a small air sampling pump and a pulsed helium valve to maintain optimum detection of compounds with good sensitivity and mass spectral resolution. Initial studies scoping the detection limits for thirty-two EPA volatile organics found that these compounds could be detected in the low- to mid-part-per-billion range. A test facility for generation of known concentrations of volatile organics in air was designed to aid in the evaluation of the ITMS for direct air sampling. A syringe pump was used to accurately meter quantities of organics introduced in a stream of air, which was subsequently introduced into the ITMS. Tests with gas standards of known concentrations showed that the test generation facility was accurate to within 5% of the targeted concentration.

Experiments to date have shown that the ITMS can be reliably and routinely employed for the rapid detection of organics in water, soil and air using direct sampling methods. The instrument is rugged and can operate for periods of six months or more without replacement of the electron filament or electron multiplier. In addition to MS/MS capabilities, the ITMS can be used to selectively ionize compounds via chemical ionization processes to aid in the detection of targeted compounds in complex mixtures. The glow discharge instrument is also rugged and has about the same sensitivity as the direct sampling ITMS. This instrument, however, is not as flexible as the ITMS and might best be used as a routine monitor for a targeted compound.

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

Rapid Detection of Drugs and Metabolites in Physiological Media

As part of an ongoing project for the National Cancer Institute to investigate the effects of environmental tobacco smoke and passive smoking, a method for the rapid detection of

markers of exposure to tobacco smoke was developed using the ion trap mass spectrometer. In this method, 1 microliter aliquots of untreated urine were thermally desorbed directly into the ITMS. Isobutane was used to selectively ionize nicotine and cotinine, a metabolite of nicotine, and fragments from collision-induced dissociation of the $(M + H)^+$ ions of each compound were quantitatively monitored. Detection limits of approximately 10 pg for each of these semi-volatile compounds in 1 μL of unconcentrated urine were observed, with a linear dynamic range of two to three orders of magnitude. These detection limits are more than sufficient for the study of urine from smokers with no sample concentration. Analysis time was less than four minutes per sample. To improve quantitative measurements, deuterated nicotine and cotinine were used as internal standards. Analysis of an EPA/NIST Reference Material, 8444, both low and high level samples, demonstrated that the direct sampling method has excellent accuracy and precision. Additional pilot studies were also conducted on the rapid detection of other nicotine metabolites, including nicotine-N-oxide and 3-hydroxycotinine. These studies indicated that this approach also shows promise for these more polar and less volatile compounds.

A similar sampling approach was used to detect a variety of drugs in urine, including cocaine, codeine, phenobarbital, tetrahydrocannabinol, amphetamine, and methamphetamine. The detection limits for these drugs were at or below levels required for drug screening purposes. Additional work is being conducted with other drugs and other matrices at present. For example, in a project for the Food and Drug Administration, methods for the rapid analysis of drugs in animals are being developed as a means of screening animals prior to slaughter to assure that the meat is safe for consumption. Two anthelmintics, phenothiazine and piperazine, are thermally desorbed from Tenax into the ITMS for selective detection using chemical ionization and collision-induced dissociation. Methods for the rapid isolation of trace drugs from biological media are being developed in collaboration with the

Separations group to provide enhanced sensitivity and to prepare isolates of metabolites suitable for chemical derivatization.

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

Development of Advanced Trapped Ion Instrumentation

The successful completion of several projects involving ion trap mass spectrometers has identified a clear need for a smaller, more portable instrument which could be used in the field, for example, for environmental monitoring. Initial design of a new trapped ion instrument has begun and the first prototype is intended to be cart portable. The instrument will consist of a novel trapped ion analyzer cell, smaller vacuum manifold, and an integrated electronics and data station. SIMION plots have been used to model the new analyzer. This new analyzer is substantially smaller than present designs, but maintains the same ion volume to retain optimal mass resolution and dynamic range while avoiding problems with space charge. The new cell is presently under construction and initial tests should begin early in 1991. The instrument will be outfitted with readily interchangeable sample inlets to allow application to a variety of sample matrices. As part of this project, we are collaborating with Scott McLuckey (Analytical Spectroscopy Section) to develop methods for detecting multiple compounds in complex mixtures under MS/MS conditions. Work is also under way to develop and demonstrate field instrumentation for direct sampling ion trap mass spectrometry based on the Finnigan ITS 40. Our studies of ITMS to date suggest that many important applications require only the sensitivity and the direct sampling components of our technology and that these promise to be achievable with the ITS 40. The work involves interfacing this instrument with our sample introduction inlets and modifying the system to provide sensitivity comparable to that observed using the ITMS. Steps are also being taken to

improve transportability and field-hardiness.

M. V. Buchanan, M. B. Wise,
*C. V. Thompson, A. V. Blalock**

*Instrumentation and Controls Division

Differentiation of Crude Oils

Direct sampling ion trap mass spectrometry (DS ITMS) has been demonstrated to be an effective method of differentiating crude oils. Twelve Middle Eastern crude oils were examined by conventional gas chromatography with flame ionization detection, combined gas chromatography/mass spectrometry (GC/MS) and DS ITMS. The chromatographic profiles of the crudes consisted primarily of paraffinic components, which made it difficult to unambiguously differentiate the crudes. GC/MS with selective methanol chemical ionization was used to preferentially investigate the aromatic compounds present without interference from the more prevalent paraffins and did yield some insight into the identity of the crude oils. Both of these methods required 30 to 60 minutes of analysis time due to the chromatographic separation step. The DS ITMS method showed remarkable ability to differentiate the crude oils in as little as three minutes total analysis time because no chromatographic separation was involved. Selective ionization with water allowed alkyl aromatics to be observed, and comparisons of the abundances of these compounds permitted most of the crude oils to be differentiated. In these pilot studies, only alkyl benzenes were monitored. The differentiation of the oils by DS ITMS should be enhanced further by monitoring higher molecular weight aromatics, such as alkyl phenanthrenes and anthracenes, which have been successfully used to differentiate oils by chromatographic methods.

R. L. Hettich, C. Y. Ma,
M. V. Buchanan, M. R. Guerin

Special Spectroscopic Studies

Special spectroscopic studies were conducted in support of many of projects within the Organic Chemistry Section and for other ORNL divisions. Most of these studies involved GC/MS with either electron impact or chemical ionization, but nuclear magnetic resonance and infrared spectroscopy were also employed. Fourier transform mass spectrometry was also used in a number of studies when conventional mass spectrometric methods were not sufficient.

Negative ion chemical ionization GC/MS was used in support of several environmental studies in the Organic Analysis group, including the identification and quantitation of technical chlordane in waste tank samples and confirmation of pesticides and polychlorinated biphenyls (PCBs) in various samples. Laser desorption FTMS was also used to characterize higher molecular weight components in waste tank samples. A novel method was developed to differentiate Arochlor mixtures based on the relative abundance of PCB homologs and pattern recognition.

GC/MS and ^{1}H NMR were used to characterize fractions from Exxon Valdez crude oil fractions in an effort to identify potentially harmful compounds. Thermal desorption methods were used with GC/MS for the analysis of organics collected from rocket exhaust in support of a program in the Special Projects Group. This method was also used to identify compounds present in air collected from a "sick" building, where occupants complained of ill effects. Various samples have been investigated for researchers in other divisions. For example, a series of products from irradiated nucleic acids have been characterized by FTMS (J. E. Turner, Health and Safety Research Division). FTMS was also used to characterize a series of isomeric pteridine-related compounds (K. B. Jacobson, Biology) and a series of complexing ligands used in radiolabelling studies (F. F. Knapp, Health and Safety Research Division).

C. Y. Ma, R. L. Hettich, M. V. Buchanan

SEPARATIONS AND SYNTHESIS

W. H. Griest

The principal objective of this group is to develop and apply separations methods for the isolation, identification, and quantitative determination of organic chemicals in complex media. An additional objective is to integrate organic synthesis and separations methods with collaborators' spectroscopic measurements so as to address specialty issues requiring knowledge of chemical processes and composition. Gas and liquid chromatography, supercritical fluid extraction and chromatography, and capillary zone electrophoresis are the principal technologies being used and/or investigated. Current chemical studies include the identification of bioactive and/or biological transformation products in complex mixtures and the identification of processes responsible for the deterioration of selected military munitions. The combination of separations and chemistry expertise has led to a major initiative in radioactive mixed waste characterization. Initial attention is being given to establishing an analytical services facility capable of generating EPA-mandated waste characterization data.

Displacement Chromatography for Trace Analysis

Investigations of enrichment for trace analysis were continued with the ORNL/UT Distinguished Scientist Research Program. Previous demonstrations that the semi-ideal model is useful for accurately predicting band profiles of trace-level compounds incompletely resolved from major sample constituents in overloaded elution chromatography have led to related studies using displacement chromatography. Unlike elution development where bands become broader and more dilute as they migrate through the column, the zones in displacement become more concentrated. At appropriate displacer concentrations and column lengths an isotachic train develops with sharp boundaries defining the various regions for the sample components. Significant band compression may be obtained for trace

constituents and this enrichment has been studied both theoretically and experimentally. The theoretical model is based upon the solution of the mass balance equations for non-linear chromatography, assuming competitive Langmuir isotherms.

Experimental studies utilized compounds in the low to sub-ppm range and were detected by fluorescence independent of the displacer which was monitored by UV absorbance. The trace compounds were pushed by the displacer front but were free to diffuse forward (i.e., the migration was not restricted by interaction with earlier eluting major components). Data were obtained for β-naphthylamine, an impurity found in β-naphthylamine, and a coumarin dye, employing various phthalates as displacers. As predicted, the trace component bands were found to be significantly narrower (hence more concentrated) compared to linear elution chromatography. Their apparent efficiencies may exceed the nominal column efficiency by 100-fold and detection limits could be improved by over an order of magnitude. Since displacement chromatography also accommodates much larger sample quantities than does elution chromatography, an overall reduction in detection limits of 100 to 1000-fold may be obtained for trace compounds for which displacement procedures may be developed.

These studies have defined some of the advantages of displacement chromatography but have also illustrated some of the difficulties in establishing the methods. The most challenging requirement remains the identification of a suitable displacer with adequate solubility, appropriate retention volume and chemical characteristics that permit selective on-line monitoring without interfering with detection of the trace substituents. For critical analyses performed on a routine basis the gain in sensitivity may well compensate any additional effort involved in methods development.

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*UT Predoctoral Program

Extraction and Isolation Methodologies

Supercritical fluid extraction is being evaluated as an analyte isolation method. The low viscosities and high solute diffusion coefficients characteristic of supercritical fluids are increasingly being exploited for the extraction and recovery of organic compounds from a variety of sample matrices such as soil, sediment, diesel exhaust and ambient air particulates. Supercritical fluids offer faster and more efficient extractions than does organic solvent extraction. In a project for Rocky Mountain Arsenal, we are evaluating the supercritical fluid extraction (SFE) of soil samples for the determination of chemical warfare agents. The chemical warfare agent simulants dimethylmethylphosphonate (DMMP, simulant for agent VX), chloroethylethylsulfide ("half-mustard" or HD/2 for agent HD), diisopropylfluorophosphate (DIFP, simulant for agent GB) and diisopropylmethylphosphonate (DIMP, another simulant for agent GB) can be extracted nearly quantitatively from soil in a 5 minute SFE using 5 wt% methanol in carbon dioxide at 3 x 10^7 Pa and 60° C. At present, the supercritical fluid extractant is depressurized in 2 mL of solvent for injection and analysis of an aliquot by GC. This off-line SFE approach produces a cleaner extract than conventional solvent extraction, but approximately the same low-ppm detection limits. Sorption of the extract onto a solid sorbent cartridge promises to increase sensitivity by one to two orders of magnitude. Another advantage of this latter approach is the complete elimination of toxic solvent wastes.

Solid phase extraction and countercurrent ultrafiltration are being evaluated as isolation methods especially compatible with Spectroscopy group methods of direct sampling mass spectrometry. Solid phase extractants traditionally have been used to achieve highly efficient recoveries of organic compounds from aqueous liquids, but before now they have not been used to extract compounds from solid biological samples. In a collaborative project with the Organic Spectroscopy group, we have been examining solid phase extraction

methods for recovering chemical warfare agent simulants from water, plant tissues, milk and meat for analysis by thermal desorption ion trap mass spectrometry. Several sorbents were compared for their ability to collect simulants from water and milk in a flow-through sampling mode. Tenax resin was found to be superior to a styrene-divinyl benzene polymer (XAD-2), a C_{18}-modified silica, and a cross-linked vinylpyridine polymer (MP-2). DMMP was the only agent for which low recoveries were obtained. Placing dialysis tubing and a drying agent around the Tenax permitted static extraction of the simulants from plant tissues and meat with separation of the resin from contaminating macromolecular constituents. Slow analyte mass transfer, however, required long equilibration times (days) using this scheme. A novel countercurrent extraction system was devised to speed up analyte extraction. The sample (as a liquid or slurry) is recirculated through an ultrafiltration cartridge at the same time that water is pumped across the outside of the ultrafiltration membrane in the opposite flow direction. The water is continuously recirculated through a Tenax cartridge to collect the extracted analyte. We expect faster and more efficient recoveries.

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Capillary Zone Electrophoresis of Nucleic Acid Constituents

Capillary zone electrophoresis has been explored as a method of separating DNA adducts and short-chain oligonucleotides. A variety of parameters influence retention behavior in capillary electrophoresis including buffer composition, pH, chemical modification of the inner walls of the capillary surface and the addition of complexing agents or micelles to the buffer. The effects of micelle concentration, voltage and solute concentration on the separation of various nucleic acid constituents were previously examined in our laboratory. These studies have been extended to include the effects of buffer composition.

Nucleic bases and pyrimidine dimers were easily resolved using phosphate/borate buffers containing sodium dodecylsulfate. Short-chain oligonucleotides (up to six base units) were also separated although isomers differing in base sequence were either unresolved or incompletely resolved. Urea, which has been reported to reduce stacking behavior, appeared to have no effect on the results. Buffers containing substituents which could complex to the phosphate groups of the nucleotides were found to approximately double migration times and reduce efficiencies. This may reflect partitioning behavior or slow kinetics in complex association and dissociation. For oligonucleotides of differing chain lengths the best separations are obtained using molecular sieving agents. We are currently investigating methods of preparing novel inorganic gels in capillaries and evaluating their suitability for electrophoretic separations of biopolymers.

