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Analytical Chemistry Division Annual Progress Report For Period Ending December 31, 1980

W. D. Shults

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CONTENTS

INTRODUCTION AND SUMMARY

W. D. Shults, Director

The Analytical Chemistry Division of Oak Ridge National Laboratory (ORNL) is a large and diversified analytical chemistry organization. As such, it serves a multitude of functions for a clientele that exists both in and outside 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, but attention is also given to needs in the analytical sciences themselves. This program is composed of medium- to long-term projects and is supported primarily by the DOE. The program constituted approximately 18% of the FY 1980 budget.

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 results or special 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. This type of activity accounted for approximately 29% of the division's budget in FY 1980.

3. **Technical Support.** The division performs chemical and physicochemical analyses and tests of virtually all types. Development of methodology is an inherent part of this activity because of the variety of analytical problems that arise in a multiprogram institution like ORNL. In general, this work is short-term in nature and comes from other divisions and programs within ORNL. A significant fraction originates outside of ORNL and involves the use of talent and/or facilities in which the division is particularly strong or unique. This type of work accounted for approximately 46% of the budget during FY 1980.

4. **Consultation, Collaboration, and Special Projects.** This work is distinguished from technical support by the nature of interaction between the division and its clientele. Work that falls in this category typically requires special attention and/or expertise and hence constitutes a collaborative effort between the "customer" and division personnel. Interactions range from performing highly sophisticated analytical measurements for or with a research staff member, to instructing others in the use of analytical equipment (plus the interpretation of data), to participating as analytical

members of technical task forces. Activities range from special studies, to program development, to the design and fabrication of analytical instrumentation for others. This work involves close interaction with the staffs of other divisions at ORNL and with non-ORNL people. Support for this activity composed approximately 7% of the FY 1980 budget.

The Analytical Chemistry Division is organized into five major sections, each of which may carry out any type of work falling in the four categories mentioned above. Chapters 1 through 5 of this report present progress within the five sections during the period January 1, 1980 to December 31, 1980. The following paragraphs summarize work in the various sections.

Analytical Methodology Section (Chap. 1). There are two groups in this section: Analytical Instrumentation and Physicochemical Analysis.

Spectroscopy continues to be prominent in the research effort of the Analytical Instrumentation group. Work is underway in microspectrophotometry, photoacoustic spectroscopy, resonance ionization spectroscopy, plasma emission (glow discharge) spectroscopy, the use of fiber optic waveguides in analytical spectroscopy, and spectroelectrochemistry. This group is also engaged in the development of in-line monitoring instrumentation for the Consolidated Fuel Reprocessing Program and for the Coal Plant Control Project. In each of these programs, the work is collaborative with personnel of the Instrumentation and Controls Division.

Several accomplishments warrant special mention this year. We discovered that delayed lasing — the time delay between pumping a Nd-YAG laser and lasing action at 1.06 μm — is a measure of optical absorbance within the laser cavity. This new approach may provide a hundred-fold gain in the sensitivity of absorbance measurements over conventional techniques. The concept of a laser power meter, based upon photoacoustic spectrometry, was brought to fruition. New work combining matrix isolation and high-resolution photoacoustic spectrometry was initiated. In-line monitors for "free acid" and uranium and plutonium, based on our concepts and research, have performed well as prototypes undergoing engineering tests. Development of a computer-controlled (remote) pipetter was completed. A laser-generated continuum light source that provides 10-ps pulses of up to 10 mJ each and separated by 8 ns was conceptualized and developed. Very sharp pulses of this type are needed as the source for the unique time-of-flight optical spectrometer that we reported in earlier annual reports.

The Physicochemical Analysis group carries out a variety of rather specialized nonroutine service and development projects and maintains a long-range research program. During this period, the group completed the study (reported last year) of the passivation of titanium electrodes, using electron spectrometry. Similar work involved the study of nickel cathodes used as electron guns in ORELA; the objective was to optimize their performance. This group completed development of a method for measuring asbestos content of various building materials and ensuring that it is less than 1%. Gypsum is a common component (and interference) in this type of measurement, but we determined that simply heating the sample at 300°C is a convenient way to remove gypsum interference. This asbestos study was published.

The highlight of the research effort in this group during the current year was the work with positron spectroscopy, which was supported initially by ORNL's exploratory studies ("seed-money") program. Most of the effort has been devoted to development of a positron source that can be used for spectrometric experiments. S. Pendyala, from the State University of New York at Fredonia, has been a close collaborator in this project. Tungsten and molybdenum moderators can be used to produce monoenergetic positrons that have an intrinsic FWHM less than 1 eV. The yields using tungsten and molybdenum are 100 times greater than those of common moderators such as magnesium oxide. We purchased a high-intensity ^{22}Na source of positrons and prepared a practical positron gun with it. We are now investigating positron spectroscopy as a surface analysis tool. The ORNL-built electrostatic electron spectrometer is being used for this work.

Previous work by this group, on the characterization of fly ash, received special recognition this year when it was published in *Science* and selected as the front cover photograph.

Mass and Emission Spectrometry Section (Chap. 2). The Mass and Emission Spectrometry Section comprises four groups: Organic Mass Spectrometry, Elemental and Ion Probe Surface

Spectrometry, Actinides and Inorganic Mass Spectrometry, and Safeguards Mass Spectrometry.

A highlight in the Organic Mass Spectroscopy Group has been the construction and performance evaluation of a three-sector mass spectrometer. This was mentioned very briefly in the last annual report as a modification of our double-focusing instrument. A unique feature of this three-sector configuration is that the double-focusing components (electric sector I plus magnet) can be operated in high-resolution mode, and metastable spectra of mass separated components obtained by electric sector II. This type of experiment is analogous to capillary column gas chromatography/mass spectrometry in that a high-resolution separation device precedes mass spectrometric identification. In this case, a high-resolution mass spectrometer is the separation device. We have successfully demonstrated this mode of operation, using a resolving power of about 14,000. We have also carried our initial experiments into photofragmentation spectrometry (PFS) with the three-sector instrument. In this mode, the ion of interest is mass selected by the doublefocusing components, and a photon beam is used to activate and fragment ions in the third field-free region so that they can be analyzed via conventional ion kinetic energy scans. A laser has been acquired so that further work in PFS can be done.

Exploratory studies were made to evaluate the potential of the ion microprobe mass spectrometer for mass spectral studies of nonvolatile organic and/or organometallic substances. The ion microprobe is attractive for this type of study because it has high sensitivity, it has the ability to select a variety of ionizing reagents, and the primary ion energy can be controlled. We observed an abundant secondary ion current that corresponded to cationized organic species and fragmentation of the cationized organic substrate. Design and construction of a source that will facilitate this type of research were initiated.

Secondary ion mass spectrometry (SIMS) allows one to perform mass and isotopic analysis on samples that are sometimes not amenable to other mass spectrometric techniques. The advantage here is that tedious chemical preparation steps may be circumvented. This year we developed methods that allow the use of SIMS for the rapid and accurate determination of lithium and boron isotopic ratios in difficult sample types. Several immediate applications of this important measurement have been made, not the least of which was the analysis of samples from Three Mile Island (TMI).

We have continued fundamental studies in SSMS techniques, with the objective of improving the precision of this type of analysis. A servo-controller was developed to maintain the spark gap width at a constant value, because gap width is ordinarily an uncontrolled parameter that leads to loss of analytical precision. The controller that we developed not only provides a constant gap width, and hence improved precision, but also has proved to be useful for long exposures, which require close operator intervention. We are also using a fast beam chopper in conjunction with the gap controller. This allows a more controlled portion of the spark pulse to be sampled and reduces inhomogeneity. Results of analyses are being monitored to compare the precision measured with these alterations in operation and the precision obtained with an unaltered mass spectrometer.

Much progress has been made toward establishing SSMS capabilities for highly radioactive materials. A surplus instrument was acquired and has now been fully tested and installed in our hot-cell laboratories in Building 2026. The shielded cubicle and transfer system has been designed, and "cold" testing of the system was done. We expect to complete this unique facility early in 1981; it should be capable of handling solid samples that read $\sim$10 mC/kg at 1 cm.

We have continued to develop and apply the resin bead technique of sample preparation for isotopic characterization and isotope dilution quantitation analysis by mass spectrometry. This technique has been extremely useful in our work with TMI samples of various types. Minor isotopes in the 1% concentration range can be measured with precision of ±0.5%, and major isotopes in the 50 to 99% range can be measured with precision of ±0.1% by this technique. We continue efforts to demonstrate the utility of the resin bead sample-loading technique as a viable analytical tool for measuring uranium and plutonium for safeguarding purposes. This year demonstration of the compatibility of this sample-loading technique with single-stage mass spectrometric measurements was completed. We acquired a quadrupole mass spectrometer and demonstrated its utility as an on-site analytical instrument. We are systematically trying to improve the precision of the resin bead technique, and we are teaching others how to use it and assisting in its implementation on a national and international basis. It is interesting to note that samples of americium, curium, and californium are now routinely submitted to us on resin beads for isotopic analysis. This approach results in the handling and transferring of much smaller amounts of highly radioactive material, while yielding more reliable analytical results.

Technical Support Section (Chap. 3). There are four groups in this section: General Analytical Laboratory, Radioactive Materials Analytical Laboratory, Transuranium Laboratory, and Reactor Programs.

Each of the groups must cope with a wide variety of analytical problems and special projects. Characteristically, they must also participate in collaborative studies with members of other divisions and programs at ORNL. An important requirement is that these groups must maintain an awareness of new developments in analytical technology and adopt them quickly, when appropriate. Development of a computer-based system for making BET measurements in either the adsorption or desorption mode has been completed. We now have surface area measurement capabilities that are based on either pressure or weight changes.

Other instrumentation-oriented projects included construction of a bipolar-pulse conductivity detector for use in ion chromatography, modification of an ion chromatograph for glove-box operation, and development of a baseline compensator for differential scanning calorimetry. Instrumentation was also developed for measuring carbon-14 in dissolver solutions and tritium in single irradiated microspheres.

New equipment of various types was acquired by each group. Our new x-ray fluorescence system, acquired last year, has been used for diverse analytical tasks on both nonradioactive and radioactive materials. This system was designed for analyses that must be performed within a glove box. Conceptualization and design of a second system for remote analysis of gamma-emitting materials were initiated this year. Of special significance has been the design and acquisition of an inductively coupled plasma emission spectrometry system. It is of unique design and incorporates both quantometer and scanning monochromator operating capabilities. This system will be operative early in 1981.

Renovation of our hot-cell laboratories has been a continuing program for the past two years and is now virtually complete. This effort is paralleled by development of microprocessor-based instrumentation for remote analysis done in the Analytical Instrumentation group. The prototype of our new computer-controlled remote pipetter is in use, and work on a remote titrator is underway.

Bio-Organic Analysis Section (Chap. 4). The work of the Bio-Organic Analysis Section is programmatic in nature, with strong emphasis on programs related to health and the environment. This section develops and provides methodology, materials, and hardware for biological and environmental studies, along with data to support these studies. There are three groups: Quantitative Methods and Applications, Isolation and Identification, and Sampling and Special Projects. Considerable overlay of technical interests exists among these groups and among other sections in the division. Because of the programmatic nature of this work, much of the effort here is directed toward acquiring information as opposed to merely collecting data. Two programs — the Life Sciences Synthetic Fuels Program and the Inhalation Bioassay Chemistry Program — reside within this section although portions of the work are carried out by other sections.

The work of this section emphasizes the recovery of organic compounds from complex mixtures such as environmental samples, coal-derived materials, and cigarette smoke — and means for determining them quantitatively. The high-performance liquid chromatographic behavior of marker compounds representing polyaromatic hydrocarbons and polyaromatic amines has been emphasized this year. Resin (Tenax) trapping of volatile organics followed by thermal desorption and glass capillary gas chromatographic analysis has been refined and implemented on a routine basis for ambient air analysis. The use of diffuse reflectance FTIR has been another focus this year and has proved to be a simple and sensitive means for examining solids and/or solutions in a KBr matrix. This technique also has potential for selective LC detection.

An important activity within this section is maintenance of a Fossil Fuels Research Materials Facility for EPA. We have computerized the data bank related to this operation this year and hosted a major workshop for a set of users of the facility.

Extensive experience with separation and identification procedures has been developed in this section and continues to be emphasized.

Currently, research centers on methods for the preparative scale isolation of biologically significant compounds and for the discrimination of structural isomers. A highlight has been the development of a procedure for distinguishing primary, secondary and tertiary amines by chemical ionization mass spectrometry; NH_4^+ and ND_4^+ are the collision gases. We have established that polar constituents, isolated from the neutral aromatics fraction of coal derived oils by our fractionation procedures, are especially mutagenic; these are primarily oxygenated compounds. Work is continuing on high-resolution LC with open capillary columns; currently we are trying to develop columns that will allow reverse-phase operation and hence provide potential utility with aqueous systems.

A major new effort is directed toward developing instrumentation for generating and monitoring military obscurants (smoke screens) that can be used in animal inhalation toxicology studies. We have prepared systems for generating and delivering diesel oil aerosol to rodents for inhalation bioassay. The physical and chemical characteristics of these aerosols must be determined relative to the starting oils and to aerosols generated in the field. The sampling and chemical characterization of hazardous solid wastes is also a new activity this year; initial emphasis is on means for recovering organic constituents from diverse solid materials.

Nuclear and Radiochemical Analysis Section (Chap. 5). This section is composed of three groups: Low-Level Radiochemical Analysis, Radiochemical and Activation Analysis, and Special Projects. All three groups perform work that ranges from routine radiochemical analysis to short-term development projects. Long-term development and research are carried out primarily in the Special Projects group.

A new sample preparation laboratory and sample receiving room were put into operation this year in the Low-Level Radiochemical Analysis group, completing several year's work toward upgrading facilities and equipment in this group. The Nuclear Data, ND-6603 spectrometer system mentioned last year is fully operational now, and a new automated high-capacity liquid scintillation counter was acquired. A concerted effort is now underway to automate the handling of analytical data generated by the various laboratories in the section. Three additional computer terminals were acquired to increase access to ORNL's DEC System 10 for data management. Much progress has been made with our ND-6620 system in the Radiochemical and Activation Analysis group, developing it as *the* data processing system for most counting equipment in the Intermediate Level Laboratories. Ultimately, we hope to have the ND-6620 system collect and analyze data and communicate it directly to the division's data management system which resides in the DEC-10.

Developmental activities within the section have continued to support a number of projects within the Laboratory, UCC-ND, and other organizations where our special capabilities or expertise is applicable. We are participating in the Life Sciences Synfuels Program (i.e., in studies related to the health/environmental impact of the gasifier at the University of Minnesota at Duluth). This work consists of activation analysis for trace elements and low-level radiochemical analysis for important naturally occurring radionuclides in feed materials, tars, and discharges from the plant. A collaborative project with IBM Corporation is underway to determine ultratrace levels of uranium and thorium in semiconductor materials. Sensitivities for these elements have been extended to about 0.01 ng/g by neutron activation analysis at the High Flux Isotope Reactor. Developmental work for the Consolidated Fuels Recycle Program has resulted in improved methods for determining carbon-14 and iodine-129 in reactor fuel dissolver solutions. Interest in the determination of technetium-99 in environmental materials has continued. Methods for analysis of technetium-99 in soils and vegetation are now fully developed and in routine use, and efforts are being made to extend the methodology to animal tissues. Studies of techniques for determining gamma-emitting radionuclides in small animals are nearing completion. This work is directed toward determining the biological radionuclide assimilation of wild animals living on the Oak Ridge reservation. A new method for electrolytic enrichment of tritium was also developed this year. It extends our sensitivity to the millibecquerel level and has been used for analysis of well waters from the Three Mile Island nuclear power station.

Other Divisional and Staff Activities. Chaps. 6 and 7 contain information that reflects the work of the division as a unit. Information about the quality assurance and safety programs is presented in Chap. 6, along with the tabulation of analyses rendered. Publications, oral presentations, professional activities, educational programs, and seminars are cited in Chaps. 7 and 8. Approximately 109 articles and 43 reports have been published, and 145 oral presentations were given during this reporting period.

1. ANALYTICAL METHODOLOGY

W. S. Lyon, Section Head

Research and development activities in the Analytical Instrumentation group of this section continue to concentrate (but not exclusively) on laser action and its applications. Delayed lasing, for example, is being studied; a program in resonance ionization spectroscopy for element-specific photoionization of samples subsequent to the mass analysis of their respective isotopes is underway; testing of the optoacoustic laser energy meter developed last year has continued; a new program in matrix isolation optoacoustic spectroscopy using laser excitation started; and equipment has been assembled for study of time resolved laser spectroscopy.

In-line sensor development has continued with work either completed or in final stages for a free acid monitor, electrochemical in-line sensors, uranium and plutonium monitors; a study of possible means of detecting I_2 in dissolved fuel solution was made. Work on the remote instrumentation for analyses in highly radioactive solutions continued. Other ongoing research includes analytical application of fiber optic waveguides, spectrochemical studies at the Transuranium Research Laboratory, and spectroelectrochemical studies in chloroaluminate melts. Detection of amines and inorganic fluoride in gas chromatography was investigated, and possible improvements in coal beneficiation studied.

In the Physicochemical Analysis group, major advances have been made in positron spectroscopy: improvements in yield of moderated positrons, demonstration of elastic scattering, and use of the ORNL technique for low-energy positron diffraction at Brandeis University. A new program has begun to use the facilities at the Holifield Heavy Ion Research Facility for x-ray and electron spectroscopy; preliminary experiments are now underway. A number of researchers in other divisions have been given assistance by group members who have used combined techniques of transmission and scanning electron microscopy, optical microscopy, x-ray fluorescence, and x-ray diffraction. Some of the materials studied in these collaborations are asbestos, SYNROC, bacteria, resin beads, silver zeolites, Nb-based alloys, and molten salt battery components.

ANALYTICAL INSTRUMENTATION

H. H. Ross, Group Leader

Application of Lasers to Analytical Chemistry

Delayed laser action and its applications. We have observed that when a Nd-YAG laser is pumped with a short-duration (~50 ns) pulse at 532 nm, it will begin lasing anywhere from 0.1 to 10 µS later at a wavelength of 1.06 µm. This delayed laser action is due to the kinetics that govern the time-dependent excited state populations in this four-level laser host. This phenomenon can be used to determine rate constants that connect different energy levels of the Nd^{+3} ion: we have determined the multiphonon relaxation rate between $^4G_{7/2}$ and $^2G_{7/2}$ + $^4G_{5/2}$ states of the Nd^{+3} ion (1). This rate constant, as determined by our technique, is 1.6 × 10^6 s^{-1}. This value agrees well with the results of others who employed different measurement scheme .

We have found that this delayed lasing characteristic can also be utilized for optical absorption determinations. Because the time delay between pumping and lasing is also dependent on threshold energy of the laser cavity and therefore losses within the cavity, intracavity absorption measurements can be performed by determining this time delay. At high pump levels (and thus short delay times), the sample absorbance is linearly related to the delay time. An experiment has been set up to measure the time delay between pump and laser output pulses as a function of intracavity absorption (2). Separate photodiodes and discriminators produce timing signals from the pump and laser output pulses. The time difference between the two timing pulses is converted into a proportional voltage by a time-to-amplitude converter and measured with a pulse-height analyzer. In the present configuration, each channel of the pulse-height analyzer corresponds to 1.5 ns, or an absorbance of about 0.001. An absorbance cell within the cavity can be filled with a blank or sample solution to make a determination.

The functional relationship between delay time and concentration of an absorber was studied by measuring the time delay for a series of solutions of copper sulfate. Excellent agreement was found between measured delays and a theoretical curve based on the previously measured YAG relaxation rate constant (1). The delay changes by ~80 ns on going from the blank solution to a solution with an absorbance of 0.5. With our present (preliminary) setup, a milliabsorbance unit, or 0.001 absorbance, can be measured. We expect that with further improvements the detection li it can be reduced by at least two orders of magnitude while still maintaining the linear relationship between absorbance and time delay. Thus, this novel technique could overcome the nonlinear responses observed in the typical intracavity absorbance experiment. Primary improvements needed to achieve this greater sensitivity are the reduction of parasitic losses in the laser cavity and greater pump energy reproducibility. This measurement scheme could have application in trace chemical analysis due to its ability to measure very low absorbance values. *(J. M. Ramsey, W. B. Whitten)*

Laser spectroscopic studies. The study of analytical applications of resonance ionization spectroscopy (RIS) has continued (3) in cooperation with G. S. Hurst's group in the Health and Safety Research Division. We have continued the study of RISA, RIS with amplification (4), which can effectively cause one RIS active atom to emit, for example, 10 or more electrons during the time of a laser flash. After extensive study, it was found that the scheme mentioned previously (3), which involves the use of NO, does not effectively neutralize an RIS-formed lithium ion, and work with this gas has been stopped. In a cooperative study with T. A. Callcott's group at The University of Tennessee, we have made the first studies of applying RIS to the element-specific photoionization of samples subsequent to mass analysis of their respective isotopes. Samarium atoms, effusing from a hot source chamber, were photoionized by a two-photon RIS process; the resonant laser was tuned to 436.4 nm to excite the 5 s → 7 p transition followed by photoionization from that state (5). Using a time-of-flight mass analyzer and a 10-ns laser pulse, it was possible to observe seven isotopes of samarium, having an abundance of 3% or greater. In these first studies, the efficiency of ionization or the confirmation of expected isotopic abundances was not checked. Working with the Mass Spectrometry group of the Analytical Chemistry Division, we have purchased a

N_2-laser-pumped tunable dye laser system and will repeat this study of the RIS-mass analysis of samarium with a magnetic mass spectrometer to better establish the precision of the technique with respect to the above characteristics. The study will be followed by similar studies of gadolinium and dysprosium to evaluate the element-specific nature of this new technique.

Detection of single plutonium atoms by an RIS process is being studied. This work is a cooperative effort with C. E. Bemis, Jr., Physics Division, and personnel of EG&G, Santa Barbara, California. The concept, using a two-photon RIS scheme (5) and generating plutonium from the alpha decay of ^{244}Cm, was discussed last year (3). The plutonium recoil is rather weak, 100 keV, so the gas in the RIS chamber will have to be light (He) and at low pressure (1.3 to 2.6 kPa). During this period it has been demonstrated that one electron can be detected under such conditions; a new chamber for carrying out this study has been designed, fabricated, and assembled. Preliminary testing of the chamber is presently underway. For counting of single atoms, the electron counter can be operated in a Geiger mode, but both proportional and Geiger modes of operation will be evaluated.

Further studies of laser-induced nuclear polarization (LINUP) have been made. The work is a cooperative effort with C. E. Bemis, Jr., and J. R. Beene, Physics Division, and S. D. Kramer, Health and Safety Research Division. As discussed last year (3), these studies have provided the first direct experimental proof and measurement of the large deformation expected *for the nucleus of fission isomers (6).* The study involves absorption of photons tuned to resonant bound-bound transitions and therefore can give spectral information of short-lived (μs to ms) lifetimes. This year the effect with ^{240m}Am was verified with a more refined experimental setup. Consideration has also been given to the study of other short-lived species by this technique. Attempts to synthesize ^{242m}Am ($t_{1/2}$ = 15 ms) for study have not proven successful by the synthetic routes studied. It is probable that francium can be studied by the LINUP technique; the results of such a study will yield new information about the optical spectrum of this element. *(J. P. Young)*

Optoacoustic spectroscopy. ***Optoacoustic laser energy meter.*** This device detailed in last year's report (7) has received further characterization by testing of repition rate and optical pulse-length effects on calibration, further response linearity testing, determination of the actual detection limit, and construction of a finalized prototype unit. These steps were necessary to complete development and to produce a working model.

The OA laser energy meter response for short optical pulses was tested using a nitrogen laser with a pulse length of 8 ns FWHM. The energy meter calibration factor observed was unchanged, even though these pulses differ in duration by 125-fold from our 1-μs laser. Thus, as expected, this device measures energy/pulse and not peak power.

At fast repetition rates (≥30 pps), calibration errors occur because each acoustically stretched pulse begins to overlap with the next signal pulse in the train. With the microphone ac-coupled, response errors are negligible below 30 pps, but beyond that repetition rate the energy meter will underestimate slightly the actual energy/pulse.

Upon close scrutiny the overall response factor for our energy meter showed a slight elevation at low-laser-input energies; the response factor (mV/mJ) increased approximately 15% over the 3.5 decade input energy range tested. This seemed suspect, so the thermopile used as a standard for these data was calibrated using electronic substitution power (joule heating) as a primary standard. When the original data were then corrected using this standardization, the OA energy meter response was constant within the ±5% scatter of the data points. The low-input energy extreme of data (0.67 μJ) does not honestly represent the detection limit of our instrument. The pulse-to-pulse amplitude instability of the dye laser measured contributes a great deal to the overall noise level observed. The true instrumental detection limit was measured with a stable helium-neon laser, attenuated with neutral density filters and modulated with a mechanical chopper. The signal-to-noise ratio approaches unity for an input pulse energy of 0.24 μJ.

Finally, the breadboard energy meter was converted into a prototype instrument. A printed circuit board was designed and fabricated, and a chassis box assembled and wired. Additional units of the OA energy meter could now be easily constructed.

The optoacoustic laser energy meter is simple and inexpensive. It is suitable for quantitation of the ultraviolet, visible, or infrared output of any pulsed laser. Such coherent light sources find wide use in many research and development areas of chemistry, physics, and biology. The only limitations on use of this device are the minimum laser pulse energy detectable and the maximum pulse energy the target will withstand without deterioration. *(R. W. Shaw)*

Matrix isolation OAS. In a new effort this year, we are examining the utility of piezoelectric (PE) detection of OAS for matrix-isolated (MI) species. The analytical application of matrix isolation and Shpol'skii frozen solution sampling for high-resolution optical spectroscopy has been reviewed by Wehry and Mamantov (8). Many organic compounds diluted in frozen matrix samples exhibit significantly narrower spectral bandwidths than are obtainable at room temperature. Thus, MI sampling can be a powerful method for the analysis of multicomponent samples where spectral selectivity is paramount.

Wehry, Mamantov, and co-workers have employed fluorescence and Fourier transform infrared (FTIR) spectroscopies for detection of MI samples. The former method results in subnanogram detection for many PAHs, with ultimate sensitivity achieved for compounds with high fluorescence quantum yields. Unfortunately not all compounds of interest exhibit strong fluorescence. Notable examples of weak- or nonemitters are partially hydrogenerated PAHs (important by-products found in coal conversion products); heteroatom-substituted aromatic materials from the pyridine, pyrrol, furan, and thiophene families (some known to be carcinogens and others suspected as contributors to the toxicity of fossil fuel-related materials); and polychlorinated biphenyls (the subject of intense environmental concern). For nonfluorescent compounds, FTIR has been used as a complementary technique, but the detection limits reported are substantially higher ($\sim$100 ng) than those for fluorescence detection. For organic compounds that absorb light strongly, but are only weakly fluorescent, the excited state photophysics must be dominated by radiationless processes. This fact makes them prime candidates for OA spectroscopy, wherein signal strength is derived from energy released by these same dark processes. We have combined these two techniques, MI sampling and OA spectroscopy, to capitalize on the benefits of both. MI sampling permits high-resolution spectroscopy for large molecules, while OA spectroscopy provides sensitive detection for nonfluorescent compounds.

The interface between these two methods is PE detection. PE transduction for OA methods has been promoted recently by workers at Bell Labs (9). Very sensitive detection of OA spectroscopy for room-temperature liquids and powders was achieved using a pulsed laser and PE ceramic transducers. In that work, both the ceramic transducer and the sample were bonded to a quartz spacer or "buffer" slab. Acoustic disturbances created optically in the sample were transmitted by the spacer to the detector with minimal acoustic impedance mismatches. Based on the reported fractional absorption detectability of 10^{-5}, we conservatively estimate a detection limit of about 1 ng by MI/OAS for a nonfluorescent molecule with $\epsilon \sim 10^4$ and a molecular weight of 200.

We began with room-temperature experiments to familiarize ourselves with PE detection of OAS before moving to low-temperature conditions and the associated experimental difficulties. Two types of PE transducers were utilized, X-cut crystalline quartz and a lead zirconate titanate (PZT) disc. Samples were placed directly on the X-cut quartz since it is transparent. For the opaque PZT disc, samples were placed on a glass window to which the PZT was acoustically bonded. The chief advantage of the former technique over the use of an independent ceramic transducer bonded to a slab is that the problems associated with maintaining an acoustic bond between the substrate and the transducer at low temperatures are eliminated. The PE quartz substrate serves all the functions of sample holder, acoustic buffer slab, and transducer. The voltage pulses produced optoacoustically were processed with a gated integrator.

Laser OA spectra were recorded for Nd_2O_3 powder for both its 510- and 579-nm bands. The samples were prepared as mulls in mineral oil and smeared on the transducer surface. For these fluid samples, a cover plate seems to be required to constrain the sample. Without such a cover the optically driven expansions preferentially compress the air over the open sample rather than the quartz substrate on the opposite side. It is hoped that this will not be necessary with low temperature matrices, which are much more rigid.

Several modifications of the experimental setup were made to improve the signal-to-background ratio. The final arrangement yielded a S/N of about 50 for this weak absorber. The X-cut quartz and PZT transducers have similar acoustic responses, with the ceramic device somewhat more sensitive. For comparable experimental conditions, the signal-to-noise ratios observed for Nd^{+3} spectra are about the same.

Having achieved reasonable room-temperature success, low-temperature experiments were begun. We decided to prepare simple Shpol'skii frozen solution samples using a liquid nitrogen-shielded, liquid helium optical Dewar. The samples were prepared by freezing liquid films on the quartz substrate in liquid nitrogen. Subsequent spectra were also measured at 77 K. The OA spectrum of a frozen pentacene saturated solution in decane was attempted first. Pentacene has an extinction coefficient of 5900 l mol^{-1} cm^{-1} at 596 nm, but it is only sparingly soluble in decane. No OA signal was observed as the laser was scanned over the suspected absorption region. However, a fluorescence excitation spectrum was recorded for this sample. Several excitation bands were measured with linewidths of 10-50 cm^{-1}. The inability to detect OA signals is most probably due to the small amount of pentacene probed (low concentration and thin sample).

MI/OA spectra of phenanthrene have been attempted recently with greater success. Its solubility is much higher than pentacene and $\varepsilon \sim$ 14800 at 293 nm. Because it was necessary to utilize *second* harmonic generation to produce the ultraviolet light necessary for phenanthrene spectroscopy, much less intensity could be brought to bear on the sample. As we scanned the absorption region, pulsed acoustic response was observed with an oscilloscope and was seen to *increase* and *decrease* with the visually observed fluorescence and phosphorescence intensity. No quantitative results have as yet been achieved, but *clearly* the method was successful for phenanthrene. For this experiment a charge-sensitive preamplifier capable of operation at 77 K was designed and used. Because it can be located very near the sample (i.e., in the Dewar), cable capacitance was eliminated and more sensitive detection was accomplished. The preamplifier failed after several cool-down/warm-up cycles and will need to be improved for better reliability.

More effort is needed in development of better sample preparation methods, quantitative measurement of spectra of several compounds, and improvement of the cryogenic preamplifier before this technique can be evaluated for its analytical utility. *(R. W. Shaw, G. Mamantov, H. B. Howell)*

Time-resolved laser spectroscopy. This project was initiated last year to determine the viability of temporal spectroscopic measurements in quantitative and qualitative chemical analyses (10). The primary emphasis until now has been on the conception and development of instrumentation that is capable of providing the necessary information while maintaining simplicity and reliability (11-13).

The initial experiments will use a mode-locked argon-ion laser as a fluorescence excitation source and a cross-correlation detection scheme. This laser source provides short-duration pulses ($\sim$100 ps) at a high repetition rate ($\sim$100 MHz). The detection system must have correspondingly high temporal resolution and the ability to utilize data from the large number of experiments being performed per unit time. The cross-correlation detection scheme has such capabilities when implemented with microwave electronic components. In addition to adequate temporal resolution, a time-resolved fluorometer must have good luminance sensitivity. This will be achieved by introducing single-photon counting techniques into the cross-correlation detection scheme.

The single component that limits temporal resolution of the instrument is the photomultiplier tube. In attempting to perform these experiments in the single-photon-counting mode, the photomultiplier tube must have high gain ($>10^6$) along with a broad measurement bandwidth. An RCA 31024A tube was selected for these experiments.

A new biasing circuit was designed and constructed for this photomultiplier tube. The circuit utilizes a ground plane, which is cemented to the tube socket, to obtain the necessary high-frequency response. Single-electron emission from the photocathode produces an output pulse of $\sim$1.2 ns FWHM and $\sim$100 mV peak amplitude across a 50-ohm load resistance. Both of these characteristics are adequate for this application.

The mode-locked argon-ion laser was tested to determine its performance. Transform-limited optical pulses from such a laser should be of the order of 100 ps duration. These short-duration pulses are difficult to measure electronically. Measurements using a high-speed photodiode and sampling oscilloscope reveal pulses with a 140-ps FWHM and also some pulse substructure on the trailing edge. It is difficult to deduce whether this pulse substructure is optical in origin or is an electrical reflection from an impedance mismatch. A nonlinear interferometric experiment has been set up to determine if the electrically measured pulse substructure exists in the optical pulses. For this experiment, a Michelson interferometer was constructed using porro prisms as retro reflectors rather than mirrors. The porro prism reflectors provide a beam displacement in the interferometer, eliminating optical feedback from the interferometer into the laser. Such feedback disturbs mode-locked operation. The nonlinear medium used to obtain the second-order optical correlation function is a two-photon absorber, α-NPO. Our first attempts at measurements with this setup were frustrated by mechanical instabilities. These instabilities cause fringes to fluctuate at the output of the interferometer, generating intolerable amounts of noise in the two-photon-induced fluorescence signal when attempting a point-by-point measurement. This problem was overcome by driving the optical time-delaying element of the interferometer at a constant rate with a synchronous motor. The scanning causes any interference fringes at the nonlinear absorber to move rapidly across the sample, thus translating the measurement noise to a higher frequency. The high-frequency noise can then be effectively removed with a low-pass filter in the detection electronics. This approach also allows tracing of the second-order optical autocorrelation function continuously on a strip chart recorder.

Results of the nonlinear autocorrelation experiments indicated that the optical pulses did, in fact, have a small shoulder on one of their edges. This shoulder was largely removed by adjustment of the mode-locker frequency, but little change was observed in the electronically detected signal. Thus, the pulse substructure was attributed to electrical reflections in the associated transmission lines. The optical correlation measurements also yielded an accurate determination of pulse duration. When the laser was well mode-locked, correlation measurements consistently produced correlograms with durations of less than 100 ps. Assuming the optical pulses can be described by a Gaussian-shaped envelope, these measurements imply that the actual pulse duration is shorter than 70 ps. Although this number is smaller than the typical quote of 100 ps for a mode-locked argon-ion laser, it is consistent with sampling oscilloscope measurements, when the response time for the electronics is taken into account. These measurements indicate that performance of the mode-locked argon-ion laser is more than adequate for our future studies. *(J. M. Ramsey)*

In-line Sensor Development

We are continuing our work on the development of in-line chemical measurement systems for the Consolidated Fuel Reprocessing Program in cooperation with the Instrumentation and Controls Division. Instrument research that was described in previous reports is now in the prototype stage; new work is primarily directed toward the in-line determination of plutonium at high concentrations and uranium at low levels.

Free acid monitor. The prototype free acid monitor, which is a complete redesign of the original working model (14), is essentially complete. It is anticipated that bench testing and calibration will begin soon.

Electrochemical in-line sensors. The initial phase of this project was completed and the results summarized in an ORNL/TM report (15). The loss in sensitivity caused by organic deposition on the vitreous carbon electrode could not be corrected without mechanical resurfacing. This failure precludes the electrochemical determination of plutonium in Purex streams. The platinum electrodes, however, can be restored through anodic and cathodic excursions so that qualitative detection of hydrazine, hydroxylamine, or nitrite ion appears practical.

Application of electrical conductivity to the measurement of acidity is being extended to organic Purex streams. An experimental flow cell (cell constant ∼200 cm^{-1}) that can measure acid concentrations as low as 0.05 *M* in 30% TBP-dodecane streams was constructed and calibrated. The strong dependence on TBP concentration will make it necessary to calibrate the monitor with each batch of TBP-dodecane. The utility of the proposed monitor is being evaluated in a solvent extraction test facility.

Uranium and plutonium monitor. The continuous in-line determination of uranium in both aqueous and organic streams by spectral methods has been investigated and described in two reports (16,17). The spectrum of uranium in various aqueous streams is affected by changes in HNO_3 concentration. Therefore, a dual-wavelength photometric procedure was developed to compensate for sample acidity. However, measurement of uranium in TBP-dodecane streams is independent of HNO_3 concentration and also is not significantly affected by fluctuations in other organic stream constituents such as TBP, NPH, and DBP around design concentrations. A simplified linear calibration equation based on a single uranyl absorbance maximum is, therefore, sufficient to calculate uranium concentrations in organic streams. A multiwavelength filter photometer has been fabricated by the Instrumentation and Controls Division to monitor uranium in both aqueous and organic streams. The photometer consists of a stationary visible light source and a PM tube separated by a rotating filter wheel. Five interference filters are set in the wheel to produce pulsed monoenergetic light as the wheel rotates. The wavelengths of light used for analysis are selected according to the type of stream and element, either uranium or plutonium, to be determined. In the case of uranium, 416- and 426-nm filters are used to compensate for aqueous streams. In addition, a 530-nm filter is used to monitor stream turbidity or radiation darkening of cell windows. A microcomputer is used to record independent absorbances and to perform background correction and calculations. The remaining filters will be selected so that Pu(III) and Pu(IV) can be determined simultaneously in streams containing both uranium and plutonium. To date, the photometer has been calibrated for aqueous and organic uranium-containing streams. The instrument can monitor 2-200 g/liter U in aqueous samples and 2-100 g/liter U in TBP-dodecane using a 1.3-mm flow cell. The day-to-day reproducibility of measurement was ±5% over a 30-day period. Photometric analyses of prepared organic and aqueous samples compared favorably with results using a standard Cary-14 spectrophotometer; a correlation coefficient of 0.999 or greater was observed between the two sets of results.

The equipment and space have been obtained to begin a similar spectral study of plutonium in aqueous and organic streams. When optimum wavelengths and calibration algorithms are determined, the multiwavelength spectrometer will be available for in-line plutonium measurement.

Radiation damage to optical cables. Because many in-line spectral analyses are contingent on the use of fiber optic cables, a study of their transmission characteristics and resistance to radiation is in progress. Cumulative ^{60}Co gamma-ray exposures up to 10^6 Gy have been used to produce permanent changes in optical transmission. In general, radiation damage progressively reduces the transmission of quartz optical fibers at wavelengths below 400 nm. Transmission of visible light (400 nm to 800 nm) is not seriously affected until a total dose of 10^6 Gy/m has been accumulated. Coupling losses of multifiber cables have also been studied. Single-fiber quartz cables 1 mm in diameter are presently under investigation because of their potential for making low-loss joints.

Low-level uranium detection in waste streams. A program has just begun to use time resolved fluorescence to detect 10-ppm levels of uranium in the presence of quenching agents and impurities that fluoresce. A very short laser pulse (1 ns) from a nitrogen laser will be used to provide the excitation energy and time pulses. The laser is on hand, and the high-speed timing circuitry is being acquired. Several studies have been conducted to date, using a standard fluorometer to examine the effect of various ions on the fluorescence of trace uranium under constant excitation conditions. At constant hydrogen ion concentration but increasing nitrate concentration, the uranyl fluorescence decreased to essentially zero at a nitrate concentration of 0.5 *N*. Severe quenching of the uranyl fluorescence was noted in aqueous samples containing 1 ppm of Fe(III) or 20 ppm of Mn(II), Cu(II), or Ni(II). There is experimental evidence to indicate that temporal resolution of the fluorescence following a very short excitation pulse should reduce or eliminate such quenching or competing fluorescence observed in conventional instrumentation. *(J. E. Strain, D. T. Bostick, J. M. Ramsey)*

Iodine analysis. In the Consolidated Fuel Reprocessing Facility, pieces of spent fuel elements will be roasted in air; the products will be dissolved in nitric acid. Most of the resulting NO_2 and fission product iodine will have been volatilized by this time, but some will inevitably remain in solution. Since the presence of too much I_2 in the solution will interfere with subsequent purification steps, it seemed advisable to develop an in-line instrument to monitor the concentration of I_2 remaining in the dissolved fuel solution.