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Mixed Mode High Performance Liquid Chromatographic Determination of Explosives and Metabolites

Last year, we reported the development of a mixed mode reverse phase/anion exchange high performance liquid chromatography (HPLC) method for the determination of explosive compounds and trinitrotoluene (TNT) metabolites. This method has been extensively applied this year. Our analytical procedure for aqueous leachates and soils or composts was subjected to the U. S. Army Toxic and Hazardous Materials Agency Level IA Certification. It now is being applied to the analysis of explosives processing wastes composts and their EPA Synthetic Precipitation Leach Test leachates. The composts are from a field composting experiment designed to decontaminate lagoon sediments at the Umatilla Army Depot. Considerable biotransformation of the TNT to monoamino derivatives is being observed. The leachates and also organic solvent extracts are being tested for bacterial mutagenicity and aquatic toxicity by collaborators in the Health

and Safety Research and Environmental Sciences Divisions. The HPLC analytical method also has been applied to 168 samples of deer, quail and rabbit tissues extracted by other collaborators in the Environmental Sciences Division. No explosives or TNT metabolites were found in any tissues within a detection limit of 0.1 mg/kg. Surrogate standards, matrix spikes, and blanks were extensively used for quality assurance.

The mixed mode HPLC method has been extended to the determination of energetic nitroesters (nitroglycerin and diethyleneglycoldinitrate), stabilizer (diphenylmethylurea) and their degradation products in munitions components as a part of a predictive surveillance study (see below). Nitroesters were found in trace concentrations (ca. 0.01 wt%) in the case wall material of one-month-old M829 rounds, and in low percent concentrations in the case walls of rounds subjected to severe accelerated environmental exposures. Nitrated diphenylamine degradation products of the stabilizer also were observed in the latter.

J. E. Caton, C.-h Ho, W. M. Caldwell, W. H. Griest

Radioactive Mixed Waste Characterization

A continuing activity in this group has been the preparation of radioactive samples for organic analysis. This activity concerns samples which require preparation in radioactivity zoned facilities, using modifications of EPA SW-846 methods. This preparation of organic extracts for volatile or semivolatile organic compounds usually results in sufficient decontamination that the final analysis can be conducted by the Organic Analysis group in nonzoned conventional GC-MS or GC laboratories using EPA SW-846 or Contract Laboratory Program instrumental procedures. This year, analyses and reporting were completed for the Melton Valley storage tanks, and for additional inactive nuclear waste tanks. In a new project, almost 280 samples were received from the DOE Fernald plant for analysis of volatile organic compounds

and toxic metals. These were received at Building 2026 and were prepared (as required) and distributed to other ACD groups for analysis. Sample documentation was a difficult task because nuclear material accountability as well as chain of custody had to be maintained in sample transfers, and the return shipment of materials classified as limited quantities of radioactive materials entailed much additional HP monitoring, repackaging and paperwork.

We are now expanding our radiochemical facilities into an additional laboratory room for conducting organic solvent extraction and concentration. The changeroom/bathroom has been completed, allowing our staff to changeout without having to move through a regulated zone to a changeroom on the lower floor. We are establishing the capability to conduct the EPA Toxicity Characteristic Leaching Procedure (TCLP) zero headspace extraction of volatile organic compounds in radioactive samples requiring a radiochemical hood environment. A state-of-the-art HPLC with ternary gradient capability, automatic sample injector, diode array UV detector, and PC data system also was purchased and installed. It will be dedicated to the analysis of radioactive samples for constituents not suitable for GC or GC-MS analysis, e.g., herbicides in TCLP leachates.

R. L. Schenley, J. E. Caton, W. H. Griest

Predictive Surveillance of Munitions

A project for the U. S. Army Armament, Munitions, and Chemical Command is aimed at understanding the causes of and developing predictive models for the deterioration of an adhesive joint and nitrocellulose case wall in the M829 120 mm kinetic energy antitank round. Laboratory studies of "coupons" cut from the case wall of the M829 round and centered around the adhesive joint identify important factors in the deterioration of the M829 round. A major accomplishment this year was the acquisition and installation of a custom-designed and fabricated environmental chamber which is

temperature- and humidity-controlled and explosion-proof. Coupon exposures to different temperatures and humidities have established humidity as an important factor in the deterioration of the adhesive joint and case wall. At elevated temperatures, the deterioration is severe. The nitrocellulose in the case wall apparently is depolymerized quickly at 85° C, but at moderate temperatures (<50° C), the deterioration in strength and hardness is largely reversible and perhaps is due to solvation and swelling. Addition of propellant to the coupon exposures reduced the reversibility of the deterioration effects, probably through reactions of the nitrocellulose with oxides of nitrogen and solvation of the adhesive by nitroesters emitted from the propellant. Coupon tests of liquids to which the full-up rounds may be exposed during deployment (such as diesel and turbine fuel, turret hydraulic fluid or cleaning agents) showed little effects, but a common production line degreaser (methylethyl ketone) rapidly caused adhesive disbonding.

Accelerated environmental exposures and subsequent physical tests of full-up M829 rounds are being conducted by the Milan Army Ammunition Plant to develop the database for predictive modelling. The exposure experiments are approximately 60% complete, but initial evaluation of the data suggests that round-to-round variability may limit the confidence of a mathematical model for predicting environmental effects on the rounds. A study of this variability and its causes and effects on modelling is in progress.

A scoping task nearing completion this year is evaluating the feasibility of an indicator strip which is affixed to the side of the M829 round and which changes color when the case wall materials are nearing the point of failure. Because both nitroester migration from the propellant and moisture contribute to deterioration, color change indicator chemistries for these factors were surveyed. The main requirements are compatibility with the case wall material and the formation of a visible color change from stable reagents. Work to date suggests that the Griess reaction (involving the formation of a diazo dye) would be suitable for indicating nitroester

accumulation, and studies now are centered around adapting the reaction to a solid surface patch. Several inorganic salts dramatically change color with hydration state and appear useful as a reversible case moisture indicator. The main problem is in controlling the sensitivity of the indicator. This may be overcome with semipermeable membranes.

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Characterization of Exxon/Valdez Spilled Oil

The exposure of large numbers of cleanup workers to spilled oil over several months of cleanup operations suggests the need for an assessment of any unusual occupational health hazards. To address this issue, we subjected weathered spilled oil and hold oil from the Exxon/Valdez to biodirected chemical fractionation and target chemical analyses based on extensive earlier biodirected separations of natural and synthetic crude oils. Potential inhalation, ingestion, and dermal contact hazards were considered. Simulated distillation and also analysis of volatile organic compounds showed a considerable reduction in organic vapors available for inhalation after the spilled oil had weathered. However, a large spill would release large quantities of benzene into the environment in the early stages of the oil spill. Analysis of toxic metals and 4-6 ring polycyclic aromatic hydrocarbon dermal tumorigens in the oils and Ames bacterial mutagenicity testing (by collaborators in the Health and Safety Research Division)

of chemical class fractions of the oils did not reveal any unusual hazards in the weathered oil relative to the hold oil. Overall, the results suggest that the weathered spilled oil should not pose occupational health hazards different from typical petroleum crude oils.

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SPECIAL PROJECTS

R. A. Jenkins

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

Tobacco Smoke Studies

Our studies continue to focus on the chemistry and measures of exposure to environmental tobacco smoke (ETS). This includes the evaluation of ion trap mass spectrometry for the determination of airborne and urinary nicotine (Spectroscopy group), a comparison of area versus personal sampling strategies for exposure assessment, and the preparation of a monograph on the chemistry of ETS. A special study is also under way to determine whether dibenzo(a,l)pyrene is present in mainstream cigarette smoke.

Laboratory studies described in the previous annual report demonstrated that our breathing zone personal sampling device and our stationary area sampling device provided equivalent results when sampling the same environment. Field studies were performed this year to determine the influence of sampling strategy on exposure assessments. Thirty public areas in the metropolitan Knoxville area were sampled for a single day each by both methods. The types of locations sampled included laundromats, restaurants with salad bars, transportation waiting areas, cocktail lounges, offices, bowling alleys and pool hall/video game/pinball parlors. The area monitors, typically two each mounted in a briefcase for unobtrusive sampling, were employed in a stationary manner. The personal monitors were worn by individuals who periodically moved through the environment in a manner appropriate for that particular environment. We found that the nicotine concentrations versus sample location were log normally distributed, and ranged from 0.2 - 90.6 $\mu g/m^3$ for the personal sampler, and from 0.0 - 72.9 $\mu g/m^3$ for the area monitor. The relative standard deviations for multiple samples acquired in each location were typically high, suggesting a great deal of spatial inhomogeneity in the locations being sampled. Within the range of sampling variability, the stationary area samplers yielded nicotine levels comparable to those determined by mobile personal samplers over a wide range of field conditions.

Considerable progress has been made toward the preparation of a monograph on the chemistry of ETS for the Center for Indoor Air Research (CIAR). The principle objective is to provide a comprehensive tabulation and review of data generated in studies of ETS exposure. A secondary objective is to provide background information on smoke chemistry, sampling and analysis methods and non-ETS sources of indoor air contaminants as an aid for future research. Special attention is being given to respirable particulate matter, nicotine, carbon monoxide, volatile organic chemicals, trace organics (primarily polycyclic aromatic hydrocarbons and N-nitrosamines), oxides of nitrogen, and formaldehyde.

A special study is under way to determine whether dibenzo(a,l)pyrene

(DBALP) is present in mainstream cigarette smoke. DBALP has recently been found by others to be 100-1000 times more carcinogenic than is benzo(a)pyrene. This implies that concentrations in cigarette smoke as little as one part per billion might contribute to its carcinogenicity. Our initial approach involved the traditional combination of precipitation, liquid-liquid extraction, multiple liquid chromatographic isolation steps, radiotracer (benzo[a]pyrene-^{14}C) recovery, and final analysis by fluorescence detection high performance liquid chromatography (HPLC). The approach suggested the presence of DBALP in one sample at a concentration of approximately 20 ppb but gas chromatographic data indicated that the HPLC peak ascribed to DBALP may be due to some other chemical. The extensive sample processing resulted in low recoveries and may have introduced contaminants. We are currently developing a new method which minimizes sample processing and relies on thermal desorption gas chromatography mass spectrometry (Spectroscopy group) for final measurement. Cigarette smoke, diesel particulate matter and possibly additional materials will be analyzed.

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C. E. Higgins, R. L. Moody

Aerosol Generation and Characterization

Characterization of exhaust from test scale rocket motors from hand-held anti-tank weapons systems has continued. The purpose of the effort is to provide both a data base for health risk assessment and an input into improved computer model projections of exhaust products. For this study, the concentrations of both major and minor vapor and particle phase constituents are being determined. Since many of the potential species are reactive, real-time monitoring systems to determine levels of particulates, ammonia, oxides of nitrogen, hydrogen cyanide, carbon monoxide and dioxide, and hydrogen chloride are used. Analytical methods validation experiments were performed using free burns of small

quantities of the candidate propellants in a small chamber. Samples for the actual characterization studies are collected from firings of scaled down test motors in a 19.6 m^3 chamber at the Army's Signature Characterization Facility (ASCF) at Redstone Arsenal in Huntsville, Alabama. Data from the most recent burns of a particular propellant formulation indicated that CO levels reached 85 ppm in the chamber, while NO reached only 1.3 ppm. Particulate phase lead reached 16,000 $\mu g/m^3$, suggesting a significant health risk from this component.

This has been a joint project with the Computing and Telecommunications Division, whose staff have examined existing computer models, to determine the extent to which such models can predict the concentrations and mole fractions of major and minor toxic constituents produced. Computer modeling was performed with the NASA-Lewis CET-86 version. This approach obtains estimates of equilibrium concentrations by minimizing free energy. The predicted mole fractions for CO were typically 20 - 35%, except for the predominantly inorganic formulation. The model correctly predicted only minor amounts of ammonia and essentially no hydrogen cyanide. Predicted mole fractions did not vary a great deal with such input parameters as exit/throat area ratios or small changes in the heats of formation of the various compositions. The accuracy of the predicted CO/CO_2 ratios was low for all but one of the formulations. In general, if the model were to be used in its present state for health risk assessments, it would be likely to overestimate exposure to CO.

Work has continued on the generation of cigarette smoke test atmospheres. The University of California - Davis (UCD) is carrying out a study on the effects of ETS on the lung development of rodent neonates. Our responsibility has been to develop a system for the generation of a controlled atmosphere of simulated ETS, using as a surrogate sidestream cigarette smoke (SS) which has been diluted sufficiently to mimic levels encountered in ETS environments. The atmosphere will be used to expose rodents at the UCD.

We generated the test atmosphere by collecting the SS from reference cigarettes which are being puffed once

per minute using a small smoking machine. The cigarette is enclosed in an ORNL Sidestream Generator, a glass assembly which channelizes the SS using laminar flow air currents. The collected SS is then dispersed into a 1.4 m^3 chamber, through which the air flow is ca. 500 L/min. From that point, a portion of the diluted SS is routed through a 1.5 m long stainless steel tube, where it is mixed with ambient air, further diluting it into a second, 0.4 m^3 chamber. Flow can be easily varied through the second chamber to produce the desired particulate concentration. The system is capable of achieving Respirable Suspended Particulate (RSP) concentration ranges in the second (exposure) chamber of ca. 100 - 1300 $\mu g/m^3$. Real time monitoring systems employed include nondispersive and electrochemical CO monitors, and light scattering and piezobalance particulate mass monitors. Nicotine will be determined by collection on XAD-4 resin, followed by extraction and analysis using GC with nitrogen specific detection. This system was set up at UCD in the late summer, and the staff there is currently fine tuning the system prior to animal inhalation exposures.

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Field Analytical Technology

Field analytical methods are becoming an increasingly important component of environmental restoration activities. We are currently collaborating with the Spectroscopy Group to develop fieldable instrumentation and methods and we continue to carry out special studies in environmental monitoring.

Work on fieldable instrumentation has centered on the development of solid sorbent sampling for use with the Ion Trap Mass Spectrometer (ITMS). When the ITMS is used in the direct sampling mode, the majority of the sampled stream is vented to atmosphere. We are examining the possibility of collecting the vented material to allow for repeated or

confirmatory analysis following field screening. We chose to evaluate a resin combination for this work, thus adopting the same philosophy as we previously used for collection of air samples with the "original" triple sorbent trap (TST). The sorbent combination evaluated was Carbotrap C, Carbotrap, and Carbosieve S-III. The first two resins are classified as graphitized carbon black and the third resin is classified as a carbon molecular sieve. The combination of all carbon-based resins allows for heating of the trap during thermal desorption to 350° C. This permits a faster and more complete desorption. For this evaluation we chose parameters, where applicable, which are used during actual ITMS water sample analyses. Analyte recoveries from spiked water samples analyzed originally on the ITMS and reanalyzed from the sorbent trap on the GC/FID system averaged 77% for a five-minute sample purge and 110% for a ten-minute sample purge for the 34 EPA target compound list (TCL) volatile organic compounds. The results of this preliminary study are very encouraging, and suggest that such a trap could be used to effectively collect and stabilize volatiles purged from soil and/or water samples in the field; then only these small traps need be returned to the laboratory for analysis.

A special study was carried out this period to support an environmental remediation effort. Initial sampling and analysis of air above a Superfund Site in Ashland, Massachusetts, suggested the presence of dimethyl mercury (DMM) in the soil. DMM is a highly toxic organo-mercurial, formed by microbial metabolism of mercury-containing dyes under anaerobic conditions. A significant release of DMM during remediation activities, such that perimeter levels would exceed 10 $\mu g/m^3$, would be sufficient to halt work at the site. The Army Corps of Engineers asked us to determine the efficacy of two approaches suggested by the USEPA for the determination of airborne DMM. One approach involved using a Jerome real-time mercury monitor modified to detect only DMM. It was necessary for us to evaluate the response of the system in the presence of a number of contaminants thought to be present at the site, including volatile organics. In

addition, we had to develop a procedure for calibrating the response of the instrument at the 1 - 2 $\mu g/m^3$ level. A number of approaches were tested. The most convenient proved to be the generation of standards in Tedlar bags. In general, the organics did not interfere with the determination. However, the reproducibility of the system response was minimal. Another evaluated approach involved a portable GC using a photoionization detector. Because of the potential for a number of volatile organic compounds (VOC's) to be released from the soil as a result of remediation activities with concomitant air contamination, the primary concern for GC-based analysis was possible coelution of these components with DMM. A number of target VOC's were examined for interference with DMM using a Photovac 10S10 GC/PID acquired for this project. The 10S10 uses a wholly encapsulated 10 m CPSIL-5 capillary column maintained at one of three temperatures, 30°, 40°, or 50° C, under isothermal conditions. We found that the major interfering VOC was benzene, which nearly coeluted with DMM at all of the column temperatures and carrier gas flow rates examined. The 10 m column was replaced with a 30 m DB-5 megabore capillary column which, since it was mounted externally to the GC, was kept at room temperature. Alteration of the carrier gas flows resulted in good (near baseline) separation of the benzene from the DMM. Operating at the highest sensitivity setting, we achieved a limit of detection of 5 $\mu g/m^3$ for DMM, or about one-half of the action level. We traveled to the Superfund site to train contractor personnel in the use of the systems. While the performance of the systems was initially acceptable, it became clear that the EPA procedures were inadequately rugged to operate under the range of environmental conditions encountered in the field.

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ORGANIC ANALYSIS

M. P. Maskarinec

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

The primary functions of the group are supported by four interdependent efforts: 1) sample receipt and tracking; 2) sample preparation; 3) gas chromatographic and gas chromatography/mass spectrometric analysis and; 4) reporting and quality control. In each of these areas, both staff and equipment capabilities have been expanded and/or upgraded during the previous year. In addition, we have been successful in our efforts to obtain certification to perform drinking water analyses from the State of Tennessee. We also spent considerable time and effort preparing for the DOE Tiger Team review.

Sample Receipt and Tracking

The efforts of the group are highly dependent on sample handling and tracking. Our sample tracking/chain-of-custody procedures have been in place for well over twelve months, and the efforts during this period have been primarily directed at refinement of the process. A laboratory hood has been dedicated primarily to sample receiving, due to the possible hazardous nature of virtually all of our samples. New chain-of-custody forms have been designed and implemented; this complies with EPA guidelines and includes additional information for samples received from outside the Laboratory. We are in the process of designing new sample tracking

methods as workloads shift and new QC requirements are added. Our current efforts are primarily being directed at improvements to the data management system which are necessary and vital to maintain quality.

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Sample Preparation

Several major changes have occurred in the sample preparation laboratory. The most important by far has been the need to implement the Toxicity Characteristic Leaching Procedure (TCLP, Method 1311). This procedure is to be applied to waste samples for the determination of hazard based on toxicity. The test replaces, in large measure, the dilution/extraction methods used in the past, and greatly expands the number of waste types which require testing. The test is complex, expensive and labor intensive. The result of the test is an extract, which is an aqueous medium. The extract is analyzed for volatile organics, semivolatile organics, pesticides, herbicides and the eight RCRA metals.

The implementation of the TCLP strained the sample preparation area in almost every way possible. The sheer space requirements forced the dedication of one full laboratory, which still needed significant physical alteration. Equipment was procured at an estimated cost of $20,000. Because of the extraction of the semivolatiles and pesticides, samples were generated which needed attention by the water preparation lab. This added substantially to their routine workload. Finally, there are waste samples to which the TCLP cannot be applied, including oils, waste solvents, and large metal pieces. Therefore, the previously used dilution/extraction systems are still in use. As a measure of the impact of the TCLP implementation, the following numbers of samples were received in CY 1990: January-August, 0; September, 12; October, 65; November, 84; December, 95.

Other methodology improvements have been made in the sample preparation area. We added several pieces of equipment to upgrade sample preparation efforts. This equipment was procured from Organomation, Inc., and includes two "S-evap" units, which replaced manual Kuderna-Danish evaporators, two "N-evap" units, which replaced manual nitrogen blowdown, and two "Roto-X-tract-L" units, which are currently replacing manual continuous liquid-liquid extractors.

This equipment has provided several advantages over previous manual techniques. The S-evap is capable of performing the Kuderna-Danish concentration in less than half the time required by the manual technique. A similar advantage is seen with the N-evap. From the standpoint of solvent consumption, the S-evap has the capability of recovering the methylene chloride as it is evaporated. Experience to date indicates that the recovered solvent (which formerly went up the hoods) is sufficiently pure that it can be reused. This has reduced our solvent consumption by ca. 80% The N-evap allows control of the nitrogen flow to each sample individually, whereas the previous device did not have this capability. Consumption of nitrogen has been reduced by ca. 75%.

In terms of hood space, 24 Kuderna-Danish evaporators can now be placed in a hood which formerly had 8, and 24 nitrogen blowdowns can be done where 6 were possible previously. Twenty continuous extractions can be carried out in a California hood which previously had 8. This consolidation of space has also had a positive impact on safety. For example, in the previous situation, each continuous extractor was equipped with a Variac, heating mantle, and stirrer, all of which have been displaced by the new unit. Now one power cord per 10 extractors has replaced 24 cords per 8 extractors. In addition, the extraction unit has sensors which shut down the heater if the bath goes dry and shuts off both the heater and the cooling water flow if a water line develops a leak.

Data quality has been improved as well. Extraction of water samples using the new unit has proven to be much more efficient due to a higher rate of

solvent flow through the sample. Variability has been reduced since the heating unit is under temperature control; each extraction is performed at exactly the same rate. Temperature control has also resulted in increased precision of the concentration steps. Finally, the reduction in manual operations, with the attendant reduction in the need for empirical judgement, has improved the overall reliability of the preparation steps.

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Gas Chromatography

The gas chromatography laboratory is currently staffed by four chemists and one technician. Eight gas chromatographs are in place, five of which are equipped with automatic sample injectors. Five of the instruments are equipped with electron capture detectors and flame ionization detectors. Two automated purge-and-trap samplers are now available for analyses of volatile compounds. Six systems have capillary capability (either narrow bore or megabore); the remaining two instruments use packed columns. Seven of the eight gas chromatographs have considerable downtime, due to the age of the instrument and also to the increased numbers of highly contaminated samples. The laboratory contains a Nelson Analytical PC-based data system, which is currently being updated.

A Varian 3500 gas chromatograph was recently purchased. This instrument is equipped with single splitless injection, dual narrow bore columns, two electron capture detectors and dual data acquisition capabilities. This enables samples to be analyzed and confirmed on two different columns with a single injection, thus saving time and amount of sample extract used. This system is devoted to samples analyzed under Drinking Water (EPA Method 508), NPDES (EPA Method 608) RCRA

(EPA Method 8080) and CLP methodologies, primarily on very clean matrices.

Methodology used in the gas chromatography laboratory includes SW-846 (RCRA) methods (method 8080 is usually used for samples requiring pesticide/PCB analyses, almost 800 samples in 1990); NPDES/CLP (608); Drinking Water (508); TCLP (1311/8080); and waste oil PCB methods. The two gas chromatographs equipped with automatic purge-and-trap samplers are used to screen volatile samples before gas chromatography/mass spectrometry analysis; one instrument is devoted to screening TCLP extracts and the second instrument is used to screen waste dilutions and soil samples. BTX (Benzene-Toluene-Xylene) analyses are also performed on this instrument.

Acrylamide in water samples was analyzed using a modification of SW-846 method 8032. This method involves bromination of the acrylamide double bond and extraction with ethyl acetate. Gas chromatographic analysis is performed according to SW-846 method 8000. The method is intended to detect acrylamide in groundwater at the part-per-trillion level. In practice, we were able to obtain reliable quantitation limits of 10 ppb after modification of the method. The primary modifications were the replacement of diethyl phthalate with tetrachloro-m-xylene as the internal standard, and the use of two megabore capillary columns rather than the prescribed packed columns. Almost 400 samples were analyzed and/or reanalyzed using this method. In general, the performance has been good in terms of recovery, sensitivity, and reliability.

Ethylene glycol test kits (Chemetrics) are now used for water samples. The test requires approximately ten minutes and can detect 1 ppm ethylene glycol in water. Since relatively few samples are submitted, and those that are submitted usually require immediate turnaround, this has allowed us to provide better service while freeing up a gas chromatograph which was previously dedicated to this analysis.

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

Gas Chromatography/ Mass Spectrometry

The GC/MS laboratory performs routine analyses primarily on environmental samples. Currently, four staff members are assigned to the laboratory, with an anticipated addition of one or two chemists in the near future. Four instruments are available, two each for volatile analysis and semivolatile analysis. All instruments are maintained on vendor service contracts; this has allowed the instruments to be operated with minimal down time. Two additional VOA GC/MS systems will be purchased soon. One of the instruments will be dedicated to the 524.2 drinking water method, the other will be used to increase our capacity for VOA TCLP analysis.

One of the volatile organic systems has been converted to a wide bore capillary column. A 75m Restek column is being used and has allowed us to shorten our run time by a factor of two compared to the packed column method. The importance of the reduction in run time comes from the QC requirement for a GC/MS tune once every twelve hours. The shorter the analytical run time, the more samples which can be analyzed within the 12-hour window.

A new purge and trap autosampler equipped with a water management system has been added which we hope will reduce the problem of carryover of water to the capillary column. This has its primary effect on the gases and early eluting analytes. The autosampler is presently being evaluated. It runs unattended resulting in increased laboratory sample throughput, reduced operator time and lower cost per analysis. In addition, the unit possesses the capability of adding the surrogates and internal standards to the sample, improving analytical accuracy. We intend that this unit will be dedicated to the analysis of relatively clean water and soil samples.

In the analysis of semivolatile organics, the primary modifications to the systems have been the result of the implementation of the TCLP. Two cryogenic oven controllers have been ordered for reducing sample cycle time.

A portable computer has been purchased, along with software and a modem to be used for monitoring the systems from remote locations. We believe that the systems can be tuned in the evening, allowing additional sample throughput and further increasing instrumental efficiency.

M. P. Maskarinec, S. H. Harmon, G. S. Fleming, S. F. Glover, J. C. Montgomery, P. L. Crawford

Reporting and Quality Control

Significant efforts during the past year were devoted to improving the quality of the work of the group. Much of this effort was directed by the Tiger Team preparations, but other signs of improving quality can also be seen. For example, performance on external evaluation samples improved throughout the year, culminating in a perfect score on the third quarter EPA sample. As already mentioned, certification was obtained from the State of Tennessee for performing drinking water analyses. This certification was a result of satisfactory performance on external samples for two consecutive periods, as well as an on-site laboratory evaluation.

One of the major problems, in terms of QA, has been an inadequate system of data review. This has been partly due to staff limitations and partly due to a lack of formality in the review process. As a result, several steps have been initiated to prevent reoccurrence of data review problems. New formats are being designed with more obvious notations of holding times. All data are being reviewed by at least two levels of supervision prior to release. All QC samples are now reported directly to the division QCO. Finally, an attempt is under way to allow electronic transfer of all QA/QC data.

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

ORNL/UT RESEARCH PROGRAM

G. A. Guiochon

Research in separations science has continued. During the past year, we have:

- moved the thrust of our theoretical effort from the study of the properties of the equilibrium-diffusive model to the study of the kinetic model of chromatography;

- begun the investigation of new practical problems, e.g., the influence on the separation achieved of a difference in the solubility of the sample components in the injected solution and in the mobile phase, or of the difference in the viscosity of the chromatographic bands and of the pure mobile phase;

- continued our work on the determination of equilibrium isotherms, with emphasis on the binary competitive adsorption isotherms;

- applied our theoretical results to the solution of separation problems involving enantiomers;

- obtained some important new results from our modeling of capillary zone electrophoresis;

- derived a general method for the characterization of the surface of porous and nonporous adsorbents and applied it to samples of nonporous alumina used for the manufacturing of ceramics.

Theory of Non-Linear Chromatography

There are three theoretical approaches of increasing complexity to the solution of the problems of non-linear chromatography: the ideal model, the equilibrium diffusive model and the kinetic model. The ideal model assumes that the column efficiency is infinite, i.e., there is constant equilibrium between the stationary and the mobile phase and no axial dispersion, so the changes in the band profile during elution are due to the non-linear behavior of the equilibrium isotherm. This model has closed form solutions in a number of cases. These solutions are accurate caricatures of the profiles obtained with high efficiency columns. Their study gives a schematic overview of the consequences of the non-linear effects in chromatography.

The equilibrium-diffusive or semi-ideal model takes into account the smoothing influence of axial dispersion and of the mass transfer resistances on the band profile by lumping these contributions into a single apparent dispersion coefficient. This model has approximate analytical solutions which are valid only at low sample sizes, but it is easily solved numerically. The solutions obtained agree well with experimental results for single component bands because it is relatively easy to determine single component equilibrium isotherms. Competitive isotherms are more difficult to account for, while band profiles are quite sensitive to minor errors in these isotherms (see next section). Therefore, excellent agreement between calculated and experimental band profiles of the components of binary mixtures is obtained in some cases, but significant differences are observed in others. The various approaches to solving this model and studying the properties of its solutions have been reviewed. We have studied the details of the interactions between bands for mixtures of two or several components.

When the kinetics of mass transfer in the column, the kinetics of adsorption-desorption, or more generally the kinetics of the retention mechanism become slow (e.g., in affinity chromatography), the equilibrium-dispersive model fails to account for the band profile. A different approach must be followed and we have to use a model of chromatography which takes into account the kinetics of these phenomena. Two types of models are available, using either a single kinetic equation with a lumped rate coefficient, or a set of equations when a detailed model of the mass transfer kinetics can be written.

We have begun a comparative study of the properties of the various kinetic models. The most important simple kinetic models are the Thomas model, which uses the Langmuir kinetic equation and neglects axial dispersion, and the linear driving force model, which uses a linear kinetic equation. Both models consider a slow kinetics of retention but rapid mass transfers in the column. We have generalized the latter model into the "reaction-diffusive" model by incorporating a term accounting for the

axial and the apparent dispersion (i.e., for the resistances to mass transfer between phases).