In view of the probable near-opacity and high radioactivity, 10^4-10^8 C kg^{-1} h^{-1}, (10^8-10^{10}

ℓ/h) of this solution, it appeared that an indirect approach might be best (e.g., measurement of the optical absorptivity of I_2 vapor over the solution, using the broad 520-nm I_2 band). To do so, however, requires that a remedy be found for an obvious difficulty: overlapping of the I_2 band by the broad NO_2 band at 410 nm. A possible solution was found in the fact that as the gas temperature rises, NO_2 dissociates (into colorless products) before I_2 dissociates. Exploratory work was therefore undertaken to find, under simulated working conditions, (1) whether any substantial proportion of the I_2 remaining after sparging would be oxidized to HIO_3, which cannot easily be eliminated; (2) whether sufficient I_2 vapor exists over a dissolver solution to make an optical absorption measurement possible; and (3) whether NO_2 and I_2 dissociate at the expected temperatures in the presence of air, H_2O vapor, HNO_3 vapor, etc.

Two-day refluxing of 1 µg of iodine with 3.5 *N* HNO_3 at 80°C oxidized only 0.006% of the I_2 present. Thus, only a tiny fraction of the remaining dissolved I_2 would be converted to nonvolatile HIO_3. The absorptivity of a 12.5-cm column of the I_2 vapor over a solution of 100 µg iodine per ml of 3.5 *N* HNO_3 was measured as a function of solution temperature. Optical density of the vapor ranged from 0.003 at 22°C to 0.042 at 80°C. Measurements of the dissociation behavior of I_2 vapor at high temperatures were made under two sets of conditions: (1) constant vapor pressure of iodine in the absorption cell and (2) constant mass of iodine in the absorption cell. In the first case, crystals of iodine were placed in the thermostatted reservoir of the cell (e in Fig. 1.1). I_2 vapor at a fixed vapor pressure diffused through the narrow (~0.25 mm) annular gap between the reservoir and the heated side-arm of of the cell. This construction made it possible to maintain a temperature difference as great as 750°C between the two portions of the cell. It is evident from the figure that all of the vapor in the side-arm exists at the temperature of the furnace; the light used for measurement traverses only hot gas. In the constant mass measurements, iodine crystals were sealed into a fused silica cylinder, which was inserted into the furnace. For the NO_2 measurements, several milligrams of NO_2 (plus air) were sealed into a similar quartz cylinder.

The net result of these measurements was that by the time a temperature of 600°C was attained,

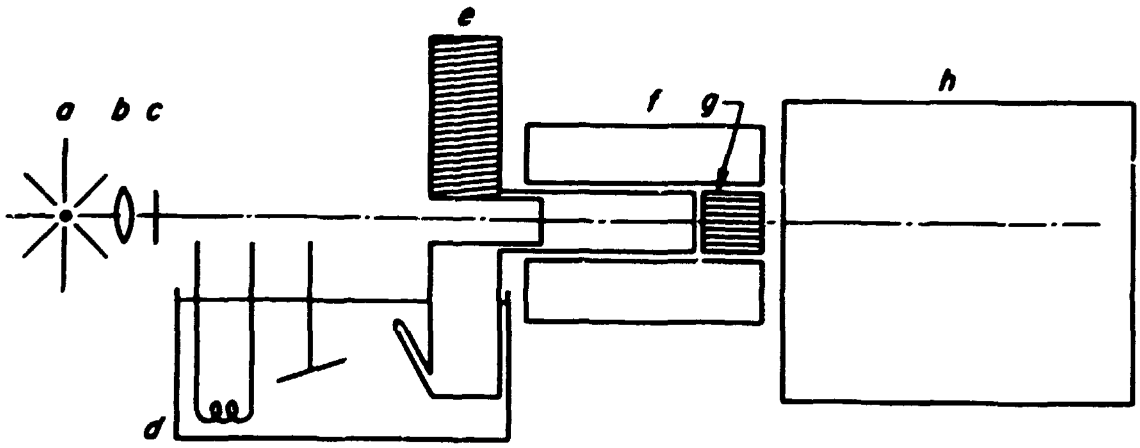

Fig. 1.1. Apparatus for measuring light absorption at high temperature. a - light source; b - collimating lens; c - filter; d - thermostated ethylene glycol bath; e - cell for constant sample temperature absorption measurements (upper portion heated); f - furnace; g - mechanical collimator; h - monochromator and detector.

the NO_2 had essentially been destroyed, but more than 50% of the I_2 molecules remained intact. *(C. Feldman)*

Remote instrumentation development. Work is continuing on the project initiated last year to develop specialized instrumentation for the unique needs of the ACD. The laboratory instrument designed to measure tri-*n*-butylphosphate and described in a previous report (18) has been used routinely for approximately one year by the analytical support group at the Transuranium Laboratory. Excellent performance has been reported. A documentation package for the instrument was prepared and placed in the ORNL Master Analytical Manual file. Two additional units were constructed and are being used by various groups within the Technical Support section of the ACD. The results of this development effort have been published (19).

The main objective for this year was the development of a prototype pipetter for delivering highly radioactive sample aliquots in a remote environment. Central to the general project plan is the use of a microcomputer-based instrument controller. New designs will incorporate advantages inherent in microcomputer-based control: stand-alone operation, application flexibility, and documentation of operation.

The Data General Corporation microNOVA MP/100 microcomputer was selected as the general instrument controller for this project. Housed in the MP/100 chassis are the mN602 16-bit central processing unit, 32K words of random access memory, a digital input/output board, an asynchronous serial communications port, and the power supply. Operator interaction with the system is by a keyboard/printer terminal. Digital communication with the pipetter is via a specially designed interface board also housed in the MP/100 chassis.

The principle of operation for the pipetter is displacement of liquid with a screw-driven plunger. A 1.8-degree stepping motor is used to rotate the 1/4-20 drive screw, allowing digital control of the plunger movement. The plunger is dimensioned to deliver 1000 μl over a travel of 2.540 cm. Combination of the above specifications produces a possible volume resolution of 0.25 μl (incremental resolution of 6.4 μm). A signal related to plunger position is generated by a linear variable differential transformer (LVDT) coupled to the plunger. Prior calibration of the LVDT in terms of millivolts per millimeter of translational motion enables confirmation of plunger position to be made.

Software for control of the pipetter is written in BASIC language. The operator has the option of performing any of several operations: filling the pipette, emptying the pipette, pipetting solutions, refilling the pipette, or printing out a record of operations for a particular sample. Prompting messages from the controller regarding status facilitate operator interaction during all operations. Assembly language software, invisible to the operator, provides digital communication with the pipettor through the specially designed interface hardware.

Reliability of solution pipetting is directly related to the accuracy and precision with which the plunger can be positioned. Data collected for these variables indicate a delivery accuracy and precision of 0.3 μl and 0.4 μl, respectively, for volumes ranging from 100 to 500 μl. A report describing the prototype system is being prepared for publication (20).

Work is underway toward the construction of a hot-cell version of the remote pipetter. The control program will be stored as firmware (i.e., in erasable programmable read-only-memory (EPROM) semiconductor memory devices). This still allows the flexibility inherent in microcomputer-based controller design while alleviating problems associated with magnetic data storage devices). *(L. N. Klatt, D. E. Goeringer)*

Analytical Applications of Fiber Optic Waveguides

Two methods of measuring optical absorption spectra with fiber optic waveguides are under development. Both techniques use optical fibers to obtain spectroscopic dispersion in the time domain. In one method, variation of the velocity of a light pulse with wavelength is used to obtain the needed dispersion. Various wavelength components of a polychromatic light pulse are detected sequentially after they have traversed a long optical fiber. The wavelength of a particular component of the spectrum is determined by its time-of-flight through the fiber. The second technique is called time delay multiplexing. In this method, the light pulse to be measured is first dispersed spatially by a conventional diffraction grating; then the separated spectral components are focused onto an array of optical fibers of incrementally increasing lengths. All fibers lead to the same detector. Light of each wavelength interval is delayed by a different amount of time, corresponding to the length of the fiber through which it passes. The detector thus measures sequentially the wavelength components of the pulse.

Prototype instruments based on the two techniques have been described in a previous report (21). Construction and evaluation of a 30-channel time delay multiplex spectrometer have been completed. This instrument uses a 600-groove/mm diffraction grating to disperse and focus the input pulse onto an array of 30 fibers, with lengths ranging from 1 to 59 m. The time delay between channels, determined by the 2-m length increment, is about 10 ns. Spectral resolution is determined by the way the fibers are arranged at the focal plane of the grating, 3 nm per channel for the present configuration. Absorption spectra of uranyl nitrate and cobalt chloride obtained with this instrument are in good agreement with those measured on a conventional spectrophotometer. A description of this instrument has been published in a recent article (22).

A laser-generated continuum light source with sub-nanosecond duration is being developed so that the two time-domain spectrometers previously constructed can be operated in a single-pulse mode. A mode-locked neodymium-glass laser has been constructed from a Korad K-1 power supply and laser head. The output of the laser is a train of pulses, 8 ns apart, with individual pulse energies of up to 10 mJ. Duration of the pulses, measured by a two-photon correlation technique, is about 10 ps. When the laser pulse train is focused into a 15-cm cell of carbon tetrachloride, a bright continuum, which extends from 450 to beyond 800 nm, is generated which extends from 450 to beyond 800 nm. The time dependence of the continuum is again a series of pulses shorter than 1 ns. The final step in the source development will be to switch a single pulse from the mode-locked laser output to avoid overlap between successive spectra. *(W. R. Whitten)*

Spectrophotometric Studies at the Transuranium Research Laboratory

In cooperation with J. R. Peterson of The University of Tennessee, R. G. Haire of the Chemistry Division, and various visitors to the Transuranium Research Laboratory, studies of transuranium elements and related compounds have continued (23). In general, spectral techniques are used for the identification and characterization of compounds that are of interest to the heavy element research program of the Office of Basic Energy Science. Because the samples to be studied are often 1 to 10 μg in size, special techniques have been developed to obtain absorption and/or luminescent spectra on such small samples.

Studies of the chemical consequences of radioactive decay in the bulk-phase solid state have continued, and based on our spectral studies, significant advances have been made in the understanding of these processes. The first paper describing β^- decay of $BkBr_3$ to $CfBr_3$ has been published (24). A second paper describing α and β^- decay in the series $Es \rightarrow Bk \rightarrow Cf$ has been written. In this second paper, it is postulated that it might be possible to infer the crystal structure of einsteinium halides by spectral study of the progeny halides. Presently, the structure of einsteinium halides cannot be experimentally determined by x-ray methods because of the extreme radioactivity of einsteinium. It is now known that in the decay of EsX_3, where X is F, Cl, Br, or I, only high-temperature forms of the respective BkX_3 and CfX_3 are observed, based on spectral analysis. Before making these assessments, it was found that one can see spectral differences in f-f transitions in actinide compounds that are related only to the crystal structure of that compound; thus, it was proven possible to determine crystal structure by spectral determination. It has further been established that within the precision of our spectral measurements (possibly ±10% since it is a single-beam instrument) all progeny compounds are accounted for. It has been previously thought that not all the $BkBr_3$ expected has been seen in the decay of $EsBr_3$. This is not correct: the apparent lack of $BkBr_3$ can be explained because of insensitivity of the spectrum of the high-temperature form of $BkBr_3$ (24). The spectral study of chemical consequences of radioactive decay has expanded to a study of Es_2O_3 and to other forms of radioactive decay. No conclusive results are yet available in the latter study, but the first spectra of Cf_2O_3 were obtained by examining samples of Es_22O_3 that were several years old. It has since been found that the spectrum of this form of Cf_2O_3 is probably a high-temperature form of Cf_2O_3 not easily made directly from californium. Using our knowledge of samarium bromide spectra, we are studying the effect of neutron radiation on the chemical composition of $^{147}SmBr_3$. This isotope was chosen because it will not transmute with neutron irradiation. This study is an evaluation of our ability to prepare μg samples of halides, irradiate them at the High Flux Isotope Reactor, retrieve them, and follow their subsequent chemistry.

In cooperation with G. W. Beall, Chemistry Division, spectral studies of various actinides doped into $LaPO_4$ have been carried out. Lanthanide orthophosphates are found in nature in the form of the mineral monazite, which contains stable concentrations of actinides; synthetic analogs of this substance represent a promising primary containment medium for the isolation of high-level nuclear wastes. The doped crystals were prepared by a flux technique, and from the crystals grown in air, it was found that U(III) or (IV), Pu(IV), Np(IV), Am(III), and Cm(III) are the stable oxidation states of these actinides as grown in $LaPO_4$. A paper describing these studies has been written.

Spectrophotometric determinations have been applied to various miscellaneous studies as well. By spectral analysis it has been reasonably established that Bk(II) has been prepared by the reaction of $BkBr_3$ with lanthanum or berkelium metal. An absorption peak at 935 nm seems to be characteristic of this oxidation state. Cation-cation complexes of NpO_2^+ with other cations in the solid state have been studied by spectral observation of the μg-sized crystals. A group headed by P. G. Huray of The University of Tennessee is doing magnetic studies of transcurium compounds; the identification of the actinide species present in their instrumentation can be made, directly, by spectrophotometry. Several times this identification has proven to be useful. *(J. P. Young)*

Atomic and Molecular Spectroscopy

Spectroelectrochemistry in chloroaluminate melts. Halide melts are widely used industrially and are currently of particular importance in the areas of molten salt batteries and catalysis. We have successfully developed and applied spectroelectrochemical techniques at an optically transparent electrode to the study of electrochemical reactions in chloroaluminate melts ($AlCl_3$-NaCl mixtures). Although we have only used these techniques with chloroaluminate melts, they are sufficiently general to be easily adapted to other molten salt systems. Thus, this research effort has resulted in development of a general capability for the study of electrode reactions in molten salt media. Details of the experimental apparatus and instrumentation have been published (25).

The chemistry of sulfur in chloroaluminate melts is of considerable interest as it relates to the development of a sodium-sulfur(IV) molten salt battery (26,27). Spectroelectrochemical studies of the oxidation of sulfur in this medium have provided considerable information about polyatomic sulfur cations and their chemical and electrochemical reactions. Discussion of this system is conveniently presented in terms of the three oxidation steps observed as elemental sulfur is oxidized to S(IV).

A previous report (28) summarized initial results for the first oxidation step. Data obtained during the past year have shown that the chemistry is considerably more complex than previously proposed. Electron spin resonance (ESR) and uv-visible spectroelectrochemical studies have indicated that at least two radical cations and two or more diamagnetic sulfur cations are formed in the first oxidation step. The diamagnetic species were previously thought to be S_{16}^{2+} and $^{2}S_{8}^{+}$; S_8^+ and S_4^+ were the proposed radicals. Hyperfine ESR data obtained by Low and Beaudet (29) for the chemical oxidation of sulfur in 65% oleum have shown that the radical previously thought to be S_4^+ is probably S_5^+. Attempts to obtain analogous ESR hyperfine splitting data for ^{33}S in chloroaluminate melts were unsuccessful. Gillespie et al. (30) reported the results from an x-ray diffraction study of a salt containing a polyatomic sulfur cation prepared by chemical oxidation of elemental sulfur in liquid SO_2. This cation was thought to contain S_{16}^{2+}, but was shown to be S_{19}^{2+}. This species possesses an absorption band corresponding to a band observed in the spectroelectrical experiments, strongly suggesting that S_{19}^{2+} is also formed in chloroaluminate melts. Based on this supporting information and the results obtained from numerous experiments designed to ascertain concentration, temperature, and potential dependence of the observed spectroscopic data; the reaction sequence for the first oxidation step can be summarized by the following scheme:

$$\begin{aligned} S_8 &\rightleftarrows S_8^{+} + e^- \\ 2S_8^{+} &\rightleftarrows S_{16}^{2+} \\ S_8^{+} &\rightleftarrows S_8^{2+} + e^- \\ S_8^{2+} + S_8 &\rightleftarrows S_{16}^{2+} \\ S_{16}^{2+} + S_8 &\rightleftarrows S_5^{+} + S_{19}^{2+} + e^- \\ 4S_8^{2+} + S_8 &\rightleftarrows 8S_5^{+} \end{aligned}$$

The two electrochemical reactions are thought to occur at slightly different oxidation potentials.

The second oxidation step results in the formation of monovalent sulfur, present as S_2^{2+}. The formation of this species was observed by uv absorption spectroelectrochemistry. Analysis of absorbance-potential data according to the Nernst equation for a variety of reactions suggests that the reactant for this oxidation step is S_8^{2+} and/or S_5^{+}. There is some spectroscopic evidence for the formation of S_4^{2+} as an intermediate. A proposed reaction sequence for the second oxidation step is given below:

$$\begin{aligned} S_8^{2+} &\rightleftarrows 2S_4^{2+} + 2e^- \\ 4S_5^{+} &\rightleftarrows 5S_4^{2+} + 6e^- \\ S_4^{2+} &\rightleftarrows 2S_2^{2+} + 2e^- \end{aligned}$$

The third oxidation step yields S(IV) in the form SCl_3 as the product. Spectroelectrochemical data indicate that at least one other species, probably S(II), is present in addition to S_2^{2+} during this oxidation. The reaction sequence thus appears to be $S_2^{2+} \rightarrow 2S(II) \rightarrow 2S(IV)$.

In summary, it is reasonable to depict the oxidation of sulfur in acidic chloroaluminate melts in terms of a decreasing number of S-S bonds and increasing chloride complexation as the formal oxidation state of sulfur increases. Each sulfur oxidation wave, then, probably consists of a series of closely spaced sequential oxidation steps rather than single multielectron steps. A manuscript detailing this research has been submitted for publication (31). *(V. E. Norvell, G. Mamantov, L. N. Klatt)*

Specific detection of amines in gas chromatography. In the gas chromatographic (GC) analysis of Synthoil fractions, it was desired to know which of the ether-soluble bases (ESB) were amines and which were not. To determine this, the ESB mixture was treated with trifluoroacetic anhydride, which forms fluorine-containing derivatives with primary and secondary amines. The GC effluent was split; part went to the helium glow detector (HGD) (32), which was used to detect fluorine, and the remainder went to the flame ionization detector (FID). Whenever a peak on the FID tracing represented a primary or secondary amine, there was a corresponding peak on the HGD tracing. Other types of compounds produced no peaks on the HGD chromatogram unless they contained fluorine originally. A paper describing this work has been published (33).

Determination of inorganic fluoride. The detection limit achieved for fluorine by exciting a deposit of diphenyldifluorosilane (ϕ_2SiF_2) on the cathode of a helium glow discharge (34) was reduced to 50 pg. Although sensitivity was found to increase with glow discharge current up to 80 mA, further increases (e.g., to peak values of 250 mA) converted the discharge to a conventional arc, which made the detection of fluorine impossible. It was found that the sensitivity of this procedure was reduced when the ϕ_2SiF_2 was accompanied by unreacted ϕ_2SiCl_2 reagent. A solution to this difficulty is being sought.