Analytical solutions of the Thomas model have been derived for the elution problem by others. We have compared these solutions to numerical solutions of the Thomas model and of the reaction-diffusive model. The solutions of these two models converge when the contribution of the axial dispersion becomes small compared to that of the reaction kinetics. However, when the mass transfer kinetics is the rate-determining step (i.e., fast reaction, slow mass transfers) or when the rates of the mass transfer and the reaction kinetics are of the same order, important differences between the solutions of the two models are observed. Finally, if the reaction kinetics is very slow and the height of a transfer stage becomes comparable to the column length, the "split peak" phenomenon takes place. Part of the solute does not have time to interact with the stationary phase and elutes as a sharp unretained peak while the rest of the solute elutes as a very broad band. Numerical solutions of the two models predict the entire band profile while the analytical solution of the Thomas model remains unable to predict the profile of the unretained part of the split peak.

G. A. Guiochon, M. Z. El Fallah, S. Golshan-Shirazi**, A. M. Katti***, J. V. H. Schudel****

*UT Postdoctoral Program
**University of Tennessee
***UT Predoctoral Program

Study of Equilibrium Isotherms

As shown by comparative studies of the experimental band profiles and the profiles calculated with the equilibrium-diffusive model and the experimental isotherms, a proper representation of the competitive behavior of the components of the mixture is necessary for an agreement between experimental and theoretical profiles. We have begun systematic investigations of competitive equilibrium isotherms.

Experimental results have shown that single component data are rarely well accounted for by a single Langmuir

isotherm. In many cases, a bilangmuir isotherm or the sum of a Langmuir and a linear isotherm give a much more accurate fit of the data and, accordingly, a much better agreement between calculated and experimental band profiles.

Binary equilibrium isotherms can be determined by frontal analysis, a method which requires much time and large amounts of solutions and compounds but gives accurate results. As we are trying to develop methods which could be applied to practical problems, we have investigated the simple wave method, based on the properties of solutions of the system of mass balance equations for a multicomponent system. Data are acquired more rapidly and easily, with much smaller amount of chemicals, but are more difficult to account for.

Experimental results have shown that when the single component data are well accounted for by a Langmuir or a bilangmuir isotherm, the competitive isotherms are well represented by using the competitive Langmuir or bilangmuir models, provided the column saturation capacities for the two components are equal. If these capacities are different, the Langmuir competitive model is no longer consistent with thermodynamics and should be replaced by the Levan-Vermeulen model, which gives good agreement between calculated and experimental band profiles. However, experimental data seem to be better accounted for by a Fowler isotherm model, a much less suitable type of equation for the numerical calculations of band profiles.

The Langmuir model is the simplest isotherm derived by statistical thermodynamics. More complex equations can be derived, either for single components or for mixtures. Further experimental investigations are in progress to select isotherm models appropriate for the particular conditions of chromatography at high concentrations.

G. A. Guiochon, M. Diack, E. V. Dose*, M. Z. El Fallah*, S. Jacobson**, A. M. Katti**, J. Zhu****

*UT Postdoctoral Program

**UT Predoctoral Program

***University of Tennessee

Theory of Optimization of Experimental Conditions in Preparative Chromatography

Since the competitive Langmuir model permits the calculation of band profiles which are usually in satisfactory agreement with experimental results, these profiles can be used for the calculation of optimum conditions. Two approaches are available: the numerical approach using a Simplex optimization procedure and an approach based on the use of the analytical solution of the ideal model, introducing semi-empirical corrections for the influence of the finite column efficiency on band spreading. We have continued the work begun last year and calculated the optimum conditions for maximum production rate of compounds of given purity, using both methods.

We have derived practical rules for the determination of optimum conditions in the touching band case or the overlapping band case and compared the trade-offs in the two. We have begun a comparison between the performance achieved in displacement and in overloaded chromatography. This last work showed that the major advantage of displacement over elution chromatography is not in the production rate at a certain degree of purity but in the concentration of the fractions recovered. The choice between the two methods under which preparative chromatography can be carried out depends very much on the specifics of the case considered, and general conclusions are not possible at this stage. Further investigations are in progress.

G. A. Guiochon, E. V. Dose, S. Golshan-Shirazi**, A. M. Katti****

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Experimental Investigation of Individual Band Profiles at High Concentration

As reported in the first section, we have recorded experimental band profiles in the case of different binary mixtures, measured the equilibrium isotherms and compared the two sets of individual profiles. Experiments were conducted

with 2-phenyl-ethanol and 3-phenyl-propanol on C18 chemically bonded silica, with phenol and catechols on C18 bonded silica, with different N-benzoyl [D and L] amino acid derivatives on a BSA bonded silica column (BSA = bovine serum albumin), and with cis- and trans- androsterone on C18 bonded silica.

In all cases, the individual profiles are determined by collecting approximately a hundred fractions and analyzing them for the two components. In the case of enantiomers, the detector has the same response factors for the two components. The total profile is obtained from the fraction analysis. It can also be derived from the detector response, using a calibration curve (in non-linear chromatography the detector response is most often not linear). The agreement between these two total profiles validates our procedure.

In all cases, when the proper isotherm model is used, excellent agreement is achieved between calculated and measured profiles. However, minor deviations between the isotherm data and the model equation used lead to very significant differences between calculated and measured band profiles.

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Study of Some Practical Problems in Preparative Chromatography

Differences between band profiles predicted by the theory of non-linear chromatography and experimental results are not infrequent. They deserve a systematic investigation because they illustrate the possible deviations between actual practice and the theoretical models used to account for the behavior of chromatographic columns. We have investigated two such cases.

Size exclusion chromatography is widely used in biotechnology to extract a fraction rich in some desired protein from a fermentation broth, after lysing the cultivated bacterias. We wanted to

investigate the phenomenon of column overloading in size exclusion chromatography and possibly the non-linear behavior of the isotherm. We found that column overloading in size exclusion chromatography takes place at rather moderate concentrations and that the band profiles recorded become poorly reproducible without apparent reasons. We have shown that fingering takes place when the concentration of the sample component in the band increases enough and the viscosity of the band becomes significantly higher than the mobile phase viscosity. This classical phenomenon causes long tailing and sometimes a multi-modal rear profile of the elution band. We have also shown that the intensity of this phenomenon can be considerably reduced either by using a mobile phase having the same viscosity as the sample solution or by pushing the sample by a rectangular plug of a solution having the same viscosity as the sample solution and a sufficient width (i.e., ca. 1/3 column volume).

Significant deformations of band profiles have been reported in preparative chromatography when the column is overloaded with a component which is poorly soluble in the mobile phase, if a solvent with a higher elution strength than the mobile phase is used to dissolve the component and increase the amount injected. Eventually, band splitting may take place. This behavior was observed in the case of cholesterol and other low-polarity compounds (e.g., related sterols) separated on C18-bonded silica, with acetonitrile as the mobile phase, when the sample was dissolved in a nonpolar solvent, such as dichloromethane, at concentrations exceeding the solubility of its components in the mobile phase. Cholesterol solubility and retention depend strongly on the local concentration of dichloromethane. The dichloromethane contained in the sample solution elutes as a nonretained band while it dilutes in acetonitrile in the process. As a result, part of the cholesterol is carried unretained to the column exit by the dichloromethane band, part is left behind the dichloromethane band and elutes late as the expected overloaded cholesterol band, and part is spread in between these two peaks. Separation of

cholesterol from its impurities becomes impossible at high column loading.

We studied the dependence of the band deformation and of its splitting on the volume and concentration of the sample, the composition of the mobile phase and the column temperature. A model taking into account the dependence of the solubility of cholesterol and of its isotherm parameters on the mobile phase composition (ratio of dichloromethane and acetonitrile) was worked out. This model permits the computer simulation of the band profiles for a single compound or for a mixture of two components. The results of the simulations are in good agreement with the behavior observed experimentally.

G. A. Guiochon, M. Czok, P. Jandera**

*UT Postdoctoral Program

Capillary Zone Electrophoresis

We have derived a new method for data handling in capillary zone electrophoresis. This method of separation, generally used for the analysis of proteins and DNA restriction fragments, is undergoing a very rapid development. Its adoption in clinical laboratories and for quality control in pharmaceutical laboratories is hampered, however, by the difficulties of quantitation. The quantitative results (relative peak areas or relative concentrations of the sample components) derived under the best possible experimental conditions have a standard deviation which is rarely better than ca. 8%. We have shown that the internal standardization for capillary zone electrophoresis should be based on the linear relation between the effective volume of solution injected for each ion and the inherent mobility of this ion. This relationship is not proportional and two standards are needed. Their use permits the analyst to establish this relation quantitatively for each sample and so to correct the analyte concentrations for variations in each injection. The computational method given is most simple. The relative standard deviations of relative concentrations derived from the results of manual injections are lower than 1%,

which is at least as good as current performance in liquid chromatography.

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

*UT Postdoctoral Program

Surface Properties of Ceramic Powders

We have derived a new numerical method for calculating the adsorption energy distribution function from adsorption isotherm data. We have shown this method to be robust with respect to quasi-Langmuir adsorption isotherms, the type most often observed in inverse gas chromatographic experiments involving energetically heterogeneous stationary phases. The stability of the method and the accuracy of its solutions have been demonstrated using simulated data. The principle of this method is based on the determination of the experimental isotherm of some test compounds on the studied adsorbent, using the Elution by Characteristic Point procedure. The accuracy of this determination has been investigated in detail. Systematic series of determinations of experimental data and simulation studies have established its degree of reproducibility.

We have used this method for the determination of the energy distribution of diethyl-ether on activated alumina. This distribution is composed of two narrow bands at 11.04 and 12.68 kcal/mol. The variances of these bands are 1.66 E-5 $kcal^2/mol^2$ and 1.00 E-6 $kcal^2/mol^2$, respectively. The monolayer capacity is 5.36 E-6 mol/g for the low energy band and 2.53 E-6 mol/g for the high energy band. Further investigations using 1-chlorobutane have shown significant differences for the adsorption energy distribution of this probe on alumina samples of different origins.

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

*UT Predoctoral Program

5. QUALITY ASSURANCE, SAFETY AND TRAINING

QUALITY ASSURANCE/ QUALITY CONTROL

W. R. Laing,
S. K. Holladay, P. L. Howell

This was the year to document plans, operations, and methods. The ACD Quality Assurance plan (QAP) was completed last year and the focus has been on group plans. Eight individual group QAPs were completed as well as the Research and Development plan. With the three plans completed last year, all ACD QAPs have now been written.

Work continued to document how we operate with standard operating procedures (SOPs) and with standard analytical methods (SAMs). Thirty-two new SOPs were written and another thirty-two were revised. These procedures covered such key areas as receipt, handling, storage and disposal of samples, data management and review, and record keeping. Fifty-one SAMs were written describing instrument operation and analytical methods.

A chemical hygiene plan and a training plan were written for the division. Chemicals were hazard labeled and a carcinogen inventory was completed.

Division groups were audited six times to check training, nuclear materials, and environmental compliance. Fifteen analysts were certified for special nuclear material measurements based upon meeting established criteria by their performance on QC samples. In October, the DOE Tiger Team did a comprehensive environment, safety, and health audit of ORNL. As we document

our activities, train employees, and gain from experience, the result is fewer audit findings. Of the 400 findings by the Tiger Team, there was only one minor finding for ACD.

The division requested certification by the State of Tennessee for drinking water in September 1989. After completion of the application form, successful analysis of two series of performance evaluation samples, preparation of an EPA QA plan, and an audit, certification was awarded for the inorganic and the organic laboratories. The low-level radiochemical lab has had certification for several years.

Two hundred quality control (QC) solutions were distributed by the QC laboratory to the ACD inorganic, organic and radiochemical analysis laboratories in 1990. Of the 4590 results reported, 97% were acceptable. Monthly inorganic control solutions were purchased from Analytical Products Group (APG), Belpre, Ohio, and submitted as blinds. Results were reported to APG and statistically evaluated with 30-plus laboratories throughout the country. All DOE analytical chemistry laboratories operated by Martin Marietta Energy Systems, Inc. participate in this monthly program. Of the 700 inorganic results reported during 1990, 99% were acceptable. The ACD organic group also participated in the program. Of the 376 results reported, 96% were acceptable.

Laboratories performing environmental compliance analyses continued to participate in EPA administered performance evaluation (PE) programs in addition to the internally administered ones. The average score for three inorganic Contract Laboratory Program (CLP) PE sets was 84.6% (out of a possible 100%). The average score for four organic PE sets for the same period was 81.7%. The Low-Level Radiochemical laboratory scored an average of 101% on 124 measurements in matrices on round robin samples from the Environmental Measurements laboratory. The inorganic group also participated in the Water Pollution Study performance evaluation 024 and the Discharge Monitoring QA performance study 010. A total of 95 results were reported and all were acceptable.

Drinking water certification was granted by the Tennessee Department of Health and Environment to the inorganic group for analysis of arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, nitrate, and fluoride. The organic group was certified for analysis of trihalomethanes and volatile organic chemicals. The Low-Level Radiochemical laboratory was recertified during this period. In order to satisfy the requirements for certification, the inorganic and organic laboratories participated in Water Supply performance evaluation studies 025 and 026. A total of 158 analyses were performed, with 90% considered acceptable.

The double-blind spiking program continued in which quality control samples were prepared by the QC Officer and submitted to ACD by the customer alongside routine environment samples. A total of 127 samples were submitted during the year.

A quality control document was approved by division management which summarized responsibilities and described requirements for glassware, standards, reagents, water, sample analysis, instrumental operations, internal quality assessment, external quality assessment, data handling, statistical data evaluation, control charting, data reporting, out-of-control events, and corrective actions. Statistical evaluation and control charting became cheaper, more frequent (bimonthly instead of quarterly), and better documented through the adoption of the Statistical Analysis System Quality Control software. Modifications to the AnaLIS QC software enabled laboratory personnel to access QC data immediately.

ANALYTICAL IMPROVEMENT COUNCIL

C. E. Higgins

The Analytical Improvement Council (AIC) activities this year have pertained largely to improvement in communication in ACD. One project was to determine those questions on the Energy Systems' communication survey for which ACD's responses were less favorable than those for ORNL, and to suggest a plan of remedial action. The largest area where ACD needed to increase favorable responses was that of communication. Great improvement subsequent to the communication survey has been achieved by the holding of regular meetings on the group and section levels. Also, informal luncheon meetings are held in which small groups of nonsupervisory personnel meet with the division director. These meetings are informative and provide real two-way communication in the absence of workers' immediate supervisors. Additional improvement in communication has been achieved by the distribution of ACD staff meeting minutes to ACD personnel. AIC has set a regular meeting time each month, with an allotment of a few minutes for ACD employees to present suggestions, ideas, or problems needing attention. A survey of division employees has been initiated to ascertain how to improve communication within the division; it is in process and yet to be summarized.

Other projects relate to the storage and labeling of chemicals. One project suggested by AIC for ACD and ORNL, but independently in progress throughout Martin Marietta Energy Systems, proposed the computerization of the chemical inventories. Another, not suggested by AIC but endorsed as a worthwhile Performance Improvement Process (PIP) project, involved the use of computers for National Fire Protection Association hazard labeling of chemicals. This program has become increasingly applied throughout Energy Systems.