A platinum furnace of improved design was fabricated to implement a second approach to detecting fluorine in the glow discharge (i.e., volatilizing small quantities of fluorine-bearing compounds immediately upstream from the discharge). The new furnace is a 3- × 4- × 5-mm platinum block with a shallow depression in the top surface. The bottom of the block is welded to a Nichrome heating element. The solution (1-5 µl) is deposited on the block, the solvent evaporated, and the assembly inserted into the discharge chamber. The block is then heated by passing 40 amperes through the Nichrome element for about 30 s. The best results (i.e., prompt, high, and narrow peaks) were obtained by generating HF as the volatile species. Although a residue containing 100 ng of fluorine as NaF gave no response when heated alone as above, a satisfactory emission peak (685.6 nm) was obtained when the solution was treated before evaporation with a pH 3 citrate or phosphate buffer. Since this approach to the analysis of water samples eliminates the liquid/liquid extraction step, efforts will be continued to maximize its sensitivity. *(C. Feldman)*

Coal Plant Control Development

The Analytical Chemistry Division is cooperating with the Instrumentation and Controls

Division in a multidisciplinary team effort to improve the practice of coal beneficiation. Coal beneficiation is a generic term used to describe any number of processes by which run-of-mine coal is treated to reduce the sulfur and mineral content, and thereby, produce a product that can be utilized either for the production of coke or as a clean fuel for electric power generation. This project is part of an effort by the Department of Energy and the Laboratory to increase the production and use of coal. Our responsibility is in the area of analytical instruments. The first phase of the project involved an assessment of the state of the art. Four activities were completed as part of the assessment process. An introduction to coal preparation was obtained from an intensive training course conducted by personnel of United Coal Companies, Grundy, Virginia. Several coal beneficiation plants located in Kentucky, West Virginia, and Virginia were visited. Each plant possessed unique elements of advanced technology in coal beneficiation. Major findings from these visits were that (1) private industry is using computers and programmable logic control systems to automatically operate coal beneficiation plants, (2) operator and plant employees readily accept the use of this technology, (3) nuclear-based density gauges perform satisfactorily for the measurement of coal-water and magnetite-water slurry densities, (4) an on-line ash monitor yields data comparable to ASTM laboratory procedures, and (5) the fine coal (<6 mm) beneficiation circuits offer the greatest potential for improving coal beneficiation processes.

Literature review has concentrated on quality control measurements for ash, sulfur, and moisture. Instrumentation for on-line measurement of ash is commercially available and has been successfully operated in coal beneficiation plants worldwide. An on-line sulfur monitor, based upon measurement of prompt gamma rays resulting from thermal neutron capture, has been developed and will be field tested in the coal-blending facility at the Monroe, Michigan, steam plant operated by Detroit Edison. This unit also contains an on-line microwave moisture monitor. An expanded version of this system, which provides an on-line multielement capability, will be field tested at the TVA steam plant at Kingston, Tennessee.

Numerous process control instruments developed for use in other industries appear directly applicable to the coal beneficiation industry, and engineering evaluation and testing of these devices in a coal beneficiation plant are required before a major instrument development program is undertaken.

These findings, along with aspects of the coal beneficiation industry reviewed by other members of the project team, have been compiled in a state-of-the-art report. *(L. W. Klatt)*

PHYSICOCHEMICAL ANALYSIS

L. D. Hulett, Group Leader

Positron Spectroscopy

Positron gun. The positron spectroscopy program described in the previous annual report (35) has been continued. We have found that monoenergetic positrons can be generated by exposing specially prepared tungsten surfaces to positron emission sources, such as ^{22}Na or ^{58}Co. The high-energy positrons enter the tungsten and become thermalized. A certain fraction ($\sim 0.1\%$) is then re-emitted into the vacuum. Escape of the thermalized positrons is believed to be due to the "negative work function" effect described by Nieminen and Hodges (36). In a recent publication (37) we have shown a very strong correlation between positron yield and theoretically calculated work functions for surfaces of tungsten, molybdenum, and iridium. Mills (38) has reported experiments that show yields from copper moderator surfaces to be proportional to the square root of the absolute magnitude of their work functions. The "negative work function" concept for positrons that have entered a solid and become thermalized refers to their potential energy, which is determined by the difference between attractive forces of the surrounding electrons and repulsive forces of the nuclei. For certain metals there is a net repulsion, such that the positron is spontaneously ejected. The average velocity with which the positron leaves the moderator surface is proportional to the square root of the potential energy. One would expect the yields of positrons that escape from the moderator to be determined by competition between the rates of annihilation and rates of escape. Thus, there is a rationale for the finding of

Mills (38) that the yield is proportional to the square root of the negative work function.

We have investigated the effect of thickness and material of the window that contains the radioactive source on the yield of monoenergetic positrons ejected from the moderator (39). We did this in preparation for a changeover from a ^{58}Co source, which is windowless, to a ^{22}Na source, which is encapsulated behind a 12 μm Ti foil. Films of varying materials and thicknesses were placed between the ^{58}Co source and the tungsten moderator such that the fast positrons had to pass through the foils before entering the moderator. The dependence of moderated positron intensity on window thickness was found to follow a universal curve. When data were plotted as the logarithm of intensity vs window thickness, expressed as mg/cm^2, all points fell on the same curve, regardless of material. The curve was linear, for the most part, and was reminiscent of Feather plots (40) used many years ago to estimate end-point energies of beta emitters. The data did not constitute a true Feather plot, however. From the universal curve we showed that a 12 μm Ti window decreases the moderated positron intensity by no more than 22% (39).

When the new ^{22}Na source was loaded in our monenergetic positron gun we found that the moderated positron intensity increased by a factor proportional to its fast positron flux. For given activity, the yield of fast positrons from ^{22}Na is almost six times that of ^{58}Co. The half life is much more convenient also: 2.6 y compared to 71 d for ^{58}Co. We then tried to improve moderator efficiency. In the first attempt we used [110] surfaces of single crystal tungsten. The resulting count rate from the gun was about 120,000 cm^{-2} s^{-1}. Next we used dendritic tungsten for which the specific surface area is much higher. Count rates were slightly higher, 137,000 cm^{-2} s^{-1}.

We gratefully acknowledge the expert help of Y. K. Chang and H. Harmon of the ORNL Solid State Division for providing the tungsten single crystals and also preparing their surfaces and Dr. J. J. Cuomo of IBM Corporation for preparing the dendritic tungsten surfaces. *(J. M. Dale, L. D. Hulett, S. Pendyala (41))*

Positron scattering. Work is now in progress to evaluate the use of low-energy positrons as a surface analytical tool. The first experiments involved the scattering of a monoenergetic beam from surfaces of tungsten and silicon. Resulting spectra were compared with those for electrons reflected from the same surfaces. The monoenergetic positron gun can be made to output an electron beam by simply reversing the potential. The electron beam is slightly broader in energy distribution, having a FWHM of 3.1 eV, compared with 2.1 eV for positrons. In Fig. 1.2 the spectra of electrons and positrons scattered from tungsten are superimposed for comparison. Intensity of the elastic peak for the electrons has been normalized to that of the positrons. Elastic peaks for both positrons and electrons occurred at approximately 785 eV, which was the acceleration potential of the gun. Positrons and electrons left the gun with energies slightly different from 785 eV because of opposite signs in work functions. Energies of the elastic peaks of both positrons and electrons have been shifted to 785 eV in Fig. 1.2.

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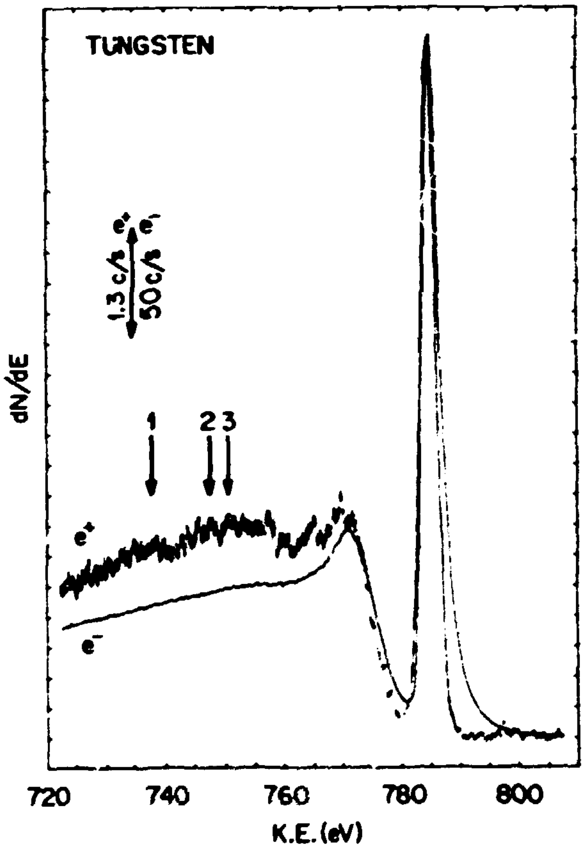

Fig. 1.2. Spectra of positrons and electrons scattered from a tungsten surface. Primary beam energy = 785 eV. Relative to primary peak, the intensity of inelastically scattered positrons is greater than that for electrons.

Structures occurring at energies less than 785 eV in Fig. 1.2 are due to inelastic collisions of positrons and electrons with the tungsten surface. The main energy loss peak for both particles occurs at an energy about 15 eV lower than that of the elastic peak. We believe it to be due to the collective excitation of valence electrons, a process related to the plasmon excitation effect that has been documented for free electron metals such as aluminum and magnesium (42). "Plasmon peaks" are universally observed in x-ray photoelectron and Auger electron spectra. Behind each main peak there is always a discrete energy loss peak that is wellresolved and that occurs at energies about 15-25 eV lower. Theoreticians have predicted for many years that positrons also went through such energy losses. The spectrum in Fig. 1.2 is the first explicit demonstration of this. For energy losses greater than 15 eV, the electron spectrum decreases monotonically in intensity. Corresponding regions in the positron spectrum are higher in intensity and appear to exhibit structure, however. The arrows in Fig. 1.2 denote energy loss points of 34, 37, and 47 eV where the spectrum appears to have its maximum structure. It is possible that the structure is due to excitation of 4f and 5p electrons, which have binding energies corresponding to the energy loss points of the arrows. If this is true, we may have the means of an analytical technique. *(J. M. Dale, L. D. Hulett, S. Pendyala (41))*

Low-energy positron diffraction. The tungsten moderator technique has been used by a Brandeis University group to design a monoenergetic positron gun for low-energy diffraction work. We were aware of this group's efforts, and when we developed the tungsten gun, we suggested that they try it in their experiments. They used it with essentially immediate success; they recently published the first recording of a low-energy positron diffraction (LEPD) pattern (43); Cu (100) was the first substrate used, Cu (111) has also been reported (44). The LEPD patterns show different structures from LEED, thus giving complementary information. We now have assurance that low energy positron spectroscopy will have at least a small beneficial impact on surface analysis. We are continuing to explore applications. An ultra-high vacuum bell jar is being assembled for the purpose of doing combined positron-electron spectroscopy on the same surfaces *in situ*. More comparisons of positron and electron energy loss spectra, such as in Fig. 1.2, will be made, threshold spectra will be studied, and LEPD/LEED measurements will be done. *(L. D. Hulett, J. M. Dale, S. Pendyala (41))*

Heavy Ion Spectroscopy

The Holifield Heavy Ion Research Facility is scheduled to become operational in January 1981. In addition to its use for fundamental studies in nuclear, atomic, and molecular physics, this facility is committed very strongly to applied research. The Solid State and Metals and Ceramics divisions have facilities under development for materials research, and the Analytical Chemistry, Chemistry, and Physics divisions have organized a joint effort to evaluate analytical methods. X-ray and electron spectroscopy induced by heavy ions and heavy-ion lithography will be studied. In preparation for this we have done some preliminary experiments using the Oak Ridge Isochronous Cyclotron as a source of argon ions. The V, Cu, Nb, Ta, and Pt targets have been bombarded with ions having energies of 36.0, 56.4, 76.6, and 103 MeV.

The x-ray fluorescence spectra, recorded with an energy dispersive spectrometer, observed in our preliminary heavy-ion experiment were qualitatively the same as those recorded routinely in our scanning electron microscopy (SEM) work in which specimens are bombarded with electron beams having energies of 10-30 keV. There were certain differences, however. For vanadium we saw $K\alpha$ and $K\beta$ peaks. For copper and niobium we saw $K\alpha$ and $K\beta$ and the L peaks. For tantalum and platinum the K peaks were of too high an energy to be detected, but we saw L and M peaks. For a given spectrum the order of intensities was always seen to be $L>K$ or $M>L$: that is, the intensity fell off as the energy of the line increased. For ion-induced spectra the rate of fall-off is greater than that seen for spectra induced by electrons in the SEM. For any given peak (e.g., K) the intensity falls with increasing atomic number, for either electron or ion bombardment. A common explanation, qualitative in nature, can be given for the effects seen in both types of spectra: to induce x-ray transitions, core electrons must be removed from the target atoms, being bombarded; electron "holes" must be produced in K, L. and M orbitals in order to induce their respective fluorescence spectra. Hole production by a bombarding electron seems easy to imagine: its force field is felt by electrons of the target atoms, and some of them are oriented so that their binding energies are overcome. For a given core level, such as K, the binding energy increase with number and shielding from the force field of the incoming electron increases with the additional outer electrons. Therefore, it is logical that cross sections for x-ray excitations by electron bombardment should go down with increasing atomic number; also, since the L and M shells are closer to the outside of the atom they should be successively easier to ionize. The parallel behavior of the ion-induced results can also be explained in terms of "penetrability" of the target atom by the incoming particle. Present models for core hole production by ion bombardment involves a collision complex with molecular orbitals containing electrons of both the ion and target atom. Holes in the ion are transferred to the target atom. For a mechanism such as this it seems reasonable that K-vacancies should be more difficult to produce than L-vacancies, which, in turn, are more difficult to produce than M-vacancies. As the atomic number of the target atom increases, penetration by the ion becomes more difficult, and cross section goes down. Thus, we can qualitatively explain our experimental results.

Heavy-ion excitation of x rays is known to produce satellite structures in spectra that are dependent on chemical states of the target atoms (45). This will be a subject of our next experiments, which will be done with a wavelength dispersive spectrometer. The energy dispersive spectrometer used in our preliminary work did not have sufficient resolution to study satellite structures. We hope to develop heavy-ion XRF as a molecular as well as an atomic spectroscopy. We will also do some heavy-ion lithography in future work. *(L. D. Hulett, J. P. Young)*

Special Studies

Transmission and scanning electron microscopy. We have been using electron microscopy and x-ray diffraction to evaluate the oxide films produced on Incoloy 800 and 406 stainless steels. The films are being studied by J. D. Redman of the Chemistry Division because of the tritium containment problems anticipated in both fission and thermonuclear reactors. The film on the Incoloy 800 was mainly $MnCr_2O_4$ while the film on the 406 stainless steel was composed of at least two phases, a layer rich in silicon at the metal interface and an outer layer rich in Fe_2O_3. Deposits removed from the inside surface of the tube were examined by transmission electron microscopy. A variety of materials varying in thickness, size, and shape were observed; some less than 0.2 μm in diameter while some single-crystal films 2.5 μm were observed. Some deposits gave single-crystal patterns that indicate hexagonal crystal structures.

C. B. Finch, Metals and Ceramics Division, grew single crystals of gehlenite ($Ca_2Al_2SiO_7$) using even- and off-stoichiometric melts. Three crystals were analyzed quantitatively by electron-induced fluorescence with the SEM using the FRAME program for calculations of Al, Si, and Ca present. Relatively constant Ca:Al:Si atom ratios at random points in a given sample were observed. The silicon concentration was less than expected, but it was observed that the melt surrounding the crystals assumed a glassy texture while the crystals were being grown.

We have examined by TEM, SEM, and EDS many mixtures of sodium and uranium oxides for R. E. Adams, Engineering Technology Division, and G. W. Parker, Chemical Technology Division. These studies are related to the Aerosol Release and Transport Program at ORNL. This project involves studying the behavior of aerosols, in secondary containment environments, released under liquid-metal-cooled fast breeder reactor accident conditions. It has been demonstrated that the sodium and uranium oxides do mix as shown by electron-induced x-ray fluorescence and mapping, as well as by images obtained in the transmission electron microscope.

R. L. Walker and W. H. Christie of the Mass and Emission Spectrometry section have reported an effective method for the concentration of uranium in single ion-exchange resin beads. These beads can be used very conveniently as point sources in mass spectrometer analyses. The SEM was used to follow the course of thermal emission spectrometric analysis of uranium samples loaded on the single beads of anion resin. This study revealed that after heating 2 min or longer, the decomposed beads tended to shrivel and crack, but most retained their spherical character. It was observed that, as a function of time, the beads became smaller due to evaporation and solution of carbon in rhenium. Thus it appears that this point-source bead gives up its contents in a controlled, predictable fashion, which is a very desirable feature in the development of accurate mass spectroscopy techniques.

The consolidation of NaCl crystals while under stress in brine solution is being studied in an effort to better understand processes taking place in salt dome nuclear waste storage sites. When a saturated brine solution, in equilibrium with small NaCl crystallites, is placed under stress, there is a change in the distribution of particle sizes such that average dimensions become larger. A. J. Shor and C. Baes of the Chemistry Division are studying the mechanism of this consolidation process. Dissolution of small particles followed by acretion of the larger, and sintering of two or more small particles are considered as a likely path. Particles of near-uniform size distributions were prepared by sieving. The initial distribution was approximately normal (Gaussian). Optical microscopy showed that sieving removed the very small and extra-large particles, leaving a distribution resembling a "square wave." These specimens were then dispersed in brines and placed under stress. In examination of the consolidated particles we found optical microscopy to be less than satisfactory because of contrast and depth of field limitations. Both of these problems are absent in scanning electron microscopy, but another difficulty arises because of the necessary vacuum environment. The liquid phase must be removed, and there is strong evidence that drying artifacts grow in. Consolidation specimens using dodecane as the dispersal liquid were performed. Evaporation of the dodecane before placing the specimen in the microscope showed no evidence of residue artifacts. SEM photos suggested that sintering had occurred by merging of salient corners of some of the particles with flat sides of others.

The vacuum system on the AMR-900 scanning electron microscope is being redesigned using conflat flanges and, in a few cases, Viton O-rings. The new valving system will have ultrahigh-vacuum, air-operated valves that will operate through the automatic valving system of the AMR-900. The sample chamber on this instrument is very large. There will be a number of conflat feedthroughs of various types and sizes that will permit an x-ray photoelectron spectrometer, a microradiography system with variable energy sources, an electron energy-loss spectrometer, possibly an electron diffraction system, high- and low-temperature systems, and other equipment to be installed. These systems will be manipulated by bellows-sealed feedthroughs. The improved vacuum level should facilitate the electron spectrometry attachments and allow the microscope to be operated with reduced downtime spent on cleaning of the column and apertures and other maintenances. *(P. L. Ball, R. V. Dunn, R. L. Sherman)*

Optical microscopy. A new Olympus stereo microscope has been received and is now in operation. It has a Dolan-Jenner Industries, Inc., "Fiber-Lite" high-intensity illuminator for reflected light and a transmitted light illuminator. Visual magnifications from 3.5X to 160X and photographic magnifications from 5.25X to 120X can be obtained. Polaroid 10- × 12.7-cm film or 10- × 12.7-cm cut film can be used.

It is often very informative to examine samples on this microscope before doing scanning electron microscope (SEM), transmission electron microscope (TEM), x-ray diffraction (XRD), or x-ray fluorescence (XRF) work on them. If desired, certain colors or shapes of particles can be separated manually to concentrate a particular phase. Because the SEM does not show color, it is often desirable to prepare the sample on a stub and take a color picture of it before starting SEM work. Such a picture is sometimes very helpful in characterizing the particles in a sample.

Optical microscopy has been used in some studies of the Ames test method, in that the chemical mutagenic activity of pollutants is assessed by their effects on a special strain of bacteria that have been bred such that they are not able to synthesize histidine, which is essential for their growth and reproduction. Normal bacteria are able to synthesize this compound, but in this special strain the gene that allows them to do so has been bred out. In administering the Ames test, bacteria are placed in an agar dish containing the suspected mutagenic material. If there is no mutagenic activity, the bacteria will not grow and multiply, but if there is, colonies of reproductive activity will be seen. This will have been caused by the diffusion of mutagenic components through the cell walls of the bacteria and into their nuclei. The DNA of the genes will have been attacked, causing them to revert to forms that enable the bacteria to synthesize histidine. A statistical analysis of the rate of production of revertant colonies is taken as a possible measure of the mutagenic activity of the material being tested. Before mutagenesis can occur, however, components of the material must be transported to the cell walls of the bacteria, and this should be determined by the way in which the material interacts with the agar. Materials that are highly insoluble in agar, for example, may never reach the bacteria and therefore may not cause reversion even though under other conditions they may be mutagenic or even carcinogenic.