SAFETY PROGRAM

S. D. Wright

A Safety Action Plan was implemented as a guide toward better safety in the Analytical Chemistry Division during 1990. The division experienced four (4) first aid cases against five (5) during the same period last year. Increased awareness of safety has been emphasized in all our Safety Meetings as a result of the above incidents.

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

Notable achievements this reporting period:

1. Safety Meetings held - 26; total attendance - 826.
2. Training Guide updates for our facilities at Buildings 2026 and 7920 continue.
3. Spring Clean-up Week activities in May included fire training at Buildings 2026 and 4500N.
4. Special seminars relating to Environmental Safety and Health were given.
5. Monthly Safety Meetings at Building 2026 were continued.
6. Nine operational safety summaries for ACD laboratory operations were documented.

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

As a result of DOE's Tiger Team Visit and ORNL's emphasis on its Environmental, Safety and Health Upgrade program, our personnel have made significant advances toward a safer working environment. These include better housekeeping, safer laboratory practices, and a much-improved attitude in general about personal safety.

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

TRAINING

H. H. Ross

Training activities within the division continue to evolve to meet the demands of DOE and Martin Marietta Energy Systems. Virtually every member of the division was personally involved in some training task during the year. It is estimated that over 1000 man-hours of training-related activity occurred in 1990. The range of such activities included evaluation of individual or programmatic training requirements, design of training agenda and/or materials, tracking and documentation of training performance, and, of course, attendance at specific training sessions.

The self-assessment training document for the Transuranium Analytical Laboratory (TAL) was completed and submitted for review. For some time the TAL staff has carried out an educational program that comprises facility, generic, and on-the-job components. However, the formal review of the self-assessment document notes that new training initiatives are required at the facility for the development of performance-based training (PBT) for accreditation (DOE Order 5480.18). The initial manpower estimate for the implementation of such a program is 5 MY. Additionally, it is conjectured that a 1.5 MY effort will be needed each year to maintain the program. Present information suggests that we will have three years to get this program in place.

A division team led by M. R. Guerin took on the task of developing a comprehensive training plan for ACD. It was the purpose of this plan to delineate overall training requirements, identify those components already in place, and define needs for future implementation. Specific training responsibilities associated with selected ACD staff were also defined. Although the scope of the plan was limited to that training provided by ACD staff, provisions were included for tracking and documenting training received through other routes. A powerful feature of the plan is that it designates standardized formats of ACD Training/Qualification Forms that match specific training functions. These forms

enhance our ability to verify, search, and update training data for every Division employee. Although the first plan was completed in October, suggested revisions will be reviewed and adopted quarterly.

In the past the division maintained a relational database, for use on a personal computer, that held the training records of ACD personnel. The database was available to ACD management staff for verifying personnel training accomplishments and for scheduling required training updates. Unfortunately, the system was difficult to maintain and use, and proved to be somewhat inflexible in the face of a changing training environment. The decision was made to change the system to a text-based data-retrieval environment. This conversion was completed near the end of the year and all existing records were transferred to the new software with few problems. Additionally, training records for the division were obtained from the TMIS database and these were added to our system as needed.

Finally, at the end of the year the division started on an evaluation of "Training Needs Overview" that will be carried out by every unit of Energy Systems. This is a massive project to upgrade compliance-based training. The first part of this task was to identify relevant laws and regulations pertaining to training. The central Training and Development Department (T&DD) staff have developed a database of over 1200 items associated with such requirements. The division is in the process of reviewing the database descriptors to determine our training responsibility identified with each work area in which we participate. At the end of this process, T&DD will cross tabulate our work activities with specific training requirements (down to the individual employee level). The expected end result is a coordinated system capable of identifying, tracking, and verifying all required compliance training for every individual in the division. The program will also inform supervisors of required training updates, or new training needed because of changing job assignments.

6. EDUCATION PROGRAMS

The division maintains liaison with the academic community through a number of joint programs. These include hosting fellowship holders from ORAU, Co-op students from the University of Tennessee, and special undergraduates from the Great Lakes Colleges Association. A newer program involves students from the service academies. In addition, graduate programs are maintained with U. T. and Clemson.

John Dale and Debra Bostick served as University Relations Coordinators for student guests and faculty during 1990.

OAK RIDGE ASSOCIATED UNIVERSITIES (ORAU) PROGRAMS

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

Brian A. Eckenrode (Michigan State University) completed research in mass spectrometry/mass spectrometry with Gary Glish and Scott McLuckey.

Sheng Dai (University of Tennessee) began an appointment with Jack Young to develop analytical sensors to be used in the electrolytic production of magnesium metal from molten chloride salt solutions.

Kevin J. Hart (Michigan State University) began research in mass spectrometry/mass spectrometry under the direction of Gary Glish.

Graduate Research Program. Rick A. Flurer (Indiana University) continued working with Gary Glish and Scott McLuckey in organic mass spectrometry.

Jocelyn Dunphy (Indiana University) completed her work with Michelle Buchanan in the investigation of laser desorption Fourier transform mass spectrometry for detection and characterization of trace levels of biological molecules isolated on chromatographic plates.

Faculty Research Program. Elizabeth A. Stemmler (Bowdoin College) did collaborative research in gas-phase ion chemistry and isometric differentiation using mass spectrometry.

Faculty Research for Historically Black Colleges and Universities. Joseph L. Russell, Chairman of Chemistry and Physics Department, Alcorn State University, worked with Larry Robinson on neutron activation analysis of environmental samples.

Student Research Participant. Kathryn L. Wohlpart worked with Rose Ramsey to develop chromatograph methods for separating and measuring transformation in DNA resulting from exposure to ultraviolet light.

CO-OP PROGRAM

Douglas L. Theobald (University of Tennessee) began a co-op assignment with Michelle Buchanan in the Organic Spectroscopy group.

GREAT LAKES COLLEGES ASSOCIATION (GLCA) PROGRAMS

Kevin H. Hazen (Coe College) worked with John E. Caton on solid phase extraction methods coupled with high performance liquid or supercritical fluid chromatography for the determination of explosives and metabolites and other polar compounds in water, tissue, or soil.

Rafat K. Alvi (Ohio Wesleyan) worked with Robert W. Shaw on laser diagnostics for chemical deposition of thin diamond films.

Nathaniel J. Schaefle (St. Olaf College) did research with W. B. Whitten on laser spectroscopy of microparticles.

UNIVERSITY OF TENNESSEE PROGRAMS

Distinguished Scientist Program. Georges Guiochon holds an ORNL/UT Distinguished Scientist appointment with the division. He maintains research groups at both UTK and ORNL. During 1990, postdoctoral researchers at ORNL included Mark Aubel, Martin Czok, Moustapha Diack, Eric Dose, and Zoubair El Fallah. Predoctoral students were Steve Jacobson, Anita Katti, Jeff Roles, and Jennifer Schudel.

Mark Aubel, Martin Czok, Anita Katti, and Jennifer Schudel completed their appointments during 1990.

Postgraduate Research. Casey Grimm (Florida State University) continued research on organic secondary ion emission with Peter Todd.

R. Timothy Short (University of Tennessee) continued research with Peter Todd on organic imaging mass spectrometry.

Brian T. Buckley (North Carolina State) completed his research with Mike Ramsey on a plasma source for multiphotoionization spectroscopy.

Lee R. Riciputi (University of Wisconsin) began research with Warner H. Christie in the use of stable isotopes with the CAMECA ion microscope.

Predoctoral Research. Michael Troutman (Indiana University/University of Tennessee) continued his work with Gary Glish on instrument development and application.

Science Alliance. Robert L. Richardson and James E. Coffield participated in the Science Alliance student program working with J. P. Young on the magnesium sensors program.

CLEMSON UNIVERSITY PROGRAM

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

SERVICE ACADEMIES RESEARCH ASSOCIATES (SARA) PROGRAM

John H. Blalock (U.S. Naval Academy) worked with J. M. Ramsey on resonance ionization mass spectrometry with a synchronously pumped mode locked dye laser.

7. SUPPLEMENTARY ACTIVITIES

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

ADVISORY COMMITTEE

The 1990 Advisory Committee was composed of:

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

R. G. Cooks, Purdue University, West Lafayette, Ind.

J. C. Giddings, University of Utah, Salt Lake City, Utah

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

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

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

CONSULTANTS

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

Minda Wang, Ohio State University, Columbus, Ohio

Dennis C. Johnson, Iowa State University, Ames, Iowa

Fred E. Regnier, Purdue University, West Lafayette, Ind.

Mary J. Wirth, University of Delaware, Newark, Del.

Robert T. McIver, Jr., University of California, Irving, Calif.

Geraldine Richmond, University of Oregon, Eugene, Oreg.

Richard N. Zare, Stanford University, Stanford, Calif.

Catherine Fenselau, University of Maryland, Baltimore, Md.

Robert S. Houk, Iowa State University, Ames, Iowa

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

Gleb Mamantov, University of Tennessee, Knoxville, Tenn.

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

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

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

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

R. K. Marcus, Clemson University, Clemson, S. C.

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

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

ACS ANALYTICAL CHEMISTRY SUMMER SYMPOSIUM

Each year the Division of Analytical Chemistry of the American Chemical Society sponsors a Summer Symposium in some topic of major research interest in the field of analytical chemistry. These Summer Symposia are usually held at a major university or research institution and attract 150-200 participants, both domestic and foreign. We hosted the Summer Symposium of 1990 in July in Oak Ridge. The attendance was approximately 225. The topic was analytical mass spectrometry.

Professor Graham Cooks of Purdue University was Program Chairman and David Donohue of ORNL-ACD was local Arrangements Chairman. The sessions were held at the Oak Ridge Associated Universities campus. Two and a half days of formal talks and poster presentations were given on virtually all topics of current research interest in

analytical mass spectrometry. An innovation this year was a special session given by graduate students; it was followed by awards for the top presentations.

The Summer Symposium of 1990 was a real success. A synopsis was published in an "A-page" article in *Analytical Chemistry* in October.

SEMINAR PROGRAM

Speaker	Title of Talk	Date
Minda Wang Dept. of Chemistry Ohio State U. Columbus, Ohio	"Recent Advances in FT-ICR Cell Performance"	1/8/90
Dennis C. Johnson Dept. of Chemistry Iowa State U. Ames, Iowa	"Electrocatalysis of Anodic Oxygen-Transfer Reaction"	1/19/90
Kevin J. Hart Dept. of Chemistry Michigan State U. E. Lansing, Mich.	"Generation of Substructure Identification Rules and Molecular Structures from MS/MS Spectra"	3/7/90
Fred E. Regnier Dept. of Chemistry Purdue U. W. Lafayette, Ind.	"Profusion Chromatography"	3/16/90
Mary J. Wirth Dept. of Chemistry U. of Delaware Newark, Del.	"Spectroscopic Studies of Solute Reorientation at the Interface of Water and Chemically Modified Silica"	4/20/90
Randall W. Nelson Dept. of Chemistry Arizona State U. Phoenix, Ariz.	"Generation of Large Ions by Laser Desorption from a Frozen Aqueous Matrix"	5/15/90

Robert T. McIver, Jr. Dept. of Chemistry U. of California Irvine, Calif.	"Peptide Sequencing with an External Ion Source Fourier Transform Mass Spectrometer"	8/24/90
Geraldine Richmond Dept. of Chemistry U. of Oregon Eugene, Oreg.	"As the Electrode Turns: SHG and the Single Crystal Electrode Surface"	10/2/90
Richard N. Zare Dept. of Chemistry Stanford U. Stanford, Calif.	"Capillary Zone Electrophoresis: An Adventure in Microplumbing"	10/26/90
Catherine Fenselau Dept. of Chemistry U. of Maryland Baltimore, Md.	"Endothermic Reactions for the Structural Analysis of Biopolymers"	11/4/90
Bobbette Nourse Dept. of Chemistry Purdue U. W. LaFayette, Ind.	"Fundamental and Applied Studies Using a Quadrupole Ion Trap Mass Spectrometer"	11/12/90
Robert S. Houk Dept. of Chemistry Iowa State U. Ames, Iowa	"Improvements in Elemental and Isotopic Analysis by Inductively Coupled Plasma Mass Spectrometry"	12/7/90

PATENTS

Scott A. McLuckey and Gary L. Glish were granted a patent in 1989 for "Atmospheric Sampling Glow Discharge Ionization Source."

AWARDS AND HONORS

Michelle Buchanan was named to the Editorial Board of *Analytical Chemistry.*

Georges Guiochon won the prestigious American Chemical Society Separations Science Award for his chemical separations research.

Shirley Cates received an Administrative Support Award at Martin Marietta Energy Systems Awards Night.

Joe Stewart received a Technical Achievement Award for pioneering development of rapid PCB extraction from soils and sediments. Joe also received a Letter of Commendation from the Environmental Protection Agency, Office of Solid Waste, for methods development.

W. H. Griest, J. L. Botts, R. N. Ceo, J. M. Keller and R. L. Schenley received the Society for Technical Communications Technical Award of Excellence for ORNL/TM-11652, "Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporator Facility Storage Tanks at ORNL".

Dub Shults received an Energy Systems President's Award for Performance Improvement Program work on the Job Opportunity System.

ADDITIONAL PROFESSIONAL ACTIVITIES

K. G. Asano

ACD Representative	Carcinogen Control Program at Y-12

D. A. Bostick

ACD Representative	University Relations Coordinator

M. V. Buchanan

Editorial Board	*Biomedical and Environmental Mass Spectrometry*
	Organic Mass Spectrometry
	Analytical Chemistry
Treasurer	American Society for Mass Spectrometry
Advisory Board	National Science Foundation Biological Centers Program
Member	Energy Systems Advisory Committee for Values
	ORNL Values Committee
Chairman	East Tennessee Mass Spectrometry Discussion Group

J. A. Carter

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

J. M. Dale

ACD Representative	University Relations Coordinator

D. L. Donohue

Chairman	Local Arrangements, ACS Analytical Chemistry Summer Symposium
Chairman	ACD Seminar Committee

J. S. Eldridge

Chairman	Membership Committee, Environmental Radiation Section, Health Physics Society
Member	Oak Ridge Reservation-Resource Management Organization: Environmental Surveillance
	Lab Committee 8 of the International Society for Methods of Air Sampling and Analysis

J. F. Emery

ACD Representative	Laboratory Emergency Sample Coordinator
	Division Computer Systems Security Officer

C. Feldman

Fellow	American Society for Testing and Materials
Member	ASTM Committee E-2 on Emission Spectroscopy, Subcommittees on Fundamental Methods, Editorial Practices, and Nomenclature

N. M. Ferguson

ACD Representative	Energy Systems Environmental Analysis Committee

G. L. Glish

Associate Editor	*Journal of the American Society for Mass Spectrometry*
Vice President	American Society for Mass Spectrometry
Consultant	Finnigan MAT, San Jose, Calif.