Optical microscopy is one of the few techniques that can be used in accounting for how the agar interacts with the material being tested. In preliminary studies we have examined some dispersions of oil, tar, and synthetic fuels and their components in agar. We feel that we can make a contribution to Ames test evaluation criteria. *(H. W. Dunn)*

Studies of silver zeolites. The containment of methyl iodide in the processing of nuclear fuels is under study by R. T. Jubin of the Chemical Technology Division. He is attempting to remove CH_3I from off-gas streams by absorption with silver mordenite (silver zeolite, AgZ). Depending on pretreatment of the AgZ, large variations in its absorption loadings of CH_3I have been observed. Regeneration procedures of the AgZ that have been studied, using 4.5% of H_2 in argon streams at 500°C, will remove over 98% of the absorbed CH_3I, but the AgZ apparently is altered such that its loading capacity is reduced. The SEM-EDX and x-ray diffraction techniques have been used to study AgZ before and after pretreatments and regeneration. The most prominent effect that we have been able to discern is the generation of free silver. Pretreatment of the AgZ with 4.5% H_2 in argon at 200°C causes silver nodules to be produced on zeolite particles. SEM-EDX examination indicates their average sizes to be 0.2 m. X-ray diffraction of the pretreated specimen shows lines corresponding to silver metal. Before pretreatment the nodules and free-metal diffraction lines were not observed. Pretreatment causes a noticeable increase in brittleness of the Zeolite pellets, possibly because the AgZ grain boundaries are weakened by the segregated silver phase. After regeneration of the AgZ, which again involves exposure to 4.5% H_2 in argon but at a higher temperature of 500°C, the SEM-EDX examination shows even larger nodules of silver; the x-ray diffraction lines of free metal are more intense. *(F. L. Ball, R. L. Sherman)*

Studies of niobium-based alloys. X-ray fluorescence can be induced by either x rays or by a beam of electrons, such as that of a scanning electron microscopy. For elements of higher atomic number [$Z>26$(Fe)] the x-ray-induced method is usually the more sensitive. For low atomic number, the electron-induced method is usually better. Both methods are nondestructive and are often used in quality assurance checks. This past year a combined application of the two methods was made to certify composition of niobium-based alloys containing Mo, Zr, and Ti. Molybdenum and zirconium were quantitatively analyzed (2-5 wt %) using AgK for excitation. A fundamental parameters program was used for matrix correction. Titanium was quantitatively measured (1-3 wt %) using the beam of the SEM for excitation. The FRAME matrix correction program, supplied by NBS, was used. The alloy specimens were being used in superconduction experiments and had been subjected to heat treatments. Our nondestructive tests verified that heat treatment had not altered their compositions. *(L. D. Hulett, J. H. Stewart, Jr.)*

Asbestos. A combined sampling analysis protocol has been developed for quantitative measurement of the chrysotile asbestos content of a wide variety of construction materials. The protocol is designed to differentiate between materials that are not asbestos contaminated and those that require costly special handling to ensure employee safety. The nature of the material determines specimen preparation techniques and the combination of analytical techniques used. The asbestos concentration range 0.5-5.0% was investigated with emphasis on differentiating between levels below or above 1% asbestos, since that is the EPA cutoff value for special handling, although the protocol could easily be extended to a much higher level. *(H. W. Dunn, J. H. Stewart, Jr.)*

SYNROC. The SYNROC ("synthetic rock") program is a major effort at ORNL, dealing with the problem of fixation and storage of nuclear waste. The goal is to incorporate the fission products as solid solutions in crystalline matrices that resemble natural minerals known to have survived weathering for millions of years. It is believed that crystalline material, of a well-defined and ordered structure, is more stable and predictable in its behavior than glasses, which are under study at other institutions. The sol-gel technique, developed many years ago at ORNL, is being used in the initial stages of the process. A solution of zirconium, calcium, titanium and barium nitrates is mixed with dilute quantities of simulated fission products such as Ru, Mo, Cs. and Nd. An ammonium donor is added to the solution, and it is extruded through a hypodermic nozzle into a heated organic medium that causes microdrop precipitation of the mixed oxides. The sol-gel particles are then washed and sintered in order to form the SYNROC material. It is desirable to use the lowest possible sintering temperature to minimize volatilization of the fission products.

XRD and SEM-EDX techniques have been used to determine the minimum temperature (575°C) at which crystallization will occur. The minerals, hollandite ($BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$), and zirconolite ($CaZrTi_2O_7$) have been found. The Ru, Mo, Cs, and Nb fission products are substituted in crystal lattice sites to the extent of about 0.5%. SEM-EDX shows the microspherical particles to be of uniform composition. Thus, it appears that the goal of simulating the highly stable natural rocks is being approached. *(P. L. Ball, R. L. Sherman)*

Support for molten salt battery program. S. Cantor, C. Vallet, and J. Braunstein of the Chemistry Division have been conducting research in several areas of molten salt fuel cell and battery technology. In the molten carbonate fuel cell program (46), Cantor has been studying a new cathode design, consisting of NiO doped with lithium, which converts it to a semiconductor of the form $(LiNiO_2)_y(Ni_{1-y}O_{1-2y})$; $y \leq 0.2$. It was necessary to determine how lithium content of the anode varied under different operating conditions of potential and LiO activity in the electrolyte. We found that x-ray diffraction is a very convenient way to specifically determine the amount of lithium in the solid solution state. Toussaint (47) has shown that the lattice parameter of NiO shrinks as lithium is substituted for Ni(II) sites and has published a calibration curve of unit cell spacing vs lithium concentration. For this type of problem the XRD method was superior to simple elemental analysis by atomic spectroscopy because in extraction of the NiO anode from the molten salt electrolyte, some of the Li_2CO_3 contaminated the outside and would have caused misleading results. The XRD parameter shrinkage method allowed us to distinguish between lithium in the solid solution state and that present as contamination.

Cantor is also studying a molten salt battery design that uses a lithium-aluminum alloy as cathode and an iron-sulfur matrix as an anode. The electrodes are physically separated by yttria felt (Y_2O_3 fibers) impregnated with a molten LiCl-KCl eutectic (48). It is desirable to determine how concentration gradients in lithium and potassium are set up in the yttria felt separator as current passes through the battery. This was done by simulating the battery by using electrolysis cells consisting of molten LiCl and KCl mixtures impregnated in yttria felt. Immediately after passing current (~0.1 amp/cm^2) through the separator matrix, the salt was quenched with helium, freezing in the concentration gradients. The cell was then sectioned parallel to its axis from one electrode to the other. The SEM-EDX method was used to determine potassium and chlorine concentrations along the axis. It was necessary to determine lithium by difference.

When an electric current flows through a molten salt cell, the ions are transported by both diffusional and electrostatic forces. Catherine Vallet has derived, and solved numerically, a differential equation that describes the concentrations of ions in molten salt cells as a function of time and distance from electrode surfaces (49,50). The equation applies universally to all molten salt cells; its parameters are the diffusion coefficient and electrical transference number of the ion being considered. Vallet has been studying a model system, consisting of mixtures of $NaNO_3$ and $AgNO_3$, as a test of the validity of the equation. Using the SEM-EDX technique described above for LiCl/KCl molten salt cells, potassium and silver concentrations were determined as a function of time and distance from electrode surfaces. Potassium ion concentrations were reduced at the anode and enhanced at the cathode; silver concentrations varied reciprocally. Concentration gradients, measured at electrode surfaces as a function of time, agreed well with those predicted by theory. *(R. L. Sherman)*

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2. MASS AND EMISSION SPECTROMETRY

J. A. Carter, Section Head

The Mass and Emission Spectrometry section is organized in three groups: Elemental and Ion Probe Surface Spectroscopy, Organic Mass Spectrometry, and Inorganic Mass Spectrometry. Each of these groups operates a number of sophisticated, sensitive instruments to perform energy-related research and development and also to provide technical support for other divisions of ORNL.

Application of secondary ion mass spectrometry (SIMS) to isotopic assay of boron and lithium in samples otherwise difficult to analyze has led to development of a reliable procedure for performing such analyses. Computerization of our ion microprobe mass analyzer has significantly enhanced our capability to perform depth profiles, both with regard to quality of analysis and to saving of substantial amounts of time. SIMS was used to investigate the nature of the resin bead–uranium–rhenium system during the course of a thermal ionization analysis.

A Kratos MS-25/DS-55 gas chromatograph–mass spectrometer data system was obtained and installed. This important acquisition will enhance both our research and support activities in organic mass spectrometry. Continued development of the mass spectrometry–mass spectrometry technique resulted in design and construction of two waveform generators. Investigation of the kinetically significant $C_7H_7O^+$ ion has continued. Work on developing an instrument to perform secondary ion mass spectrometry on organic samples has begun. A suitable source has been designed and is now being fabricated.

Work to bring the hot spark source mass spectrometer on line has continued. It has been tested under "cold" conditions and is ready for hot testing to begin. The quadrupole mass spectrometer passed laboratory evaluation tests for use as an on-site assay device to analyze plutonium and uranium for safeguards; it is now ready to be installed in a van. It has also successfully analyzed small boron samples for possible post-accident on-site determination of that element in case of a reactor emergency. Work has continued for various safeguards projects (TASTEX, WAX) concerning monitoring of nuclear facilities under international control. Evaluation of lutetium as a possible spike for tank calibration has begun; the initial results were excellent. A data network linking three mass spectrometers and computers was developed and is now in operation.

Our support to the Three Mile Island reactor site has continued this year. Samples have been analyzed for trace constituents by a variety of mass spectrometry techniques.

ELEMENTAL AND ION PROBE SURFACE SPECTROSCOPY

Quantitative SIMS analysis of difficult sample types. Last year we described the use of secondary ion mass spectrometry (SIMS) to determine isotopic boron and lithium in difficult sample types without the necessity of sample chemistry prior to measurement (1). We have now extended this method, through the use of minimum sample chemistry, to allow quantitative boron and lithium determination. A complete description of this method has been published in *Analytical Chemistry* (2). In a typical application, five samples of borosilicate glass powders containing natural boron were dissolved in aqueous HF and diluted to volume. Ten µl of each sample was then loaded onto a pyrolytic carbon planchet; a second loading of 10 µl of each sample took place at another location on the planchet. Before drying, 10 µl of a ^{10}B spike solution was injected into each sample drop of the second loading while being viewed under a low-power microscope. The two solutions were mixed by drawing the solution up into the spike pipette several times. Spiked and unspiked samples were dried as usual in a laminar flow hood and were subjected to SIMS analysis. The quantitative results thus obtained from standard isotope dilution calculations are compared with results for the same samples using conventional atomic absorption methods (Table 2.1).

Table 2.1 Determination of boron—SIMS vs AA

Sample No.	Isotope dilution SIMS (wt % B)	Atomic absorption (wt % B)
1	3.94	3.91
2	3.88	3.90
3	3.98	3.92
4	3.87	3.90
5	3.94	3.88

Application of SIMS to the quantitative determination of boron and lithium in solutions of unknown composition was examined by analyzing a radioactive liquid generated in the Three Mile Island nuclear reactor accident. The original sample consisted of a highly radioactive aqueous solution that indicated about 2.6×10^{-4} C kg^{-1} h^{-1} ml^{-1} of beta, gamma activity on contact with the sample vial surface. Prior isotope dilution spark source mass spectrometry and optical emission spectrometry provided estimates of <5 µg ml^{-1} lithium and 3400 g ml^{-1} boron in the solution. One hundred µl of this solution, after acidification and dilution, was obtained for SIMS analysis. Ten µl was removed and spiked with a 99.999 atom % ^{6}Li spike solution, and the remaining 90 µl was spiked with a 92.41 atom % ^{10}B spike solution. These solutions were allowed to stand overnight to insure isotopic equilibration. Approximately 1 µl of each was then loaded onto a pyrolytic graphite planchet along with natural boron and lithium standards. This resulted in a sample that gave a combined beta, gamma activity of approximately 2.6×10^{-7} C kg^{-1} h^{-1}. The sample was subjected to SIMS analysis using 16.5 keV, 1 nA, O_2^+ primary beam, which was rastered over an area 200 µm × 160 µm on the sample surface. Analytical results for both isotopic and quantitative analyses for boron and lithium obtained via SIMS are reported in Table 2.2. Results obtained from other techniques on aliquots of the same sample are shown for comparison. Repetitive analyses of a normal lithium standard demonstrated that the ^{7}Li/^{6}Li ratio could be determined with a precision of about 1.0%.

An advantage of the SIMS method for this kind of analysis is the fact that very low levels of radiation were actually handled due to the ultrahigh sensitivity of SIMS for lithium and boron. A further advantage is that no detectable instrumental contamination was produced during the analysis. In this analysis we estimate that less than one ten thousandths of the sample was consumed by the sputtering process. In conventional thermal or spark source mass spectrometry, a significantly higher fraction (from 1 to 100%) of the sample is spread about the instrument ion source region by the nature of the ionization process evaporation or bulk sputtering. Although we do not recommend using this approach for alpha-emitters like plutonium, we have shown that a routine SIMS instrument can be used on properly diluted radioactive samples without fear of instrumental contamination. *(W. H. Christie, R. E. Eby)*

Table 2.2 Analysis of a Three Mile Island water sample; a comparison of SIMS with other techniques

Method	Total B ($\mu g/g$)	Isotopic B $^{11}B/^{10}B$ (atom)
Isotope dilution	3314	
Spark source mass spectrometry	3565	~4
Microtitration	3211	
Mannitol procedure	3235	-
Isotope dilution	2978	
SIMS	3050	4.07
	Total Li ($\mu g/g$)	Isotopic Li atom fraction
Flame emission spectrometry	≤ 5	-
Isotope dilution	4.64	$^{6}Li \leq 0.02$
SIMS		$^{7}Li \leq 99.98$

SIMS investigation of resin bead thermal ion emitters. Secondary ion mass spectrometry and scanning electron microscopy have been used to follow the course of typical thermal emission mass spectrometric analyses of uranium samples loaded on single anion resin beads. A detailed description of this investigation has been published in the *Int. J. Mass Spectrom. Ion Phys.* (3). In our laboratory, Walker et al. (4) extended the resin bead technique to include both chemical separation and mass spectrometric filament loading. This method is finding wide application in a variety of nuclear programs. In the laboratory, each bead serves as one sample for a mass spectrometer; typically 1-3 ng each of uranium and plutonium are adsorbed on a bead. Samples loaded on resin beads result in ionization efficiencies about an order of magnitude higher than those loaded as solutions. This can be partially explained by the fact that, since the beads are 100-200 μm in diameter, they serve as good approximations to a point source for the ion optics of the mass spectrometer. Another possible contribution would be the carbon of the bead serving as a more efficient reducing agent for uranium and plutonium as compared with the traditional reduction method of heating in the vapor of an unsaturated hydrocarbon.

To investigate this matter, we used SIMS to follow a series of resin beads treated to simulate a typical thermal emission analysis. The anion resin beads (Dowex 1, 2% cross-linked) were loaded with uranium in the standard way. We chose the NBS U-500 standard ($^{235}U/^{238}U$ = 0.9997) because we felt that two peaks of equal intensity might help resolve ambiguities in the SIMS spectra, should they occur. The filaments normally used in our thermal emission work are V-shaped rhenium. Because the SIMS instrument requires a reasonably flat surface, we loaded the beads on flat rhenium filaments, which were spot welded on holders that were also suitable for direct insertion in the scanning electron microscope. The uranium-loaded beads, on filaments, were placed in an auxiliary vacuum system, whose base pressure was <1 × 10^{-6} Pa. After base pressure was reached, the temperature of each filament was slowly increased. A pressure burst signalled decomposition of the bead; heating was stopped on two filaments at this point. The others were heated to 1700° C, the normal temperature for isotopic analysis of uranium, and left there for periods ranging from 2 min to 2 h. The pressure during this time was <1 × 10^{-6} Pa. Beads were chosen to be approximately the same size; measured diameters ranged from 195 to 321 μm.

A sizable fraction of the beads was lost, which is not normally a problem with the V-shaped filaments used in the thermal emission mass spectrometer. Since little or no uranium was detected on these filaments during SIMS analysis, it seems probable that the beads left the filament early in the heating cycle, probably during decomposition of the bead.

While suitable for mounting in the scanning electron microscope, the filament holders could not be directly inserted into the ion microprobe. The rhenium filaments to which the resin beads were attached were therefore carefully removed from the multipin header to which they were spot-welded. The filaments were straightened under a low-power microscope (6X) using microtools. The straightened filaments were then attached to a flat mount 2.5 cm in diameter using conducting silver paint. Only the ends of the filaments were attached to the mounting cylinder, and great care was exercised to avoid getting paint on or near the resin beads. Bead samples mounted in this fashion presented no major difficulties in terms of sputtered ion yields for SIMS analysis. The biggest difficulty arose because of the size of the bead itself. Beads analyzed were typically hemispheres or fractions thereof. SIMS requires a flat surface for analysis, and deviations from that norm produce corresponding anomalies in the efficiency of secondary ion extraction. Some of the beads projected as much as 100 µm above the rhenium surface, and this height altered the electrostatic field between the sample and ion extraction electrode. To avoid these difficulties, the scanning circuit controlling the primary ion beam was modified to allow line scans to be made in directions both orthogonal and parallel to the extraction electrode. Y-direction scans, which moved the primary beam in a direction parallel to the secondary ion extraction electrode, produced the most reliable linear profile data.

SIMS was used to examine elemental distributions on the filaments. Complete mass scans revealed no elements present in significant quantities other than uranium, carbon, and rhenium. Ion micrographs showing distribution of carbon and uranium on the bead and adjacent filament demonstrated that both elements are confined to the region of the bead, and each ion image coincided with the location of the bead observed through the ion microprobe's optical microscope. The apparent increased concentrations of both elements noted near the center of the bead were due to the enhanced ion extraction efficiency of the pickup electrode in the region closest to it. Localized concentrations of uranium were observed on some beads; these were always at the bead/filament interface. No migration of either carbon or uranium along grain boundaries of the filament was observed for any bead-filament combination studied.

A region near the bead was scanned. The edge of the rastered area was a few µm from the bead, and the center was a little over 100 µm distant. Uranium gave too fleeting a signal to yield an ion image. This suggested that no appreciable uranium diffused into the rhenium filament. Carbon gave a uniform signal over the entire area. Rhenium displayed varying sputtered ion intensities as a function of crystal orientation, which is a common phenomenon in SIMS.

Thus, even near the bead, no significant migration of uranium had occurred. This is confirmed by linear profiles generated by scanning the primary beam across the bead (Fig. 2.1), which show both U^+ and C^+ reaching background levels a few µm from the edge of the bead. Distribution of uranium through the bead seems to be quite uniform, whereas a fraction of the beads showed enhanced U^+ signals at the edges.

A very thin layer of uranium (a few monolayers) was observed over the entire length of each rhenium filament. To preclude the possibility of cross-contamination in the filament heating process as the source of this uranium, one bead was loaded with NBS U-010 (1% ^{235}U) and heated for 30 min adjacent to two filaments upon which beads containing NBS U-500 were being heated. Only the 1% isotope was observed on the first filament, eliminating cross-contamination as a possibility.

Inspection of the back of a rhenium filament with an optical microscope revealed a disturbed region congruent with the area occupied by the bead on the top surface. Investigation with SIMS revealed a high carbon content in this area. This study was made using a O_2^+ beam at 16 keV; C^- was monitored because the intensity of this ion is about 100 times greater than that of C^+. Traces across this region were qualitatively similar to that shown for C^+ in Fig. 2.1, with the carbon signal rising more than two orders of magnitude above background in each case; U^+ was observed only as a thin surface layer. Thus carbon, with its high mobility in rhenium, diffuses through the 0.003-cm thickness of the filament in <0.5 h, while uranium does not penetrate that distance in 2 h.

SEM investigation of a bead heated for one hour at 1700° C showed a hemispherical bead skeleton in contact with the rhenium surface. It appears that the carbon of this skeleton leaves the parent body more rapidly from the area of the bead-filament interface than it does from regions not in contact with the filament. Diffusion of carbon into the rhenium substrate and evaporation of carbon from the interface region, where the bead is hottest, are two mechanisms that help explain this observation.

A by-product of this investigation revealed the capability of our ion microprobe to determine isotopic ratios on very small uranium

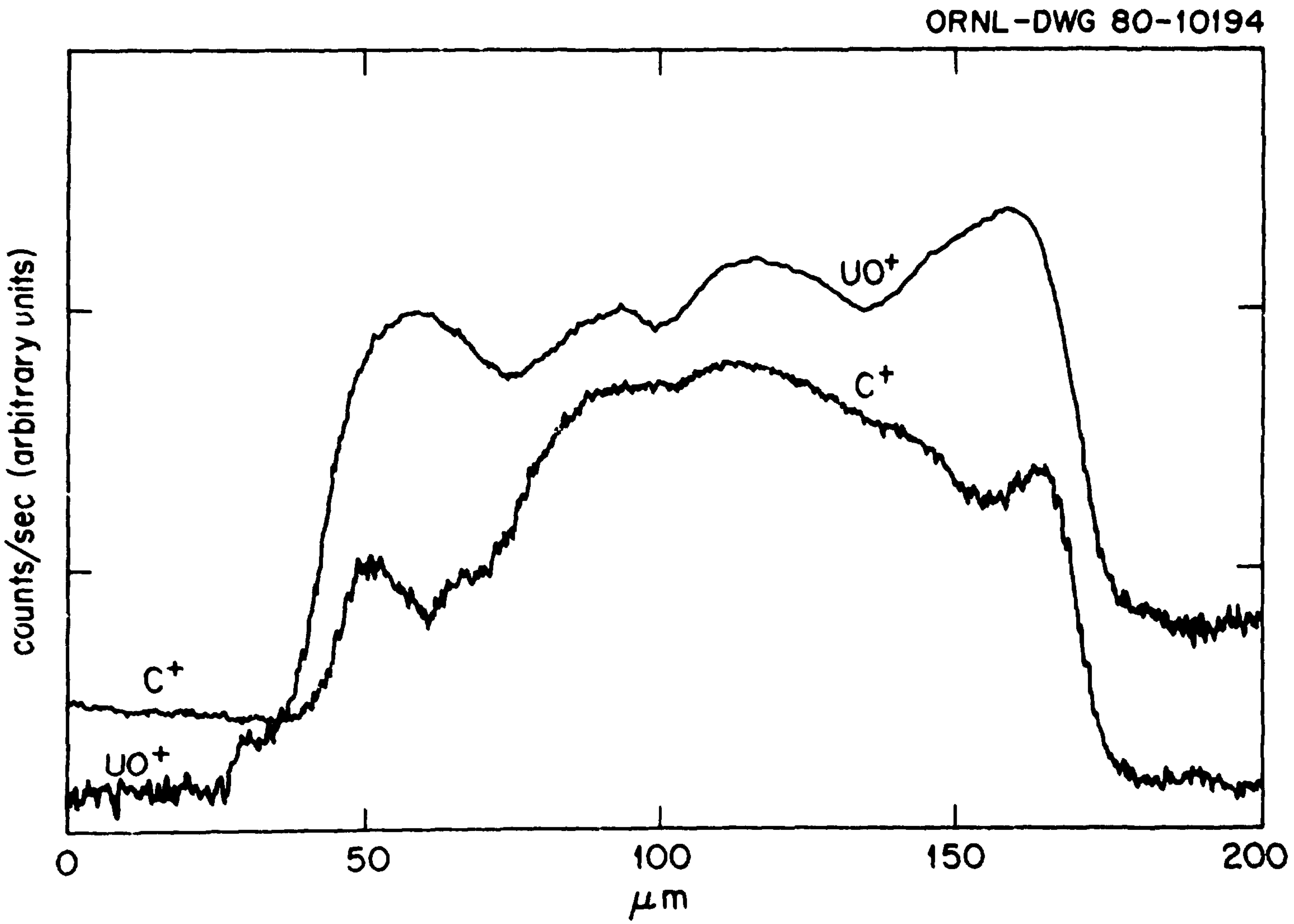

Fig. 2.1. Uranium and carbon distribution along the central diameter of a resin bead.

samples. Twenty measurements of the $^{235}U/^{238}U$ were made while in linear profile mode. We estimate sputtering a volume of 90 μm^3, while the total volume of the bead was 4 × 10^6 μm^3. Assuming a total adsorption of 1-3 ng U, this represents 20-60 × 10^{-6} ng, or 20-60 fg of uranium. The average of the ratios we obtained was 1.012 ± 0.015 (1σ); the NBS certified value is 0.9997.

We conclude from this study that ionization of uranium in the resin bead-rhenium system occurs at the filament-bead interface. We base this conclusion on the fact that uranium does not migrate away from the immediate area of the bead to any appreciable extent. In addition, the work function of the Re-C composite surface is higher than that of pure rhenium or pure carbon. The Saha-Langmuir equation was used to estimate the ratio of singly charged ions to neutral atoms expected from the three surfaces. Using work functions of 4.6, 5.43, and 5.84 for C, Re, and Re-C, respectively, we calculated that for U^+/U this ratio was an order of magnitude higher for Re-C than for carbon. The ionization potential of uranium was taken to be 6.2 eV. The fact that uranium remains uniformly in the residual carbon matrix of the bead, even though the bead is less than 1% fully loaded, indicates that uranium migrates slowly to the interface region as the bead material evaporates and diffuses into the rhenium matrix. In addition, this slow migration provides ample exposure of uranium to a reducing medium and thus minimizes its loss as oxide species. The bead thus serves as a reservoir of uranium, maintaining a fairly steady flux of neutral atoms to the region of maximum ionization over long periods.

The ion micrographs and linear profiles made during this study show no migration of uranium away from the immediate vicinity of the bead, even along grain boundaries. Optical microscopy shows that a bead is small with respect to the size of a typical rhenium crystallite (i.e., filament treated as previously described). It is thus meaningless to speak of ionization from polycrystalline rhenium in this context. McHugh (5) has demonstrated that zone-refined rhenium, as this was, shows a marked preference for (001) crystal orientation in the plane of the surface. The roughened surfaces of some of the crystallites lead us to believe that orientations other than (001) occur with enough frequency to affect ionization efficiencies of uranium from beads mounted entirely on such crystals; this finding supports those described by McHugh. Thus, if a means were available for identification of efficiently ionizing crystallites, it would be possible to load the bead directly onto the grain of choice and achieve more efficient and reproducible ionization. *(W. H. Christie, D. H. Smith, R. E. Eby)*

Depth profiling studies of photovoltaic devices. We have continued our collaborative effort with workers in the Solid State Division using SIMS to study ion implantation as a surface modification method and to develop depth profiling techniques for the study of photovoltaic devices. The general effect of dopant redistribution via laser annealing has been the subject of a recent SIMS investigation, and we have published the results of this study in *Surface Science* (6). In a continuing study we have used SIMS to depth profile in-vacuo laser-annealed samples of boron-implanted silicon. A single chip of the as-implanted material was aligned in the vacuum laser annealing apparatus so that three discrete areas could be identified and subjected to 1, 5, or 10 discrete laser pulses. Table 2.3 gives results from SIMS depth profiling studies of this sample on two dates.

Table 2.3 SIMS results for regions annealed with multiple laser pulses

Sample	Relative profile area	% B retention
	B in Si	
as-implanted	20.1	100
1-pulse	21.1	105
5-pulse	21.6	107
10-pulse	19.8	99
	^{75}As in Si	
as-implanted	56.0	100
1 pulse	52.2	93
5 pulse	46.5	83
10 pulse	38.1	68
15 pulse	37.8	67

These in-vacuo annealing results agree with previous in-air laser annealing where no boron was observed to be volatilized out of the near surface region of the silicon crystal. SIMS-obtained profiles show multiple-pulse laser annealing to achieve a nearly rectangular distribution for ion-implanted boron in silicon. Workers in the Solid State Division have shown that this type of dopant distribution has superior electrical properties in photovoltaic applications.

We have also used SIMS to perform depth profiling studies on in-vacuo laser-annealed samples of ^{75}As-implanted silicon. In contrast to the results obtained for in-air laser annealing, we found that significant arsenic loss can occur when annealing in-vacuo. Table 2.4 records the results of four depth profiles measured on the ^{75}As-ion-implanted silicon prior to laser annealing.

Table 2.4 SIMS depth profile results: ^{75}As-implanted standards

Sample	Relative profile area
1	54.1
2	60.2
3	55.6
4	54.1
Avg.	56.0 ± 2.9

A single chip of the as-implanted material was aligned in the vacuum laser annealing apparatus so that four discrete (quadrants) areas could be identified and then subjected to 1, 5, 10, or 15 discrete laser pulses. The average peak area of 56.0 ± 2.9 established the experimentally determined standard area for a known dose of 8.3×10^{16} ^{75}As atoms cm^{-2}. Peak areas determined for the regions annealed with multiple laser shots and corresponding percent arsenic retention values are shown in Table 2.3. Samples laser-annealed in air show no appreciable arsenic loss.

Quantified SIMS depth profiles for these four samples were compared to Rutherford backscatter profiles (determined by C. W. White) and were found to be in agreement (atoms cm^{-3}) within 10-15% in all cases. The SIMS profiles show a significantly faster backside drop-off for the 10- and 15-pulse samples, reflecting higher depth resolution of the SIMS technique. The results of this study have been published in *Solid State Technology* (7).

We have used the SIMS technique to study lateral and depth distribution of magnesium and silicon before and after laser annealing. Samples implanted with ^{24}Mg were examined using O_2^+ primary beams. The as-implanted samples (5×10^{15} atoms cm^{-2}, 70 keV) showed normal Gaussian depth distributions in accordance with Lindhard, Scharff, and Schiott theory. After laser annealing, significant magnesium movement toward the surface is indicated by SIMS depth profiles. The distributions are double humped with a peak near the surface (10 nm) and the main peak at about 150 nm. Studies of the lateral distribution of magnesium using ion imaging techniques show magnesium to be segregated into islands approximately 10 μm in diameter separated by 10-15 μm. These islands are completely sputtered away after removing approximately 2 nm of the sample surface. After laser annealing, consolidation and regrowth of these islands is noted. The islands are reduced in number by a factor of 2 and now extend in depth to about 10 nm. Below these depths (2 nm for as-implanted and 10 nm for laser-annealed samples), the lateral distribution is uniform. Lateral segregation observed in the as-implanted samples suggests considerable mobility for magnesium atoms due to the large degree of lattice disorder present in this solid/vacuum interface region during ion implantation. *(W. H. Christie, R. E. Eby).*

Computerization for real-time, multielement depth profiling. During the past year we have continued to improve the digital link between the PDP-11/34 computer and the ion microprobe scaler output. The scaler output was soon found to be incapable of providing high enough data rates to allow convenient mass scanning. Therefore, an analog-to-digital converter (ADC) interfaced directly to the computer was tied to the Hall-probe output of the secondary mass analyzing magnet. A chopper-stabilized operational amplifier was added to match the output of the Hall probe (0-1 V) with the input conversion range of the ADC (-5 V to 5 V). Under computer control the conversion time was 235 with a resolution of 4096 (12 bit). The digitized value was converted to a mass by means of a quadratic equation, determined by least-squares fit to a set of known masses. A second ADC was interfaced to the detector signal output. A mass scanning program was written to control these two ADCs and the automatic magnet scanning of the ion microprobe mass analyzer (IMMA).

In order to provide the best information for a limited number of elements, a peak-hopping scheme was needed. This means setting the magnet to a particular mass and collecting data via a gated scaler. A digital-to-analog converter (DAC) on the computer was tied into the magnet control circuit through a differential amplifier. Due to the limited resolution of the DAC (12 bit), a selector was added to provide varying offsets and mass ranges. After an additional gate line was added to the Anadex scaler, the multielement peak-hopping/depthprofiling software was written.

A magnet scan range, suitable for the sample being studied, is manually switch selected. The computer uses a previously stored quadratic equation to determine approximate digital-to-analog converter (DAC) settings for each mass of interest. The program then steps through the desired masses (up to 15), and the operator can observe mass centering on an oscilloscope and manually make small adjustments to the DAC settings for each mass via a keyboard if necessary. When all peaks are set up properly, the sample is shifted to the region to be depth profiled, and depth profiling is commenced.

The data logging program is set up to check a disk file for previously stored parameters. If the particular alloy type is found in the disk file, the program automatically selects correct masses to be monitored, as well as proper indexed sensitivity factors and isotopic and atomic abundances to be used in subsequent calculations. The program steps through the desired mass peaks, recording count rate data and counting times. Typically, the magnet is switched to a peak, allowed to stabilize (5 s) while data are recorded for 10 s, and then proceeds to the remaining masses. After stepping through the desired masses, recorded data are stored to disk. Calculations are done immediately, and elemental compositions are listed on the system printer. The program repeats this sequence so that compositions versus sputter depth are recorded for as long as the operator desires. When data-taking is terminated, a table is printed out showing sensitivity factor index ratios and elemental compositions as a function of time.

One of our continuing projects has been the study of oxide films on Incoloy-800 and similar alloys. In these profiling studies we have shown that the surface oxide is highly enriched in chromium and manganese. The depth profile was discontinued before the unaltered base metal composition was reached. Since our magnet scanning technique is relatively slow, we have incorporated a time interpolation routine into the calculational programs so that time-corrected depth profiles can be produced. *(R. J. Warmack, R. E. Eby, W. H. Christie)*

Cesium ion source development. Work is continuing on the cesium ion source, which replaces the normal duoplasmatron source and provides enhanced sensitivities for electronegative species and increased sputter rates. We felt the cesium source capable of better intensity than presently available for standard operation (2 to 3 mA/cm^2 in a 10–12 μm focused spot). Ion-optical studies quickly revealed that most of the beam was lost through over convergence and aperturing. Further studies showed that most of these losses could be avoided by a simple redesign of an extraction electrode. New parts have been fabricated and will be tested as soon as time can be scheduled on the IMMA. *(R. J. Warmack, W. H. Christie)*

Spark-source mass spectrometry for highly radioactive materials. A facility to provide analyses for highly radioactive alpha-emitting samples is nearing completion. A spark-source mass spectrograph has been coupled to special shielding and sample handling fixtures so that high-level solids can be safely handled and analyzed (8). Although of general utility for any hazardous sample types, the facility will be primarily used to provide badly needed analyses of undiluted nuclear fuel reprocessing solutions and solids.

Work this year has been devoted to assembly, alignment, and testing at Building 2026. Rails, allowing the mass spectrometer to be moved, were installed. A stainless-steel containment liner was then aligned with a special coupling bellows to an adjacent hot cell. The source of the mass spectrometer was interfaced to the liner. The liner and source region were then shielded with lead brick. With the mass spectrometer in position, all services necessary for its operation were installed — electrical, pneumatic, water, and vacuum. After needed repairs and modifications were complete, the mass spectrometer was thoroughly checked for satisfactory operation.

The ion source had to be radically redesigned due to remote operation and shielding requirements. Electrically actuated gimbals were designed to operate through a vacuum interface, to align the sample electrodes onto the optical axis of the instrument, and to adjust the electrode gap to provide good sparking conditions. Electrodes are loaded with remote master-slave manipulators, which will also perform any needed repair or replacement operations. The source design is based on glued plexiglass® pieces and spot-welded sheet metal parts to provide both an economical and disposable system.

Final cold testing for the entire facility is complete, and hot operation is anticipated in the very near future. Complete operating procedures are being written from both analytical and safety standpoints. Upon approval, the unit will be sealed by installing shield windows and connected with the hot cells to begin hot testing and hot operation. *(R. J. Warmack, V. H. Christie, J. A. Carter)*

ORGANIC MASS SPECTROMETRY

Ion chemistry. Our studies of the chemistry of gas phase ions have focused on the use of metastable dissociations to characterize (1) the reacting configuration of isomeric $C_7H_7O^+$ ions and (2) the reaction channels of aromatic amines. The $C_7H_7O^+$ work is an extension of that reported last year (9). The kinetic energy released (T) when a metastable ion fragmented was used as an indication of the structure undergoing reaction.

Our new results, in collaboration with Prof. B. S. Freiser of Purdue University, involve the use of ion cyclotron resonance (ICR) spectrometry. In this study the ions were generated in the ICR and photodissociated. Initial results show some conflict with our results using kinetic energy release measurements of metastable dissociations. The major difference is that the photodissociation spectrum of protonated benzaldehyde (presumably having the same structure as the $C_7H_7O^+$ ion derived from benzyl alcohol) is the same as that of *o*-cresol. This indicates they have the same structure, while our kinetic energy release measurements show that $C_7H_7O^+$ from benzyl alcohol (T = 195 meV) differs in structure from *o*-cresol (T = 350).

This inconsistency may be attributable to the fact that the ion lifetime in the ICR is on the order of milliseconds as contrasted to microsecond lifetimes in the mass spectrometric metastable dissociations. The ICR-generated ions would then have much longer times in which to isomerize. Evidence that a slow isomerization is taking place is the fact that about 40% of the ions undergo photodissociation in the ICR, and thus it is presumed that the other 60% has not undergone isomerization or has isomerized to a different structure.

The study of aromatic amines has as a goal the direct analysis of complex mixtures of aromatic amines by MS/MS, without prior sample cleanup or fractionation. To achieve this goal, it is necessary that isomeric primary, secondary, and tertiary amines have unique reaction channels so that they can be identified in the presence of each other.

The results thus far obtained are encouraging. The secondary amine, *n*-ethylaniline, shows as its major fragmentation the loss of CH_3, giving an ion at m/z 106; the isomeric tertiary amine, *n*,*n*-dimethylaniline, has as its major metastable transitions loss of NH_3 and HCN, giving ions at m/z 103 and 94.

Crude collision-induced dissociation experiments also indicated that *n*-ethylaniline can be differentiated from ring-substituted ethylanilines. If these results prove to be generally applicable, MS/MS analysis of mixtures containing aromatic amines should be feasible. *(D. H. Russell, E. H. McBay)*

Mass spectrometry/mass spectrometry with the triple-sector spectrometer. The new triple-sector mass spectrometer (10) has been modified during the year, and several ion chemistry studies have been initiated.

One of the prime areas of interest is the rapidly expanding field of mass spectrometry/mass spectrometry (MS/MS, also known as MIKES). This technique involves the operation of a multi-sector mass spectrometer as two independent mass analyzers. The first of these analyzers acts as a separator, separating out the ion of interest. The second one analyzes the fragment ions generated from the ion selected in the first step. This mode of operation can be used for analysis of complex mixtures and for assistance in determination of ion structure, among other things.

One of the principal advantages of our three-sector MS/MS instruments is the ability to use the first two sectors as a high-resolution instrument in high-resolution MS/MS (HRMS/MS). As MS/MS is analogous to GC/MS, HRMS/MS is analogous to capillary column GC/MS. Several

HRMS/MS experiments have been performed with emphasis on oxygen and nitrogen isobars (e.g., $C_7H_7O^+/C_7H_9N^+$, nominal m/z of 107). The initial results are quite promising as there was ample sensitivity at a resolving power of 15,000 to characterize both isobars at m/z 107 in a mixture containing ten parts of benzylamine to 1 part p-cresol.

We have also used the triple-sector spectrometer in the study of consecutive metastable transitions by setting the sectors to pass only those ions undergoing chosen transitions within the time range of several microseconds. With a triple-sector instrument, and thus three field-free regions, there are three possible experimental approaches to study consecutive metastable dissociations, two of which are unambiguous. This is in contrast to doublesector instruments in which only one, possibly ambiguous, experimental scheme exists.

We have thus far concentrated on only one approach, in which the first metastable dissociation occurs in the first field-free region and the second metastable dissociation occurs in the third field-free region. Primary advantage of this mode of operation is that an ion formed from a specific precursor ion can be studied without interference from other isomers, provided that they are not generated via identical fragmentations. As an example, the $C_7H_7O^+$ ion formed from ethyl phenol (m/z = 122) can be studied without interference from $C_7H_7O^+$ formed from chlorobenzyl alcohol (m/z = 142) by selecting the transition of 122^+ to 107^+ in the first field-free region and then detecting the transitions of 107^+ in the third field-free region.

Performance of the triple-sector instrument has been improved by several new additions to the electronics. Most notable was the construction of two ramp generators (11) to control scan functions. Also, a fast roll-off current to voltage amplifier with a range of four orders of magnitude has been built and added to the detection circuitry to prevent aliasing of the signal during signal averaging. *(D. H. Russell, W. T. Rainey, G. L. Glish)*

Installation of Kratos MS-25/DS-55 gas chromatograph-mass spectrometer-data system. The Kratos MS-25 double focusing, low-resolution spectrometer has been installed in the Organic Mass Spectrometry Group (9735). This instrument is being used both in support and research programs. A modified Perkin Elmer Sigma-3 gas chromatograph is interfaced to the ion source and may be used with packed or capillary columns through either a jet separator or direct inlet line. A solids-liquid probe is also used for inlet of samples. Data acquisition and processing is via a Kratos DS-55 data system.