G. L. Glish

Board of Directors	Asilomar Conference on Mass Spectrometry
Member	ORAU Traveling Lecture Program

W. H. Griest

Consultant	DOE SBIR Review
	Electric Power Research Institute
	Environmental Protection Agency IERL/TSO
	Center for Indoor Air Research

M. R. Guerin

Advisory Board	University of Kentucky Tobacco and Health Research Institute
Consultant	DOE and NCI SBIR Reviews
	PHS Office of Smoking and Health Additives

G. A. Guiochon

Associate Editor	*Analytical Chemistry*
Advisory Board	*Journal of Chromatography*
	Journal of Chromatographic Science
	Journal of Liquid Chromatography
	Chromatographia

G. A. Guiochon

Member	HPLC Permanent Committee of the International Symposia on Column Liquid Chromatography
	ACS Board, Chromatography Subdivision, ACS Division of Analytical Chemistry

R. L. Hettich

Chairman	ACD Seminar Committee
Member	ORAU Traveling Lecture Program

C. E. Higgins

Chairman	Analytical Improvement Council

S. K. Holladay

ACD Representative	Quality Control Officer
Member	ASTM Committee D-34

P. L. Howell

Member	ASTM C-26 Nuclear Fuel Cycle
	ASQC Energy Division

R. H. Ilgner

ACD Representative	Environmental Protection Officer
Consultant	Fourth Judicial District Court, Monroe, La.

R. A. Jenkins

Consultant	Federal Trade Commission, Standardized Smoking Practices
	National Institute on Drug Abuse SBIR Reviews

K. O. Jeter

Member	Analytical Improvement Council

L. N. Klatt

Member	Energy Systems Ph.D. Recruiting Team
	ACD Seminar Committee

W. R. Laing

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

S. A. McLuckey

Chairman	ASMS Ion Physics and Instrumentation Interest Group
Consultant	Finnigan MAT, San Jose, Calif.

M. P. Maskarinec

Member	EPA Working Group on Improvement of TIC Identification

M. P. May

ORNL Representative	Energy Systems Technical Training Subcommittee on Analytical Laboratories
ACD Representative	Training Coordinator
Member	Energy Systems Training Process Review Team
	ACD Facility 9735 Generator Certification Officer

J. M. Ramsey

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

R. S. Ramsey

ACD Representative	Ph.D. Recruiting Officer
Member	ORAU Traveling Lecture Program

R. S. Ramsey

Consultant	National Cancer Institute SBIR Reviews
	Center for Indoor Air Research

L. Robinson

Member	ASTM Task Group on Nuclear Methods of Chemical Analysis
ACD Representative	Radiation Control Officer

H. H. Ross

Advisory Board	*Journal of Radioanalytical and Nuclear Chemistry*
Editorial Board	*Journal of Radioanalytical and Nuclear Chemistry, Letters*
Faculty Member	Department of Chemistry, University of Tennessee, Knoxville (Adjunct Professor, Science Alliance)
Consultant	Savannah River Site, Aiken, S. C.
	GPU Nuclear, Three Mile Island, Unit-2, Middletown, Pa.
Member	Canvassing Committee, ACS Award for Nuclear Chemistry
	Fellowship Committee, ACS Division of Analytical Chemistry
ACD Representative	Training Coordinator

T. M. Rosseel

Vice President	American Vacuum Society, Tennessee Valley Chapter
Member	AVS Tennessee Valley Chapter, Scholarship Committee
	ORNL Proposal Review Committee
	Organizing Committee, 15th International Conference on X-ray and Inner Shell Processes, Knoxville

R. W. Shaw

Member	Analytical Improvement Council

W. D. Shults

Chairman	ACS East Tennessee Section
	Education Committee, ACS Division of Analytical Chemistry
Advisory Committee	Chemistry and Laser Science Division, Los Alamos National Laboratory
Member	Board of Visitors, Chemistry Department, University of Tennessee, Knoxville
	Energy Systems Analytical Managers Council
	DOE Analytical Managers Group
Review Committee	*Analytical Chemistry*

D. H. Smith

Member	ASMS Isotope Ratio Interest Group

J. H. Stewart, Jr.

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

J. R. Stokely

Chairman	DOE Site Survey Program RAD Committee
	DOE Technical Safety Appraisal Team
Member	DOE Future Analytical Support Task Team
ACD Coordinator	BS/MS Recruiting

P. J. Todd

Consultant	National Institutes of Health, General Medicine
	National Institute of Mental Health
Coordinator	ACD Awards

B. A. Tomkins

Member	ACD Seminar Committee

J. W. Wade

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

M. B. Wise

Member	ACD Safety Committee
	ORAU Traveling Lecture Program

S. D. Wright

Arrangements Chairman	Conference on Analytical Chemistry in Energy Technology
ACD Representative	Safety Officer
	Computer Systems Security Officer

J. P. Young

Fellow	American Association for the Advancement of Science
Member	Program Advisory Committee, ACS Division of Nuclear Chemistry and Technology
Organizer	Symposium on Lasers in Nuclear Chemistry and Technology, National ACS Meeting, Boston
ACD Representative	ORNL Graduate Fellow Selection Panel

8. PRESENTATION OF RESEARCH RESULTS

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

PUBLICATIONS

BOOKS AND PROCEEDINGS

Author	Author(s), Title, Where Published
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	Asano, K. G.; McLuckey, S. A.; Glish, G. L., "Negative Ion Mass Spectrometry of Phosphate Esters", *Proceedings of the 38th ASMS Conference on Mass Spectrometry and Allied Topics*, Tucson, Ariz., June 3-8, 1990, p. 924.
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Hettich, R. L.; Buchanan, M. V., "Structural Characterization of Modified Nucleic Acid Constituents by Laser Desorption FT-MS", *Proceedings of the 43rd Annual Summer Symposium on Analytical Chemistry*, ORNL, July 24-27, 1990, p. 18.

Buchanan, M. V.

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Donohue, D. L.

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Dyer, F. F.

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Emery, J. F.

Robinson, L.; Dyer, F. F.; Emery, J. F., "Experimental Capabilities of the Proposed Neutron Activation Analysis Facilities in the Advanced Neutron Source", *Proceedings of the American Nuclear Society Annual Meeting*, Nashville, Tenn., June 10-14, 1990.

Fleming, G. S.

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Glish, G. L.

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Shults, W. D.

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Lyon, W. S.; Shults, W. D.; Coleman, C. B., *A Brief History of the Analytical Chemistry Division*, September 1990.

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Stokely, J. R.	Stokely, J. R., *Analytical Chemistry Division Summary Report: Radioactive Materials Analysis Section*, ORNL/CF 90/69, March 1990.
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Thompson, C. V.	Jenkins, R. A.; Thompson, C. V.; Gayle, T. M.*; Ma, C. Y.; Tomkins, B. A., *Characterization of Rocket Propellant Combustion Products*, ORNL/TM-11643, June 1990.
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Vick, D. O.	Vick, D. O.; Landau, Larry*; Christie, W. H., *Spark Source Mass Spectrometry Software Documentation and Verification*, ORNL/TM-11328, December 1989.
Wade, J. W.	Wade, J. W.; Prestwood, S. H., *DCL Command Procedure Implementation for the Nuclear Data 9900 Data Acquisition and Processing System*, ORNL/TM 11452, January 3, 1990.
Whitten, W. B.	Dale, J. M.; Whitten, W. B.; Ramsey, J. M., *Advanced Techniques for the Chemical Characterization of Microparticles*, FY-1989 Accomplishments, March 1990.
Wise, M. B.	Wise, M. B.; Buchanan, M. V.; Guerin, M. R., *Rapid Environmental Organic Analysis by Direct Sampling Glow Discharge Mass Spectrometry and Ion Trap Mass Spectrometry: Summary of Pilot Studies*, ORNL/TM-11538, August 1990.
Wright, S. D.	Wright, S. D.; Shults, W. D., *Analytical Chemistry Division Self-Assessment Report*, September 12, 1990.
Young, J. P.	Vane, C. R.*; Rosseel, T. M.; Young, J. P.; Zuhr, R. A.*; Peterson, R. S.*, *High Resolution X-Ray Studies of the Chemical Environment of Sulfur Implanted in Silicon and Quartz*, Physics Division Progress Report, ORNL-6578, March 1990.
	Young, J. P., *Report of Foreign Travel*, ORNL/FTR-3774, October 11, 1990.
	Young, J. P.; Mamantov, G., *In-Line Sensors for Electrolytic Magnesium Cells, Quarterly Report*, ORNL/M-1323, November 12, 1990.

ORAL PRESENTATIONS

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

Speaker	Author(s), Meeting, Date
Asano, K. G.	Asano, K. G.; McLuckey, S. A.; Glish, G. L., "Negative Ion Mass Spectrometry of Phosphate Esters", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.
	Asano, K. G.; McLuckey, S. A.; Glish, G. L., "Comparison of an Atmospheric Sampling Glow Discharge Ion Source with Electron Ionization for Halocarbons", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.
Buchanan, M. V.	Buchanan, M. V.; Hettich, R. L.; Kerley, E. L.; Dunphy, J. C., "Investigation of Ionization Techniques and Substrate Materials for the Application of FTMS to Biological Compounds", American Society for Mass Spectrometry Conference on Ion Trapping in Mass Spectrometry, Sanibel Island, Fla., January 28-31, 1990.
	Buchanan, M. V.; Hettich, R. L., "Determination of Oligonucleotide Sequences and Modifications Using Laser Desorption FTMS", DOE Workshop on the Relevance of Mass Spectrometry for DNA Sequence Determination, Seattle, Wash., April 4-5, 1990.
	Buchanan, M. V.; Wise, M. B.; Guerin, M. R., "Direct Sampling Mass Spectrometry for the Rapid Analysis of Physiological Media", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Buchanan, M. V. — Buchanan, M. V.; Hettich, R. L.; Kerley, E. L.; Dunphy, J. C., "Determination of Oligonucleotide Sequence and Adducts via Fourier Transform Mass Spectrometry", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

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

Caton, J. E. — Caton, J. E.; Griest, W. H., "Determination of Explosives and TNT Metabolites in Biological and Environmental Samples by Liquid Chromatography on a Mixed-Mode C18-Anion Column", 42nd Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, July 1990.

Christie, W. H. — Christie, W. H., "The CAMECA Ion Microscope", ORNL Associate Director's Executive Committee Meeting, January 31, 1990.

Christie, W. H., "Capabilities of the CAMECA Ion Probe", ORNL Environmental Sciences Division Seminar, March 1, 1990.

Christie, W. H., "Secondary Ion Mass Spectrometry", American Vacuum Society/American Society for Materials Meeting, Oak Ridge, June 6, 1990.

Christie, W. H., "Glow Discharge Mass Spectrometry", Analytical Chemistry Division Information Meeting, June 13, 1990.

Donohue, D. L. — Donohue, D. L., "Progress in Positron Mass Spectrometry", DOE/BES Site Review, ORNL, April 9, 1990.

Donohue, D. L.; Hulett, L. D.; Eckenrode, B. A.; Glish, G. L.; McLuckey, S. A., "A Study of Energy Regimes in Positron Ionization Mass Spectrometry of Organic Compounds", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Duckworth, D. C.*; Marcus, R. K.*; Christie, W. H.; Donohue, D. L.; Smith, D. H., "Interfacing a RF Powered Glow Discharge Atomization/Ionization Source to a Double Focussing Mass Spectrometer", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Donohue, D. L.

Donohue, D. L.; Hulett, L. D.; Glish, G. L.; McLuckey, S. A.; Eckenrode, B. A., "Positron Ionization Mass Spectrometry", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Donohue, D. L.; Hulett, L. D.; Eckenrode, B. A.; Glish, G. L.; McLuckey, S. A., "Positron Ionization of Organic Molecules: Is It Worth the Trouble?", 43rd Annual Summer Symposium on Analytical Chemistry, ORNL, July 24-27, 1990.

Donohue, D. L.; Christie, W. H.; Duckworth, D. C.*; Marcus, R. K.*, "GDMS Studies of Insulators and Metals with the VG-9000", 17th Annual Meeting of the Federation of Analytical Chemists and Spectroscopy Societies, Cleveland, Ohio, October 7-12, 1990.

Dunphy, J. C.

Dunphy, J. C.; Hettich, R. L.; Buchanan, M. V.; Busch, K. L.*, "Laser Desorption Mass Spectrometry in the Analysis of Thin-Layer Chromatograms and Electropherograms", 41st Pittsburgh Conference/Exposition, New York, March 5-9, 1990.

Dunphy, J. C.; Busch, K. L.*; Hettich, R. L.; Buchanan, M. V., "Sample Substrate and Concentration Effects on the Laser Desorption Mass Spectra of Materials Contained on TLC Plates", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Eckenrode, B. A.

Eckenrode, B. A.; McLuckey, S. A.; Glish, G. L., "Reactions of the Hydroxide Anion With Substituted Nitroaromatics", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Eckenrode, B. A.; McLuckey, S. A.; Glish, G. L., "Comparison of Electron Impact and Chemical Ionization Sensitivities on an Ion Trap Mass Spectrometer", 43rd Annual Summer Symposium on Analytical Chemistry, ORNL, July 24-27, 1990.

Glish, G. L.

Glish, G. L.; McLuckey, S. A.; Eckenrode, B. A.; Flurer, R. A., "Studying Chemistry with a Quadrupole Ion Trap", American Society for Mass Spectrometry Conference on Ion Trapping in Mass Spectrometry, Sanibel Island, Fla., January 28-31, 1990.

Glish, G. L.; McLuckey, S. A., "The ORNL Explosives Detector", USSOCOM Expo 90, Idaho Falls, Idaho, March 21-22, 1990.

Glish, G. L.

Glish, G. L., "The Quadrupole Ion Trap: A Poor Man's Four Sector?" Boston Mass Spectrometry Discussion Group, March 27, 1990.

Glish, G. L.; McLuckey, S. A., "Progress in Organic Mass Spectrometry", DOE/BES Site Review, ORNL, April 9, 1990.

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E., "Analysis of Involatile Compounds with an Ion Trap Mass Spectrometer Using Electrospray and Laser Desorption", International Symposium on Applied Mass Spectrometry in the Health Sciences, Barcelona, Spain, April 17-20, 1990.

Glish, G. L.; McLuckey, S. A.; Asano, K. G., "Real-time Vapor Monitoring with MS/MS", 199th National Meeting of the American Chemical Society, Boston, April 22-27, 1990.

Glish, G. L.; McLuckey, S. A., "Separations in Space vs Time: A Mass Spectrometrist's Point of View", 12th Annual Spring Symposium, Minnesota Chromatography Forum, Bloomington, Minn., May 8-9, 1990.

Glish, G. L.; McLuckey, S. A.; Grant, B. C.; Troutman, M. R., "Comparison of Low and High Energy Collision Induced Dissociation in a Reverse Geometry Hybrid Instrument", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Glish, G. L.; McLuckey, S. A.; Van Berkel, G. J., "MS/MS and MS^n Experiments with Peptides Using a Quadrupole Ion Trap", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

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Glish, G. L.; Donohue, D. L.; McLuckey, S. A.; Eckenrode, B. A.; Hulett, L. D., "Ionization of Organic Molecules with Low Energy Positrons", 8th Asilomar Conference on Mass Spectrometry, Pacific Grove, Calif., September 23-27, 1990.