The spectrometer is furnished with movable slits to permit operation at three mass resolutions of 800, 1400, and 2800 at different slit widths with transmissions of 1, 0.4, and 0.02, respectively. The instrument is extremely sensitive because of the double-focusing configuration with hexapole lens. We have measured sensitivity as high as 3.25×10^{-9} C μg^{-1} with the electron bombardment source and a multiplier gain of 10^5.

We also use the spectrometer in chemical ionization (CI) mode with three reagent gases selectable from the console. Rapid switching between CI and electron bombardment ionization (EI) is also possible, such that both CI and EI spectra can be obtained from a single chromatographic peak. We have measured sensitivities using a packed column and found that 100 pg of methyl stearate gave a peak height of 65 mV at m/z 298 with a multiplier gain of 10^5. Under the same conditions, isooctane-CI yielded an 80-mV peak.

The DS-55 data system is composed of a Data General Nova 4X central processor with 64K of 16-bit memory, a Tektronix 4010 visual display unit, a Data General 30-cps Dasher (teletype), a dual density fixed plus removable disk drive, and a Kratos data acquisition interface capable of 50-kHz sample rate. The system is also configured to operate the Versatec printer/plotter of DS-50 system, if desired.

The system runs under control of the Data General Real-time Disk Operating System (RDOS) with a wide range of commands for handling data and peripheral hardware. RDOS supports program development tools, such as Fortran and Algol compilers, text editor, etc. The DS-55 commands provide for data acquisition and real-time processing as well as post-run processing. A variety of interscan (real-time) options allows plotting or printout during collection of data. Control of the major spectrometric operating parameters is through a matrix board that is preset for ten different programs. Foreground-background operation is possible with the VDU as console and the teletype operating in foreground. Thus, data acquisition with real-time reports and post-run processing are accomplished simultaneously.

The system has been used in support analyses for staff members in other divisions as well as in collaboration with MS-50 high-resolution analyses. We are presently starting a collaborative program with personnel from The University of Tennessee, Exxon Corporation, and ORNL Chemistry Division on the study of products obtained from pyrolysis of coals that have been deuterated in specific functionalities. We hope to reveal interesting details on the structure of coal by tracing the reaction pathways of deuterated species. We have installed a Chemical Data Pyroprobe in the chromatograph injector and a fused silica capillary column for component separation. Pyrolyses of untreated and deuterated coal samples are being carried out under various time-temperature combinations, and product compositions are determined. *(E. R. McBay, W. T. Rainey, D. H. Russell, C. L. Glish)*.

Precision triangular waveform generator (Model ORNL/79-11965). For our HRMS/MS (10), we needed a triangular waveform generator. The special requirements were (1) long-term slope stability, (2) selectable rising and falling sides to the triangle, (3) long-term dc level stability, (4) a wide selection of repeatable slopes, (5) selection of an initial or static voltage, and (6) programmable ramp limits for any slope. The generator would be used to scan either the magnetic field or the voltage between the plates of the electrostatic analyzer (ESA). Slow scan rates were needed for magnet scanning; fairly rapid scans of the ESA would permit a live oscilloscope display.

The actual instrument has the following characteristics:

1. Independently selectable rates of rise (fall) from 1 V/s to 888 V/s. A 1-2-4-5-8 sequence is used, resulting in 431 wave shapes.
2. Drift. When adequately warmed up, drift rate is 2 μV h^{-1} at constant voltage. Ramp rate reproducibility is 99.95% or better.
3. Output. ±10 V, 200 mA.
4. At maximum rate-of-rise, overshoot beyond selected cutoff voltage is 25 mV.
5. Free running or cutoff after 0.5, 1, 2, or 4 cycles.
6. Selectable initial, upper, and lower scan limits.
7. Selectable initial scan direction with error detection for illogical conditions.
8. True analog ramp.
9. Reversing and "hold" from front panel.

In our HRMS/MS work we used a signal averager to collect data. The 12-bit resolution of this device limited us to detection of errors of ±0.05%. Our measure of stability was the width of a mass peak at half maximum (WHM) for data taken over a few short cycles compared with the WHM for data taken over a period of an hour or two. Within the precision of the mass spectral experiment, it was not possible to establish that the waveform generator had drifted more than ±0.05%. *(T. R. Mueller, D. H. Russell)*

Programmable ramp generator (Model ORNL/79-9537). A ramp generator was needed for the HRMS/MS (10) work that would provide digitally addressed voltages for operation of the spectrometer by a computer and would improve the long-term stability of voltages applied to the electrostatic analyzer plates (ESA) so that higher resolution could be attained.

In the prototype, thumbwheel switches are used to enter values of the initial potential, the gain of the sweep (ramp) digital-to-analog converter (DAC), and the number of steps/sweep. In the computerized version, these values will be entered either from the control panel or from the computer. The ramp generator has a crystal-controlled clock, but there are provisions for an external clock (e.g., a computer-supplied pulse).

Dwell times of 1 to 100 s are provided to give a wide flexibility of scan rates for data aquisition. An auxiliary feature that has proven very useful is an analog voltage generator that can be switched in to replace the digitally generated signal. With a resolution of better than 1/5000, this feature allows one to locate a peak and to translate this voltage into its digital equivalent for entry into the thumbwheel switches. Other ancillary features include two switchable outputs, monitors that display sweep direction, halt/sweep mode, programmed delay active, step pulse time, and amplifier overload conditions. Outputs for "sweep increment," "sweep count," and "halt" and inputs for "start" and "stop" are also provided at TTL levels. An analog meter allows one to follow progress of very slow sweeps in terms of the fraction of the selected ramp amplitude. A provision is also included for viewing the contents of various registers on a five-digit LED readout. A preset counter allows a predetermined number of sweeps to be selected or, in the usual mode, displays the sweep count. A description of the instrument is being prepared for publication. Work performed with it was reported at the ASMS meeting in May (11). *(T. R. Mueller, D. H. Russell)*

Organic SIMS instrumentation. Development is underway on a new ionization source that extracts, accelerates, and focuses secondary ions sputtered from a surface after impact by a beam of primary ions of a few (0-5) keV kinetic energy. For some time, secondary ion mass spectrometers (SIMS) such as ion microprobes and ion microscopes have been used for surface imaging and analysis of inorganic samples. Design of the new source is better suited for nonvolatile organic molecular and pseudomolecular ions (12) from a surface where target imaging is not required.

The design requires that primary ions strike the target at 70° from the target normal. Such oblique incidence is known to improve secondary ion yield (13). By comparison, normal or near-normal incidence is used in microprobes to improve spatial resolution.

Secondary ion extraction and acceleration (up to 10 keV) are provided by two independent ion lens systems. This feature permits analysis of the effects of primary ion kinetic energy, secondary ion yield, fragmentation, etc., particularly at low primary ion energy.

Ion optics of the secondary ion extraction system were designed with the interactive ion optics program SIMION (14). Unlike conventional ion sources, we use cylindrical rather than rectangular symmetry. This is consistent with cylindrical symmetry of the accelerating optics but not with rectangular symmetry of the mass spectrometer. The advantage of this approach is that all secondary ions are kept near the mean ion axis, whereas in conventional (rectangularly symmetric) ion sources, there is no "z" focus. Secondly, generation of the transfer optics (cylindrical to rectangular symmetry) will be straightforward because a high percentage of secondary ions will be paraxial.

Sample introduction will be via direct-probe insertion through a vacuum lock, rather than the carousel approach of many microprobes. This permits minimal sample handling and rapid turnaround.

By virtue of the common source design of the ORNL single-, double-, and triple-sector mass spectrometers, this ion source is compatible with them all. The source and supporting structures will be mounted on wheels to facilitate interchange.

While there is a paucity of literature on organic SIMS, the technique appears promising for analysis of polypeptides as well as organics adsorbed to various matrices. The technique should also be valuable in analysis of catalytic effects between a metal surface and organic layer. The flexibility of the device also permits study of the mechanisms involved with organic secondary ion formation.

There may be other applications as well. For example, in preliminary studies, SIMS was found to be useful in isotopic ratio measurements (see above). Because extraction and acceleration are performed independently, this type of source may well show reduced mass discrimination in the voltage scanning techniques employed in isotope ratio measurements. In a general way, this source should serve as a tool for the development of SIMS methodology wherever target imaging is not required. *(P. J. Todd, W. H. Christie)*

High-resolution organic mass spectrometry. Several modifications to the Kratos MS-50/DS-50 system have been completed during the past year, and definite improvement in operation has resulted. Installation of a new TTY board in the Tektronix 4010 terminal with necessary software changes has converted the data system to a standard system configuration. The data system has operated without difficulty since modification. Installation of the second disk drive was completed with changes in software to permit the use of one disk for software and one disk for data acquisition and storage. Since both disks are removable, the system is much more versatile and dependable, with much greater data storage capability. Since the new Data General Eclipse system has a similar disk drive, we expect to transfer DS-50 data and/or software to magnetic tape for long-term storage and, thereby, eliminate the need for many disks. An all-glass heated inlet system was designed and installed for use with gases or volatile samples and has been used routinely with satisfactory results.

The spectrometer has been used in the static mode at resolutions up to 50,000 and in the dynamic mode at a resolution of 10,000 and a scan rate of 10 s per decade. Rather high noise levels preclude the use of higher resolutions and make tune-up difficult. Instrument performance was checked recently by a Kratos engineer, who will recommend service to bring the instrument up to original specifications.

We have used the MS-50 primarily in metastable scanning modes and for determination of appearance potentials. Data have been used in conjunction with those from the triple-sector instrument in ion chemistry studies. *(E. H. McBay, D. H. Russell, W. T. Rainey)*

Organic mass spectrometry support work. The Organic Mass Spectrometry Group has continued to give assistance to a variety of programs in need of identification of organic compounds. The major effort during this year has been devoted to projects originating in the Analytical Chemistry Division. In addition, we have handled analyses for Metals and Ceramics, Environmental Sciences, Operations, Health and Safety Research, and Biology divisions, as well as the Y-12 and ORDGP analytical laboratories. The DuPont 493B mass spectrometer has been used in the majority of these analyses, although on many of the samples the high-resolution MS-50 was also used. We have continued to give priority support to members of the Bio-Organic Analysis section of ACD, especially C.-h. Ho and B. A. Tomkins. A large number of GCMS analyses were carried out on a variety of synthetic fuel fractions with interest in identification of compound types such as hydrocarbons, phenols, amines, azarenes, etc.

Low-resolution mass spectra were also used to confirm the identity of a large number of intermediates and final products for F. F. Knapp and co-workers in the Health and Safety Research Division. All compounds were metalorganics containing Se, Te, Sn, or S in stable molecular structures of expected usefulness in diagnosis or treatment in animal tests. We were able to confirm the identity of most compounds using low- and high-resolution mass spectrometry, thereby confirming the reaction pathway for preparation of the compounds. These reaction pathways could then be used to prepare compounds containing radioisotopes for animal tests. Compounds such as substituted steroids, fatty acids and esters, barbiturates, and others gave satisfactory results.

We have also continued our support of EPA personnel at Research Triangle Park. We completed qualitative analyses on the fence-line measurements, but were not asked to quantify the results. We also assisted the Advanced Analytical Techniques Group at EPA/RTP by preparation of a series of standards containing pollutants on NBS standard urban particulate matter. These standards were to be used in evaluation of analytical procedures. *(C. A. Pritchard, E. H. McBay, W. T. Rainey)*

Data General computer system. Recently we were able to acquire a used Data General Eclipse S/130 computer system. The system consists of the following:

1. S/130 central processor (CPU)
2. 96 KB MOS Memory
3. Data General 5 MB fixed disk plus 5 MB top-loading removable disk
4. 300 LPM line printer
5. Nine-track, 800 BPI magnetic tape system
6. Diablo, 2.5 MB front-loading disk drive
7. VDU w/keyboard
8. RDOS, a real-time disk operating system

This is the third Data General system to be installed in the Organic Mass Spectrometry laboratory. The first system was based on a NOVA 2; the second on a NOVA 4. These are dedicated to the MS-50 and MS-25 organic spectrometers, respectively.

The DS-50 system has two removable, front-loading Diablo disks. The other system has a fixed disk and a top-loading removable disk. Having both types of disc drives on the Eclipse, we intend to use it as an exchange device for moving programs from one system to another. A second use will be for rapid printout of data via the line printer. The magnetic tape unit is intended for archival storage requirements.

Within the next year we will be interfacing two spectrometers to the Eclipse. It is intended that each spectrometer will have a small locally dedicated computer for its operation. These will be interfaced with the Eclipse as extensive calculation, processing, and storage needs arise. We are in the process of learning the RDOS and machine level programming techniques. *(T. R. Mueller, W. T. Rainey, E. H. McBay)*

INORGANIC MASS SPECTROMETRY

Quadrupole mass spectrometry for the Office of Safeguards and Security. We are currently evaluating a quadrupole mass spectrometer for potential use as an on-site inspection device for determination of uranium and plutonium isotopic ratios. The instrument arrived on May 9, 1980.

The instrument, a Balzers quadrupole mass spectrometer, was chosen because it is approximately an order of magnitude more sensitive than instruments from other vendors. This, plus digitizing the output of the multiplier detector, allows us to perform routine isotopic analysis of resin bead uranium and plutonium samples, which typically contain 1-3 ng of each element. A Tektronix 31 calculator, which is loaded from a cassette tape, serves as a data collection device and as a scan controller for the mass spectrometer.

The sample insertion probe, especially designed by the vendor for this application, is compact, easy to use, and reasonably foolproof. Insertion of a new sample and subsequent evacuation to operating pressure takes about 4 min. Filament pretreatment to assure reliable ion currents and to minimize isotopic fractionation requires about 5 min, and data acquisition 7 to 10 min. Thus, the total time required for an analysis is 15–20 min per sample.

The instrument is mounted in containers that ultimately will be mounted in a mobile van. The van has arrived, and installation is underway.

We made a brief study of the instrument's ability to measure boron isotopic ratios. The need for a technique to estimate total boron in water was evident at the time of the Three Mile Island incident. We have found that 100 ng of B is sufficient sample and that the $^{10}B/^{11}B$ ratio (~0.25) was measured to a precision of ±1%. Thus, through the use of an enriched ^{10}B spike, we should be able to provide on-site boron analysis if similar events in the future require it. *(J. R. Walton, D. H. Smith, H. S. McKown, H. Simmons)*

Mass spectrometry in support of International Safeguards Projects Office. The original TASTEX Task J experiment involved sampling spent fuels by Japanese personnel at their Tokai reprocessing plant and shipping the samples on resin beads to ORNL for analysis. The results of this experiment were mixed. One area of difficulty was contamination at the sampling site, where kilograms of material are handled (in contrast to the nanogram quantities on the resin beads). We thus developed a bulk sampling process more immune to such problems than the original one. In this technique, approximately 1000 beads (rather than 10) are exposed to the sample, agitated for 10 min, washed, and set aside for transfer to the mass spectrometry laboratory. We evolved the necessary hot-cell procedures, as well as the more conventional ones. J. A. Carter and W. R. Musick went to Japan to instruct Japanese staff in the technique. The Japanese subsequently took samples and are presently waiting permission to ship them. This technique is in the process of being adopted as an ASTM procedure.

The second sampling of the WAK reprocessing facility in Karlsruhe, West Germany, was accomplished by International Atomic Energy Agency (IAEA) personnel. Most of the samples have been analyzed, and difficulties still remain. We are hopeful that the bulk sampling technique described above will alleviate most of the problems.

Support continues for the IAEA mass spectrometer that we installed four years ago. D. H. Smith visited the IAEA laboratory and evaluated all aspects of instrumental performance (with D. L. Donohue, currently on leave of absence to the IAEA). The instrument was restored to original specifications, and various suggestions for improving laboratory routine were made. It was gratifying to learn that the instrument had analyzed over 2300 samples in the past year with only two days down-time.

We supplied uranium and plutonium samples to NBS for joint certification of isotopic content. These samples are on resin beads and are to be used by the IAEA in a round-robin exercise to evaluate interlaboratory results from samples loaded in this way. *(D. H. Smith, R. L. Walker, H. S. McKown, J. A. Carter, W. R. Musick, H. Simmons, H. C. Smith, E. G. Miller)*

Mass spectrometry development to improve precision. A major effort is underway to improve the precision routinely obtainable on isotopic ratio measurements. This will ultimately involve critical investigation of all phases of ion formation, transmission, and detection. The two areas that received the most attention this year were filament chemistry and mass scanning mode. It has been known for some time that emission of Pu^+ and U^+ can be enhanced by adding a layer of rhenium over the sample. Techniques previously developed used vacuum (15) or electrodeposition (16) to produce a uniform layer of rhenium over samples of uranium and plutonium. These techniques are not easy to implement in the laboratory, and it was decided to look for a simpler method. Rhenium powder slurried with sucrose was added to the filament over plutonium or uranium loaded on resin beads. It led to significant enhancement of ion emission and reduction of isotopic fractionation. This resulted in an improvement in precision of roughly a factor of two. The purpose of the sucrose was to provide the carbon to yield a Re-C solution, which has a higher work function than pure polycrystalline rhenium.

The technique has not yet been developed to the point where it is suitable for routine use; work on this project is continuing with that goal in mind. Safeguards in particular will benefit from such a development, but we hope to extend the application of this technique to samples from many sources.

The second aspect of mass spectrometry to receive considerable attention this past year was that of mass scanning. Programmatic changes were made in software controlling the sweep, such that alternate scans go up and then down in mass. This has the effect of distributing the scans of each isotope symmetrically with time and thus averaging out the effect of long-term beam instabilities.

The enhanced ion beam stability resulting from the addition of a rhenium-sucrose slurry allowed precise investigation of focusing conditions in the ion source. This led to the design and construction of a new high-voltage divider that yields more stable isotopic ratios than the previous design.

Considerations of pulse shape and signal-to-noise parameters in the detection system led to development of new divider network for the electron multiplier detector.

The single-stage mass spectrometer was converted to magnetic scanning with a view to assessing the reduction in bias achieved by elimination of voltage scanning. Results in this regard were somewhat ambiguous, but converting our instruments to this kind of scanning is still under consideration.

Another project carried out on the single-stage mass spectrometer was evaluation of a two-filament source arrangement. Precisions obtained were not as good as those obtained from resin bead samples, and 100 ng was the minimum amount of sample required to give a stable ion beam. Our conclusion was that the expenditure in time required for us to perfect the technique at ORNL was too great to make further investigation worthwhile. A "turret" source, on which such experiments will be reported, has been ordered from VG Micromass. This commercial unit allows highly accurate reproduction of filament-source geometry and should lead to better precision. *(D. H. Smith, H. S. McKown, R. L. Walker, J. A. Carter, H. Simmons, H. C. Smith)*

Mass spectrometer source improvement. In view of improved stability of the ion beam in our source as described elsewhere, we initiated an investigation into the whole question of source design. The designs of sources from other laboratories were obtained and compared with ours. An ion simulation computer program called SIMION was obtained to evaluate focusing characteristics of the various systems. This program will also be used to help develop designs worthy of experimental evaluation.

The SIMION program was modified to make it suitable for use with the input-output devices on our PDP-11 computers. Electrode configuration, equipotential contours, and ion trajectories can even be displayed on a storage visual display unit or plotted on paper. This program was of considerable help in designing the new source divider panel. *(H. S. McKown, D. H. Smith, P. J. Todd)*

Computerized operating system for tandem mass spectrometers. Interfacing of two of our multistage mass spectrometers to DEC MINC microcomputers is complete. The MINCs have visual display units with keyboards, 32K of core, and dual floppy disk drives. An assembly language code controls the sweep control panel and accepts data for a given scan. The data for each run are stored on discs under mainline (Fortran) program control. After data from all samples have been collected, they are transferred to the host computer, a DEC PDP-11/34, via locally designed communication network. Data processing and report writing then proceed automatically on the host computer. Communication is possible in both directions between the host computer and either MINC. Operation of the network is simple and has thus far been virtually error free. *(R. J. Warmack, H. S. McKown, T. R. Mueller, D. H. Smith)*

Use of a microcomputer to acquire data from a mass spectrometer and to calculate sample composition. A Rockwell AIM-65 (R6500) microcomputer was interfaced to a mass spectrometer for data acquisition and subsequent processing. A report, listing up to fifteen components and the percentage of each species present, is generated.