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Goeringer, D. E. — Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Laser Photoionization in an Ion Trap Mass Spectrometer", Optical Society of America Meeting on Laser Applications to Chemical Analysis, Incline Village, Nev., February 5-8, 1990.

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Multiphoton Ionization/Tandem Mass Spectrometry in a Three-Dimensional Quadrupole Ion Trap", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Laser Induced Ionization in the Ion Trap Detector", 43rd Annual Summer Symposium on Analytical Chemistry, ORNL, July 24-27, 1990.

Goeringer, D. E.; McLuckey, S. A.; Glish, G. L., "New Operational Modes for an ITMS", 17th Annual Meeting of the Federation of Analytical Chemists and Spectroscopy Societies, Cleveland, October 7-12, 1990.

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Griest, W. H. — Griest. W. H.; Ho, C. -h.; Guerin, M. R., "Analytical Investigation of the Exxon Valdez Oil Spill", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

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Griest, W. H.; Caton, J. E.; Ho, C. -h.; Tomkins, B. A., "HPLC Determination of Explosive Compounds and Metabolites in Compost Products", SETAC 11th Annual Meeting, Arlington, Va., November 11-15, 1990.

Griest, W. H.; Stewart, A. J.*; Tyndall, R. L.*; Ho, C.-h.; Caton, J. E.; Caldwell, W. M.; Ironside, K. S., "Chemical and Toxicological Investigation of Composted Explosives-Contaminated Lagoon Soils", THAMA Environmental R & D Symposium, Williamsburg, Va., November 1990.

Grimm, C. C.

Grimm, C. C.; Todd, P. J.; Short, R. T., "A Data Acquisition and Control System for an Imaging Secondary Ion Tandem Mass Spectrometer", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Guerin, M. R.

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Guerin, M. R.; Buchanan, M. V.; Wise, M. B, "Rapid and Microanalysis by DSITMS", National Institute of Environmental Health Sciences Seminar, Research Triangle Park, N. C., September 14, 1990.

Guiochon, G. A.

Katti, A. M.; Guiochon, G. A., "Prediction of the Profiles of the Elution Bands in Preparative Scale Chromatography", 6th International Symposium on Separation Science and Biotechnology, Fort Lauderdale, Fla., January 16-18, 1990.

Czok, M.; Golshan-Shirazi, S.*; Guiochon, G. A.; Katti, A. M.; Ma, Z.*, "Progress in the Theory of Non-Linear Chromatography", 7th International Symposium on Preparative Chromatography, Gent, Belgium, April 8-11, 1990.

Guiochon, G. A.

Newberger, J.*; Taylor, S.*; Guiochon, G. A., "Practical Laboratory Applications of the Sample Self-Displacement Technique", 7th International Symposium on Preparative Chromatography, Gent, Belgium, April 8-11, 1990.

Czok, M.; Golshan-Shirazi, S.*; Guiochon, G. A.; Katti, A. M.; Ma, Z.*, "Progress in the Theory of Non-Linear Chromatography", 199th National Meeting of the American Chemical Society, Boston, April 22-27, 1990.

Golshan-Shirazi, S.*; Jacobson, S.; Guiochon, G. A., "Comparison of Experimental and Theoretical Band Profiles in Overloaded Elution Chromatography", Keynote Lecture, HPLC '90, 14th International Symposium on Column Liquid Chromatography, Boston, May 22, 1990.

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Roles, J. L.; Guiochon, G. A., "Inverse Gas Chromatographic Studies of Ceramic Materials", 18th International Symposium on Chromatography, Amsterdam, The Netherlands, September 27-28, 1990.

Guiochon, G. A.; Czok, M.; El Fallah, M. Z.; Golshan-Shirazi, S.*; Jacobson, S.; Katti, A. M.; Ma, Z.*; Zhu, J.*, "Preparative Chromatography: An Overview", 18th International Symposium on Chromatography, Amsterdam, The Netherlands, September 27-28, 1990.

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Golshan-Shirazi, S.*; Guiochon, G. A., "Comparison of the Kinetic Models for Overloaded Elution Chromatography", 1990 Annual Meeting of the American Institute of Chemical Engineers, Chicago, November 12-15, 1990.

Hettich, R. L.

Shea, M. J.*; Compton, R. N.*; Hettich, R. L., "Laser Ablation Studies of Palladium Electrolytically Loaded with Hydrogen and Deuterium", 1990 American Physical Society Meeting, Anaheim, Calif., March 12-16, 1990.

Hettich, R. L.; Jacobson, K. B.*, "Laser Desorption FTMS for the Structural Characterization of Underivatized Pteridines", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Hettich, R. L.; Buchanan, M. V., "Examination of Sample Substrate Effects in Laser Desorption FTMS Studies of Biological Compounds", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Hettich, R. L., "Reactions of Carbon Cluster Anions with Oxygenated Compounds Using FTMS", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Hettich, R. L., "Generation and Characterization of Cluster Ions by Fourier Transform Mass Spectrometry" Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Hettich, R. L.; Buchanan, M. V., "Matrix-assisted Laser Desorption Fourier Transform Mass Spectrometry for Biological Compounds", NATO Workshop on Mass Spectrometry, Minaki, Canada, June 24-28, 1990.

Hettich, R. L.; Buchanan, M. V., "Structural Characterization of Modified Nucleic Acid Constituents by Laser Desorption FT-MS", 43rd Annual Summer Symposium on Analytical Chemistry", Oak Ridge, July 24-27, 1990.

Hettich, R. L.; Buchanan, M. V., "Determination of Oligonucleotide Sequences and Modifications by Laser Desorption Fourier Transform Mass Spectrometry", 200th Annual Meeting of the American Chemical Society, Washington, D. C., August 26-31, 1990.

Hettich, R. L., "Mass Spectrometry Capabilities of the Analytical Chemistry Division", Office of Technology Transfer Meeting with Eastman Chemical Company, ORNL, October 11, 1990.

Hettich, R. L.

Hettich, R. L.; Buchanan, M. V., "Laser Desorption Fourier Transform Mass Spectrometry for Ion Generation and Structural Characterization", DOE Workshop on Advanced Laser Technology for Chemical Measurements, Oak Ridge, November 12-14, 1990.

Hulett, L. D.

Hulett, L. D., "The Slow Positron Facility at Oak Ridge National Laboratory and Its Research Programs", Vanderbilt University Seminar, Nashville, Tenn., October 30, 1990.

Hulett, L. D.; Donohue, D. L.; Lewis, T. A.*, "Slow Positron Beam Extraction and Manipulation Using a Pulsed Gap Accelerator Technique", 11th International Conference on the Applications of Accelerators in Research and Industry, Denton, Texas, November 5-8, 1990.

Hulett, L. D.; Donohue, D. L.; Peretz, F. J.*; Montgomery, B. H.*, Hayter, J. B.*, "Preliminary Considerations of an Intense Slow Positron Facility Based on a ^{78}Kr Loop in the High Flux Isotope Reactor", MRS Symposium on Proposals Relating to a National Positron Facility, Boston, November 27-30, 1990.

Hulett, L. D.; Donohue, D. L., "Positron Microanalysis with High Intensity Beams", MRS Symposium on Proposals Relating to a National Positron Facility, Boston, November 27-30, 1990.

Ilgner, R. H.

Wise, M. B.; Buchanan, M. V; Guerin, M. R., "Rapid Analysis of Trace Organics Using Direct Sampling ITMS", Symposium on Monitoring Water in the 1990s; Meeting New Challenges, Denver, June 11-14, 1990.

Buchanan, M. V.; Hettich, R. L.; Wise, M. B., "Analytical Applications of Laser Desorption FTMS", Symposium on Monitoring Water in the 1990s; Meeting New Challenges, Denver, June 11-14, 1990.

Keller, J. M.

Keller, J. M.; Botts, J. L.; Peele, J. M.; Baggett, C. J., "Characterization of Radioactive Waste from ORNL Storage Tanks", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Kerley, E. L.

Kerley, E. L.; Buchanan, M. V., "Generation and Trapping of Electrosprayed Ions for Analysis by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Klatt, L. N.

Dale, J. M.; Klatt, L. N.; Ramsey, J. M., "Document Counterfeit Deterrence Via Substrate Tags", USSOCOM Expo 90, Idaho Falls, Idaho, March 21-22, 1990.

Laing, W. R.

Laing, W. R., "EPA Protocols vs Old Waste Tanks", DOE Analytical Managers Conference, Los Alamos, N. M., September 11-13, 1990.

Laing, W. R., "Environmental Sampling", Westinghouse Materials Corporation, Cincinnati, December 2-3, 1990.

McLuckey, S. A.

McLuckey, S. A., "The Use of Unconventional Ionization Methods with Quadrupole Ion Traps", American Society for Mass Spectrometry Conference on Ion Trapping in Mass Spectrometry, Sanibel Island, Fla., January 28-31, 1990.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "The Potential Utility of the Three-Dimensional Quadrupole as an Analyzer for Ions Derived from Biological Materials", DOE Workshop on the Relevance of Mass Spectrometry to DNA Sequence Determination, Seattle, Wash., April 4-5, 1990.

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McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "Electrospray Ionization/Ion Trap Mass Spectrometry", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

McLuckey, S. A., "Chemistry and Physics in a Mass Spectrometer: What Makes a Reaction Analytically Useful?", 43rd Annual Summer Symposium on Analytical Chemistry, ORNL, July 24-27, 1990.

McLuckey, S. A.

McLuckey, S. A.; Van Berkel, G. J.; Glish, G. L., "Quadrupole Ion Trap Analysis of Ions Derived from Electrospray", 17th Annual Meeting of the Federation of Analytical Chemists and Spectroscopy Societies, Cleveland, October 7-12, 1990.

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McLuckey, S. A.; Glish, G. L.; Grant, B. C., "Recent Advances in Explosives Detection at Oak Ridge", Annual FBI Meeting on Explosives Detection", Quantico, Va., October 16-17, 1990.

Mamantov, G.

Mamantov, G.; Tortorelli, L. J.*; Flowers, P. A.*; Harward, B. L.*; Trimble, D. S.*; Hondrogiannis, E. M.*; Coffield, J. E.; Klatt, L. N., "Investigations of Some Aspects of Chemistry in Alkali Chloroaluminate Melts", 7th International Symposium on Molten Salts, Montreal, May 6-11, 1990.

Maskarinec, M. P.

Maskarinec, M. P.; Wachter, L. J., "Organic Services", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Maskarinec, M. P.; Harmon, S. H.; Fleming, G. S., "A Retention Index System for Improving the Reliability of GC/MS Tentative Identifications", 6th Annual Symposium on Waste Testing and Quality Assurance, Washington, D. C., July 16-20, 1990.

Ramsey, J. M.

Ramsey, J. M.; Whitten, W. B.; Goeringer, D. E., "Laser-Based Detection of Atoms and Molecules in Electrodynamic Traps", American Society for Mass Spectrometry Conference on Ion Trapping in Mass Spectrometry, Sanibel Island, Fla., January 28-31, 1990.

Ramsey, J. M.; Whitten, W. B., "Fluorescence Analysis of Microdroplets: An Approach to Single Molecule Detection", Optical Society of America Meeting on Laser Applications to Chemical Analysis, Incline Village, Nev., February 5-8, 1990.

Ramsey, J. M., "Optical Spectroscopy in Electrodynamic Traps", Seminar presented at Michigan State University, East Lansing, April 12, 1990.

Ramsey, J. M.

Ramsey, J. M.; Whitten, W. B., "Ultrasensitive Fluorescence Analysis in Levitated Microdroplets", 199th National Meeting of the American Chemical Society, Boston, April 22-27, 1990.

Ramsey, J. M.; Whitten, W. B., "Looking for Single Molecules in Levitated Microdroplets", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Ramsey, J. M., "Approaching Single Molecule Detection in Condensed and Gas Phase Measurements Using Electrodynamic Traps", Department of Chemistry, University of British Columbia, Vancouver, June 18, 1990.

Goeringer, D. E.; Whitten, W. B.; Ramsey, J. M., "Resonance Ionization in an Ion Trap Mass Spectrometer", Fifth International Symposium on Resonance Ionization Spectroscopy and Its Applications, Varese, Italy, September 16-21, 1990.

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Ramsey, J. M., "Ultrasensitive Spectroscopic Measurements in Electrodynamic Traps", Chemistry Department Seminar, Indiana University, Bloomington, October 29-31, 1990.

Ramsey, J. M.; Whitten, W. B., "Fluorescence Detection at the Single Molecule Level Using Levitated Microdroplets", Waters Chromatography Co. Seminar, Boston, November 9, 1990.

Ramsey, J. M.; Whitten, W. B.; Arnold, S.*; Bronk, B. V.*, "Ultrasensitive Molecular Fluorescence Spectroscopy in Levitated Microdroplets", DOE Workshop on Advanced Laser Technology for Chemical Measurements, Oak Ridge, November 12-14, 1990.

Ramsey, R. S.

Ramsey, R. S.; Katti, A. M.; Guiochon, G. A., "Trace Enrichment by Displacement Chromatography", 14th International Symposium on Column Liquid Chromatography, HPLC '90, Boston, May 20-25, 1990.

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Ramsey, R. S.; Ho, C. -h.; Carrier, W. L.*, "Analytical Methodology for Measuring Cyclobutane Pyrimidine Dimers in UV-Irradiation DNA", 18th Annual Am. Soc. Photobiol. Meeting, Vancouver, British Columbia, June 16-20, 1990.

Robinson, L.

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

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Rosseel, T. M.; Young, J. P.; Vane, C. R.*; Zuhr, R. A.*; Peterson, R. S.*, "High Resolution HIXSE Studies of the Chemical Environment of Sub-Surface Moieties", DOE/BES Site, Review, ORNL, April 9, 1990.

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	Rosseel, T. M.; Young, J. P.; Vane, C. R.*; Zuhr, R. A.*; Peterson, R. S.*, "High Resolution Heavy-Ion-Induced X-ray Satellite Emission Study of Implanted Sulfur as a Probe of Co-Implanted Oxygen in an Oxide Substrate", 11th International Conference on the Application of Accelerators in Research and Industry, Denton, Texas, November 5-8, 1990.
Shaw, R. W.	Shaw, R. W.; Young, J. P.; Smith, D. H., "Tunable Diode Lasers for Resonance Mass Spectrometry and Very High Resolution Atomic Spectroscopy", Optical Society of America Meeting on Laser Applications to Chemical Analysis, Incline Village, Nev., February 5-8, 1990.
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	Shaw, R. W.; Young, J. P.; Smith, D. H., "Isotopically-Selective Resonance Ionization Mass Spectroscopy Using Tunable Semiconductor Diode Lasers", 43rd Annual Summer Symposium on Analytical Chemistry, ORNL, July 24-27, 1990.
	Shaw, R. W.; Young, J. P.; Smith, D. H., "Resonance Ionization Mass Spectrometry Using Tunable Diode Lasers", 200th American Chemical Society National Meeting, Washington, D. C., August 26-31, 1990.
Short, R. T.	Short, R. T.; Todd, P. J.; Grimm, C. C., "Imaging of Low-Energy Ion Beams", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.
Teasley, N. A., Jr.	Teasley, N. A., Jr., "Probal", Software Symposium, Oak Ridge, September 11-12, 1990.
Todd, P. J.	Grimm, C. C.; Todd, P. J.; Short, R. T., "A Data Acquisition and Control System for an Imaging Secondary Ion Tandem Mass Spectrometer", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Todd, P. J.

Markey, S. P.*; Shih, M. -C.*; Todd, P. J., "Focused Cesium Ion Source and Its Performance for Continuous Flow Liquid SIMS", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

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Van Berkel, G. J.

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Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Electrospray Ionization of Porphyrins Using a Quadrupole Ion Trap for Mass Analysis", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Electrospray Ionization of High Mass Molecules Using a Three-Dimensional Quadrupole Ion Trap for Mass Analysis", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Huang, E.*; Henion, J.*; Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A., "Ion Spray LC/MS Determination of Biomolecules with an Ion Trap Mass Spectrometer", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A., "Mass Spectrometric Approaches to Porphyrin Analysis", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L., "Recent Developments in the Analysis of Electrospray Derived Ions Using a Quadrupole Ion Trap Mass Spectrometer", American Society for Mass Spectrometry Fall Workshop - Electrospray Ionization, Chicago, November 5-6, 1990.

Wade, J. W.

Wade, J. W., "DCL Command Procedures - How Far Should Automation Go?", Canberra/Nuclear Data Users Meeting, Key Largo, Fla., May 7-11, 1990.

Whitten, W. B.

Whitten, W. B.; Goeringer, D. E.; Ramsey, J. M., "Laser Spectroscopy with an Ion Trap Detector", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

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Whitten, W. B.; Ramsey, J. M., "Laser Spectroscopy in an Electrodynamic Trap", 6th Interdisciplinary Laser Science Conference, University of Minnesota, Minneapolis, September 16-19, 1990.

Whitten, W. B.; Ramsey, J. M.; Goeringer, D. E.; Buckley, B. T., "Resonance Ionization of Rubidium in an Ion Trap Mass Spectrometer", DOE Workshop on Advanced Laser Technology for Chemical Measurements, Oak Ridge, November 12-14, 1990.

Wise, M. B.

Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Determination of Target Compounds in Environmental Samples Using Direct Sampling Ion Trap Mass Spectrometry", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Wise, M. B.; Ilgner, R. H.; Buchanan, M. V., "Detection and Quantification of Trace Organics in Air by Direct Thermal Desorption Ion Trap Mass Spectrometry", 38th American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, Tucson, Ariz., June 3-8, 1990.

Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Analysis of Trace Organics Using Direct Sampling ITMS", Am. Soc. Test. Mater. Symposium on Monitoring Water in the 1990's, Denver, June 11-14, 1990.

Wise, M. B.; Ilgner, R. H.; Buchanan, M. V.; Guerin, M. R., "Direct Sampling ITMS for Rapid Determination of Nicotine and Drugs in Physiological Fluids", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

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Wise, M. B.; Ilgner, R. H.; Buchanan, M. V.; Guerin, M. R., "Determination of Target Organics in Air Using Ion Trap Mass Spectrometry", 6th Annual Symposium on Waste Testing and Quality Assurance, Washington, D. C., July 16-20, 1990.

Wise, M. B.; Ilgner, R. H.; Guerin, M. R., "Rapid Determination of Nicotine in Urine by Direct Thermal Desorption Ion Trap Mass Spectrometry", 5th International Conference on Indoor Air Quality and Climate, Toronto, July 29-August 3, 1990.

Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Determination of Airborne Organics by Direct Sampling Mass Spectrometry", 5th International Conference on Indoor Air Quality and Climate, Toronto, July 29-August 3, 1990.

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Wise, M. B.; Buchanan, M. V.; Ilgner, R. H.; Guerin, M. R., "Rapid Analysis of Target Analytes in Complex Matrices Using Direct Sampling Ion Trap Mass Spectrometry", 17th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Cleveland, October 7-12, 1990.

Wise, M. B.; Buchanan, M. V.; Guerin, M. R., "Rapid Determination of Trace Organics in the Environment Using Direct Sampling Ion Trap Mass Spectrometry", SETAC 11th Annual Meeting, Arlington, Va., November 11-15, 1990.

Young, J. P.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Hyperfine Spectral Studies of f-Transition Elements by Diode Laser-Assisted Resonance Ionization Mass Spectrometry", 199th National Meeting of the American Chemical Society, Boston, April 22-27, 1990.

Young, J. P.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Hyperfine Spectral Studies of f-Transition Elements by Diode Laser-Assisted Resonance Ionization Mass Spectrometry", *Proceedings of the 199th National Meeting of the American Chemical Society*, Boston, April 22-27, 1990.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Applications of Diode Lasers to Resonance Ionization Mass Spectrometry", Analytical Chemistry Division Information Meeting, June 13-15, 1990.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Applications of Diode Lasers to Resonance Ionization Mass Spectrometry", Fifth International Symposium on Resonance Ionization Spectroscopy and Its Applications, Varese, Italy, September 16-21, 1990.

Young, J. P., "Selected Topics in Laser and Molten Salt Analytical Research at Oak Ridge National Laboratory", Seminar presented at the University of Camerino, Perugia, Italy, September 24, 1990.

Young, J. P., "Process Monitoring Studies in the Analytical Chemistry Division", Office of Technology Transfer Meeting with Eastman Chemical Company, ORNL, October 11, 1990.

Young, J. P.; Shaw, R. W.; Smith, D. H., "Applications of Diode Lasers to Resonance Ionization Mass Spectrometry", DOE Workshop on Advanced Laser Technology for Chemical Measurements, Oak Ridge, November 12-14, 1990.

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Analytical Chemistry	Anal Chim Acta	Biomed Environ Mass Spectrom	Energy & Fuels	Environ Sci Technology	Int J Mass Spectrometry	J Am Chemical Soc	J Am Soc Mass Spectrometry	J Chromatography	J Physical Chemistry	Organic Mass Spectrometry	Proposals	Other	Total
Buchanan, M. V.	6		7	2	1			2			1	3	1	23
Carter, J. A.						1					8		9	
Christie, W. H.		1											2	3
Czok, M.									1					1
Dale, J. M.												1		1
Dose, E. V.	6								4	1				11
Dyer, F. F.		1											1	2
Glish, G. L.	3		1	1	1	3		2	3	1		10		25
Goeringer, D. E.												1		1
Griest, W. H.	1				1							1		3
Guerin, M. R.					1							4	2	7
Guiochon, G.	245[a]								15	3		5	5	273
Hettich, R. L.			2					1						3
Ho, C. -h.												2		2
Katti, A. M.													1	1
Klatt, L. N.												9	2	11
Laing, W. R.													37	37
McLuckey, S. A.	4	1	1			3	1	3				1	1	15
Mueller, T. R.		1										1		2

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Analytical Chemistry	Anal Chim Acta	Biomed Environ Mass Spectrom	Energy & Fuels	Environ Sci Technology	Int J Mass Spectrometry	J Am Chemical Soc	J Am Soc Mass Spectrometry	J Chromatography	J Physical Chemistry	Organic Mass Spectrometry	Proposals	Other	Total
Ramsey, J. M.	2											2	4	8
Ramsey, R. S.	5	1										6	1	13
Ross, H. H.												2	3	5
Rosseel, T. M.												15	2	17
Shaw, R. W.												5		5
Smith, D. H.			2									2		4
Stewart, J. H.					1								40	41
Todd, P. J.									2		1	41		44
Tomkins, B. A.									1			2	2	5
Van Berkel, G. J.				2		1								3
Whitten, W. B.	1	1										1	2	5
Young, J. P.	2											2	3	7
TOTALS	275	6	13	5	5	8	1	8	26	5	2	132	109	595

[a]As Associate Editor

SUMMARY OF ANALYTICAL SERVICE WORK

ORGANIZATION	Number of Results Reported By: Analytical Spectroscopy	Radioactive Materials Analysis	Organic Chemistry	Inorganic Chemistry	TOTAL
ORNL Unit					
Analytical Chemistry	1,155	907	10,018	859	12,939
Central Management		210	587	312	1,109
Chemical Technology	6,185	6,352	12,071	2,118	26,726
Chemistry		32	953	1,568	2,553
Energy		399		1,511	1,910
Engineering Physics and Mathematics	7	32	2,479		2,518
Engineering Technology	90	34	264	35	423
Environmental and Health Protection		9,451	52,860	17,109	79,420
Environmental Sciences	22	200	15,606	7,478	23,306
Environmental Restoration		1,607	909	3,837	6,353
Finance and Materials	1,122	20	513	8	1,663
Fusion Energy		145	6,497	20	6,662
Health and Safety Research	48	497	2,435	2,289	5,269
Instrumentation and Controls	140	14		43	197
Metals and Ceramics	3,350	205	4,957	718	9,230
Physics	156	312	147	1	616
Plant and Equipment		189	6,439	661	7,289
Research Reactors	50	172	2,963	58	3,243
Robotics & Process Systems	60	9	235	23	327
Solid State		79	2,420	564	3,063
Waste Management and Remedial Actions	36	37,374	18,319	2,279	58,003
Others					
K-25		418	220	3,413	4,056
Miscellaneous	10	177	205	614	1,006
Paducah		1,166	3,725		4,891
Y-12	6,037	5,159	1,848	3,622	16,666
TOTAL	**18,468**	**65,160**	**146,670**	**49,140**	**279,438**

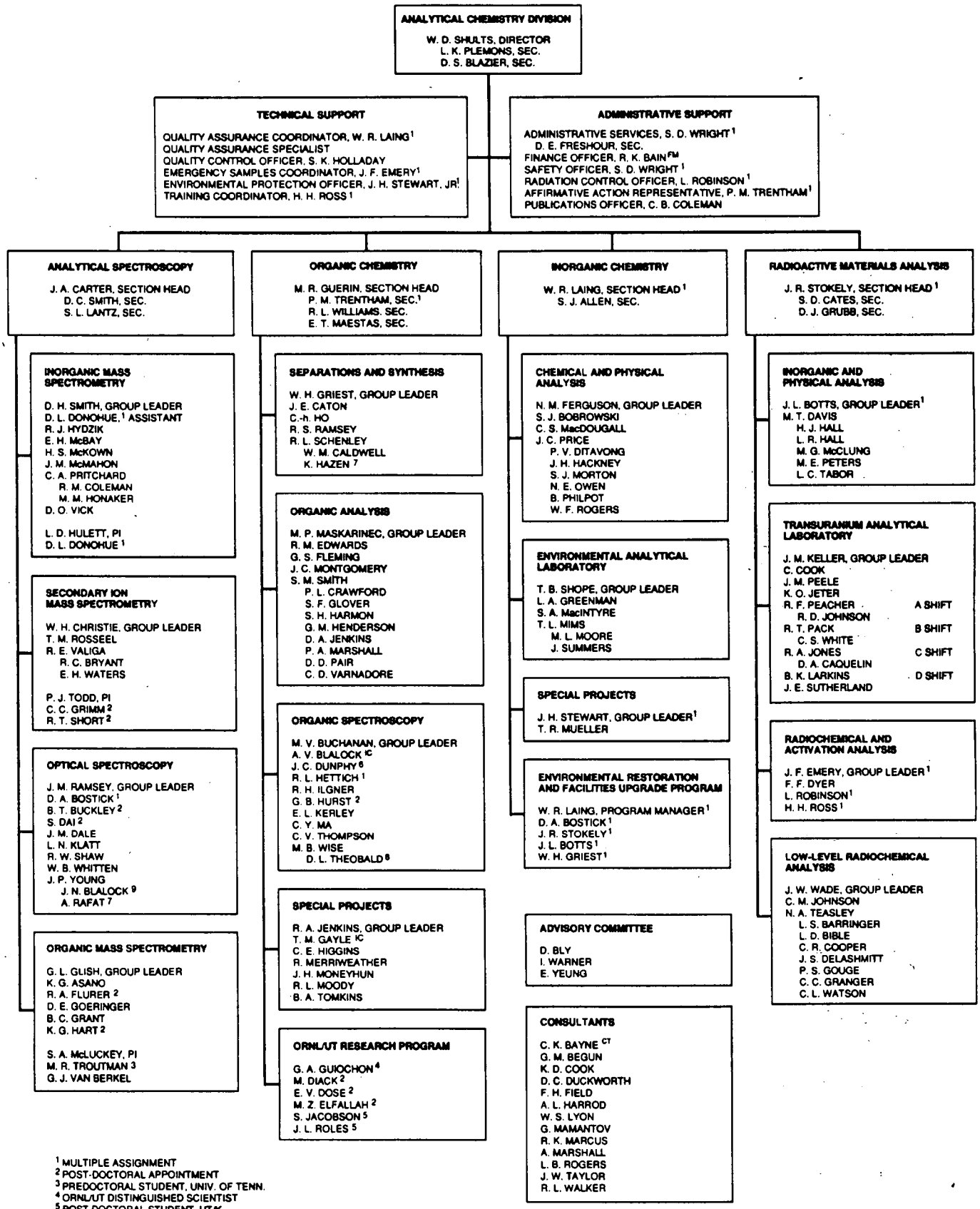
DIVISIONAL MANPOWER AND FINANCIAL SUMMARY
FY 1990

Source	$K	PY[a]
DOE programs		
Energy Research		
Basic Energy Sciences	1,592	10.5
Health and Environmental Research	571	3.7
Environmental Site Survey	10	0.0
Safeguards and Security	513	4.2
Nuclear Energy	272	1.9
Multi Program Facilities Support	117	1.7
Fossil Energy	26	0.1
Miscellaneous	339	2.4
Total DOE Programs	3,440	24.5
Work for others - federal agencies		
Department of Defense	1,333	5.4
National Cancer Institute	373	1.6
Federal Aviation Administration	74	0.7
National Institute of Health	293	0.9
NASA	29	0.1
Miscellaneous	667	6.1
Total WFO - federal agencies	2,769	14.8
Work for others - nonfederal agencies		
Protective Coating Companies	67	0.1
Uranium Ore Testing Companies	37	0.0
Center for Indoor Air Research	185	1.3
Miscellaneous	71	0.1
Total WFO - nonfederal agencies	360	1.5
Support/Services		
ORNL Divisions/Programs	5,843	80.3
Other Clients	2,028	27.9
Intra-division	1,271	
Total Support/Services	9,142[b]	108.2
TOTAL ACD COST	14,440[c]	149.0

[a]Person years

[b]Support/Services cost does not include laboratory overhead.

[c]Total ACD cost excludes intra-division charges.



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