We have a Vacuum Generators Model MM1201 mass spectrometer that has a number of programming features built in. It is used mostly for assaying cylinder gases.

The microcomputer system contains on one board the microprocessor (which forms the heart of the system), input/output (I/O) ports, a text editor, a program assembler, a rather good version of BASIC, a system monitor program, 4096 (4K) bytes of random access memory (RAM), an LED readout, a 20-column printer, as well as features that are not needed in this application. A typewriter-type keyboard that can be located up to two meters from the board provides communication between the operator and the computer. Programs can be stored on and read from cassette tapes. The recorder interfacing is also on the board, as is an interface for serial I/O via a 20-mA current loop. The I/O ports can be software programmed, bit-by-bit, to be either inputs or outputs. Interrupt detection is also provided. By combining 88 microcoded instructions with an executive routine written in BASIC, we were able to satisfy the requirements for the application. Data acquisition time is less than 100 mS/peak.

A very simple interface between computer and spectrometer was fabricated. Data are stored temporarily under machine language control; between acquisitions, a BASIC routine reconstructs the data as a variable. Background data and sensitivity factors are stored outside of the BASIC program so that they are protected if programs are altered. These data are stored and recalled via short machine language routines called by BASIC. Although only 4K of on-board RAM is used, programming allows the operator ten options for altering program execution or for listing data.

We feel that this is a very cost-effective solution to our problem. Less than six weeks elapsed from inception of the project until the first data were processed. A more detailed description of this work has been prepared for publication. *(T. R. Mueller, J. R. Sites, L. K. Bertram)*

Dissolver tank calibration using lutetium. An isotope dilution technique using lutetium has been utilized for total solution volume and solution weight determinations. This approach has been compared with conventional calibration methods, in a joint effort with the Chemical Technology Division, for accountability measurements on three batches of dissolved spent fuel from the Dresden-1 reactor. In order to make accountability calculations, the total volume or weight of a dissolver solution, as well as the concentration of uranium and plutonium, must be accurately measured. Use of other elements such as Li, Mg, and Sr has been reported for this determination, but all of these have disadvantages associated with their measurement and ubiquitous occurrence. Lutetium was selected with the following expected advantages: (1) it has two naturally occurring isotopes of widely different abundances (i.e., 175:97.4%, 176:2.6%), (2) enriched Lu is available as the isotope spike, (3) it is not produced in fission, and (4) it ionizes easily by thermal emission and could be measured without chemical separation.

The method involves addition of normal lutetium in 3 *N* HNO_3 to the dissolver solution, which is then mixed by air sparging. We added $\sim$30 mg of normal lutetium per liter of dissolver solution for these tests. Small samples were withdrawn for fissile and lutetium analyses by isotope dilution. Weighed aliquots of dissolver solution ($\sim$0.5 ml) were spiked with enriched ^{176}Lu and diluted to 100 ml. One µl of this solution containing $\sim$0.2 ng of normal Lu and $\sim$0.4 ng of ^{176}Lu spike constitutes a filament loading for the 175/176 ratio measurement on one of our two-stage high-sensitivity mass spectrometers. No chemical separation is required. Weight of the dissolver solution can be calculated from the known 175/176 ratio of normal, spike, and the measured ratio of the sample/spike mixture. For volume calculation the density must also be measured, a possible source of error. However, density is not necessary to calculate the total fissile content of the dissolver tank if solution weight is used, and this method is recommended for accountability.

The results of measured volumes for the three batches of dissolver solution by both methods of calibration are given in Table 2.5.

In the chemical processing plant, spent fuel was dissolved in tank T-555 and transferred to a feed tank, T-556. Measurements for volume and weight of solution were estimated for each tank. The conventional method of estimating volume and weight was based on differential pressure measurements across the liquid level and density probes by means of a high-precision manometer. After calculation of the solution volume, appropriate corrections were applied. In the case of the solutions in T-555, the only correction was subtraction for estimated volume of the fuel rod hulls. A potential source of error was the possibility for retention of air bubbles within the empty hulls. Correction factors applied to the solutions in T-556 included allowances for the volume of previously removed samples and for residual amounts of solution left in T-555.

Table 2.5. Results: determination of dissolver solution volume

Batch	Tank	Method Conventional	Method Lu-IDMS
4-DS-1	T-555	10.15	10.29
	T-556	12.05	12.21
4-DS-2	T-555	8.79	8.55
	T-556	8.48	9.00
4-DS-3	T-555	8.44	8.13
	T-556	9.36	9.51

The estimation of solution volume and weight by the lutetium-isotope dilution method requires no corrections and thus should have better accuracy. In the three batches tested, the lutetium method checked more closely to material balance calculations than the conventional method. Precision of the lutetium method for each of the three batches was ±1% based on three determinations. Although this is the first attempt at tank calibration using lutetium, the apparent success of these tests warrants further development and evaluation of the method for accountability measurements. *(R. L. Walker, J. A. Carter, E. G. Miller, H. C. Smith, W. R. Musick)*

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3. TECHNICAL SUPPORT

L. T. Corbin, Section Head

The 78,000 analyses performed within the General Analytical Laboratory constituted a 25% increase over last year. A corresponding increase in analytical requests forwarded to other laboratories was also noted. New equipment included a direct injection module for the Oceanographic International carbon analyzer, a cascaded multistage electronic filter for the vacuum fusion system, an arsine generator with a helium-glow discharge excitation unit, a Technicon block digester, an automatic hydride generator for the atomic absorption spectrophotometer, a Dionex model 16 ion chromatograph, and bench-top charcoal-filtered hoods. Continued support provided to outside agencies included mercury analyses for the Virginia Water Control Board; lithium, mercury, fluoride, chloride, moisture, lead, zinc, and lithium hydroxide for the Tennessee Valley Authority; and special analyses for the Three Mile Island (TMI) nuclear station.

In the Radioactive Materials Analytical Laboratory, new equipment included an x-ray fluorescence (XRF) analyzer, oxygen-to-metal analyzer, fiber optic spectrophotometer, and a pulse-height analyzer. XRF was used to solve difficult analytical problems in fuel reprocessing, waste management, and resource recovery. Support of TMI continued with the analysis of water, sludge, and metals from the reactor site. Instrumentation was developed to measure C-14 in dissolver solutions and tritium in single irradiated microspheres. Capabilities were expanded in nuclear coatings work with the addition of a superheater to the design-basis-accident apparatus and construction of an apparatus to measure chloride release from irradiated panels.

The Transuranium Analysis Laboratory performed 35,000 analyses during the year. Most of these were in support of transuranium element production, power reactor fuel reprocessing studies, and monitoring plant effluents. New equipment included a dielectric constant meter, a low-level alpha counter, and a gamma spectrometry system.

The Reactor Programs Group continued to provide analytical support to ongoing reactor technology development programs. Principal "laboratory-oriented" research and development efforts have been directed toward the Consolidated Fuel Reprocessing, High-Temperature Gas-Cooled Reactor, and Alternative High-Level Waste Forms Development programs. In addition, the group has provided development of methods to meet the needs of the service laboratories. Specific studies were thermal and mass spectrometric analyses for characterization of reactor fuel and radioactive waste forms, kinetics of thermal denitration and dehydration of uranyl nitrate hydrates, and reaction of sugar and nitric acid. Specific methods of analysis included the determinations for dibutylphosphoric acid by ion chromatography, Cr(VI) in process solutions, radiolysis products (Cl_2, H_2O_2, ClO_3^-, and ClO_4^-) in irradiated brine, gaseous products for the combustion of irradiated carbide fuel, and spark-induced by-products of sulfur hexafluoride. Instrumentation efforts were directed toward development of a bipolar-pulse conductivity detector for ion chromatography, a baseline compensator for differential scanning calorimetry, and modification of an ion chromatograph for glove-box operation and increased sensitivity and sample throughput.

Expansion of the Data Management System continued with the addition of an analysis catalog and the cost distribution program.

DATA MANAGEMENT SYSTEM

Programming for the Data Management System (DMS) began in 1975, and the system was placed in use in 1976. Four years later the system has matured and fewer additions are being made. A new analysis request sheet was designed to encourage customers to use computer-compatible sample codes.

A feature called "analysis catalog," similar to "customer catalog," has been programmed. This will allow the recall, by a single number, of frequently used combinations of analysis requests. For example, all the radionuclides reported from a routine gamma scan can be recalled as a unit.

A new program BILLST has been written to calculate analytical charges using standard times for routine analyses. This change will standardize customer costs to a greater extent and will allow more precise estimation of charges for budget purposes.

RADIOACTIVE MATERIALS ANALYTICAL LABORATORY

W. R. Laing, Group Leader

Upgrade of Hot Facilities

Work continued in several areas of our plan to upgrade equipment for hot cells and glove boxes. The status of each item is as follows:

Fiber optic spectrophotometer. A 10-m glass fiber optic bundle for the Brinkman colorimeter has been tested. It was found that the instrument light source had insufficient intensity to operate with the 10-m fiber optic. Additionally, wavelengths above and below the 500–550-nm band were severely attenuated, which would limit use of the fiber optic even with a more intense source. This test verified our previous opinion that long fiber optics must be constructed of quartz. The instrument has been transferred to the TRU laboratory for further tests with the 1-m fiber optic.

Oxygen-to-metal ratio. A new oxygen-to-metal (O/M) apparatus has been assembled, placed in an inert atmosphere glove box, and evaluated. The procedure will use water-saturated 4% H_2-Ar gas to convert an oxide sample to its stoichiometric composition in a single step. Change in weight of the sample will be used to calculate the O/M ratio.

X-ray fluorescence. The x-ray fluorescence (XRF) system for glove-box operation has been tested extensively with cold samples and is now in operation with plutonium-bearing materials. Sample preparation is done in one glove box, and the solutions, contained in mylar-covered plastic cups, are passed through a transfer port into the glove box containing the XRF unit.

Glove-box instrumentation. Several instruments have been modified for glove-box operation and are nearing the testing stage. These include a mercury porosimeter, a hydrogen analyzer, and a sealed-reflux system. Glove boxes are on order for moisture and gas release equipment.

Other instrumentation. A Tracor pulse-height analyzer and a Ludlum scaler replaced outdated counters this year. A Barber-Coleman gas chromatograph and a Shimadzu integrator have been installed in a glove-box laboratory for use with samples containing small amounts of radioactivity.

Building 2026 Maintenance

Considerable progress has been made this year on upgrading the building systems. All cell filters have been replaced. A scheduled roughing filter change for the main filter bank was delayed when it was learned that replacements for present filters were no longer available. A new system has been designed, and frames are being constructed to allow the use of less expensive disposable filters.

Cells 2 and 6, storage, mockup, and decontamination cells were cleaned thoroughly, and all unused equipment was sent to the burial ground. Cell 2 was painted. All manipulators have been refurbished with new bearings, swivels, switches, and tapes as needed. The drive mechanism for the west intercell conveyor was repaired.

An engineer was authorized to conduct a heating and ventilation audit of the building to determine whether the system was being operated properly and to make recommendations for repair, upgrade, and energy conservation. The filter changes mentioned previously were one of his suggestions. All transmitters have been recalibrated, and the controllers have been replaced with more modern units. Significant improvement in energy consumption is already evident, and additional savings should result when the roughing filters are changed and the system balance is completed.

Radioactive Materials Analysis

An x-ray fluorescence instrument, consisting of a United Scientific model 440 spectrometer and a Tracor-Northern model 4000 computer, was placed into operation during the year. A common power supply and computer control two spectrometers — one for cold samples and one located in a glove box for alpha-containing material. XRF has been applied to a number of sample types that would present formidable problems for chemical analysis. These applications include the measurement of (1) U, Pu, Th, Zr, Ru, and Re in aqueous and organic solutions; (2) Al, Ba, Si, Cs, Zr, and Ti in solutions and solids from waste fixation and resource recovery; and (3) chloride and sulfur in coal liquefaction streams. Qualitative scans have been made on a variety of metals, deposits, and vegetation.

The in-cell carbon-14 apparatus was redesigned to include a trap between the reflux condenser and the CO_2 absorber. The trap, filled with 6 M H_2SO_4, was used to scrub ruthenium from the gas stream of dissolver solution samples. At the same time, the procedure was changed to use persulfate oxidant rather than silver-catalyzed dichromate. This same apparatus was used to determine total organic carbon of dissolver solutions from carbide fuels.

Samples of water, sludge, and metal from the containment building at the Three Mile Island nuclear plant were received for analysis and distribution. As many as 30 analyses — utilizing wet chemistry, physical measurements, spark-source mass spectrometry, ion chromatography, mass spectrometry, activation analysis, and gamma spectrometry — were required for some samples.

An apparatus for the measurement of tritium in a single irradiated microsphere has been constructed. The microsphere is placed in an indentation in an anvil block, which is moved into position in a tube furnace. A solenoid-operated plunger crushes the sample, which is then oxidized by water-saturated air at 1000°C. The tritiated water produced is retained in a cold trap for counting. Recovery of tritium from labeled compounds averaged 95%, and the reproducibility of tritium results from particles with the same radiation history has been within 15%.

The volumetric uranium procedure was modified to allow titration of the reduced uranium with a 1.97 ml/cm Micrometric syringe. This modification, although less precise than the weighed titrant procedure, was adequate to meet customer needs and was used to determine the uranium content of 400 samples.

The conventional weighed titrant volumetric uranium procedure was used to analyze a dissolver solution on four occasions over a period of 33 days. The average uranium content, 76.99 mg/ml, showed no change over this period. The twelve aliquots had a relative standard deviation of 0.12%.

After observing the success of applied Teflon coatings in corrosion prevention in the General Analytical Laboratory, some equipment has been prepared for testing in the Radioactive Materials Analytical Laboratory (RMAL). An aluminum heater block and three hot plates have been Teflon-coated and will be used in glove-box and hot-cell applications.

The greatest radiation exposure to RMAL personnel occurs when waste is removed from the cells to the dumpster for burial. Although improved techniques have reduced the exposure, there remains room for improvement. A design for a shielded waste carrier has been made, and a mockup constructed for testing.

Testing of Coatings

Several nuclear coatings customers have expressed an interest in obtaining chloride release values at radiation exposures up to 10^7 Gy. A stainless steel cylinder with an O-ring seal was fabricated and conditioned with a dilute chloride solution at the high-flux radiation facility. Standards and blanks were irradiated, and recoveries of 95% or greater were obtained. Coated steel panels were tested at exposure levels from 10^5 to 10^7 Gy. Results indicated that chloride release is initially very rapid and decreases with time.

A superheater has been installed in the design-basis-accident (DBA) test facility for nuclear coatings. This addition will allow the testing of coatings at temperatures up to 195°C to more closely simulate reactor accident conditions.

Silicone rubber specimens were tested for the effects of radiation on their mechanical properties. Samples were exposed to both neutron and gamma fluxes and tested for tensile strength, elongation, and compressibility. The mechanical property tests were done by Metals and Ceramics Division personnel. *(R. F. Apple)*

GENERAL ANALYTICAL LABORATORY

R. R. Rickard, Group Leader

The number of analytical requests handled by the General Analytical Laboratory (GAL), or assigned to other laboratories, increased sharply during the year. This increase was due principally to three projects: a sample-intensive study of a biodenitrification pilot plant, an investigation into the chemical species that account for corrosivity of distillate oils, and a Laboratory-wide sampling of oils for polychlorinated biphenyl analysis. During the year, two service contracts with commercial laboratories were used during peak load periods to mitigate the impact of personnel losses. Some of the interesting analytical projects and problems encountered during the year are reported here.

General Analyses

A gas chromatograph was assembled and evaluated for the analysis of gaseous products from the combustion of uranium carbide. A test of the system using a novel single-injection technique yielded a 95% confidence limit of ±1.2% for the CO and ±0.8% for the CO_2 in a mixture of 60% CO–40% CO_2. The single-injection technique was made possible by using the reference side of a thermal conductivity detector with matched thermistors and two columns connected to the detector.

The determination of dibutylphosphoric (DBP) acid in solutions containing relatively high concentrations of nitric acid by ion chromatography had been difficult in the past. Removal of this nitrate interference has been achieved through the use of SEP-PAK® C_{18} reverse-phase resin cartridges. The resin, when wetted only with methanol, retains DBP but allows quantitative elution of nitrate with water. Approximately 90% of the DBP was eluted with methanol.

A cascaded multistage electronic filter has been added to the vacuum fusion system to remove line and high-frequency noise. It is now possible to select a setting that will pass the chromatographic peak of hydrogen, nitrogen, and oxygen without distortion, yet filter high-frequency noise components of the analyte signal. This feature significantly improved our capability to analyze metals with very low gas content.

Carbon was determined in mercuric iodide crystals by flowing oxygen through a combustion tube heated with a clam-shell furnace. A cold trap was employed to remove mercury and iodine before the combustion gases entered a Leco carbon analyzer for CO_2 measurement.

Numerous fly ash samples were prepared for analysis by inductively coupled plasma spectroscopy, using a method adapted from that used by the NURE program for stream sediments. This dissolution-leach method uses digestion with hot nitric and hydrofluoric acids. A special 2.5-cm-thick aluminum plate — with an imbedded thermocouple, recessed wells 1.2-cm deep for Teflon beakers, and coated throughout with Teflon — maintained the digestion temperature desired for consistency.

Operator input of simulated distillation data was eliminated by employing a BASIC language program written for a Sigma-10 chromatographic data system. The data system, with a printer/plotter, removed a potential source of error and shortened analytical time.

Salt samples from a proposed waste depository were analyzed for sulfate, carbonate, moisture, and weight loss at different temperatures. Other salt samples subjected to gamma radiation were analyzed for hydrogen peroxide, chlorine, perchlorate, and chlorate content.

Extensive analyses were made on "as-received" middle-distillate oils from the Ft. Lewis coal liquefaction plant in order to determine which chemical species accounted for accelerated corrosion rates. Total oxygen, nitrogen, chlorine, sulfur, and iron were determined in both the oils and water wash solutions. Water washes of oils appeared to reduce corrosivity of the oil by stripping significant percentages of chlorine, lesser amounts of sulfur, and the same order of magnitude of nitrogen (on an atomic percent basis). Further studies are in progress.

Environmental Analyses

A biodenitrification pilot plant required approximately ten thousand analyses over an extended operating period. Ethanol (a food supplement for the working bacteria), nitrate, nitrite, ammonia, total organic carbon, and phosphate were determined daily on six to twelve samples over a six-month period.

Photographic waste solutions were analyzed for silver and cyanide content in support of studies dealing with waste solution cleanup. Cyanide was distilled from the solutions and measured with an ion-selective electrode. Silver, both soluble and insoluble, was determined by atomic absorption spectrophotometry.

A joint effort of the Analytical Chemistry Division and the Environmental Sciences Division (ESD) with the Tennessee Valley Authority, was undertaken to evaluate the effectiveness of analytical methodologies for making measurements of trace elements in leachates of coal-type materials. Analyses of leachates prepared by ESD for arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc content have been completed by our Environmental Analyses Laboratory and a TVA laboratory. Results of the study indicated good interlaboratory agreement.

Organic material in certain waters and soil leachates imparts a color that interferes with the methyl thymol blue procedure for sulfate. Programmatic needs dictate that sulfate analyses not be compromised by employing clarifying treatments that form sulfate from other sulfur species. After many tests, a SEP-PAK® C_{18} reverse-phase resin cartridge was found to remove the organic interference at pH 1.7. Such pretreatment proved acceptable and solved a long-standing problem.

Assembly of an arsine generator coupled to a helium-glow discharge excitation system has been completed, evaluated, and put into service. The unit has met all expectations for determining total arsenic and the arsenic form (speciation).

TRANSURANIUM ANALYSIS LABORATORY

J. H. Cooper, Group Leader

Most of the effort of the Transuranium (TRU) Production Plant this past year was directed toward production of transcurium elements and the study of power reactor fuel element reprocessing. These two programs generated the majority of samples analyzed by the Transuranium Analysis Laboratory. Two different campaigns for the production of californium (about 1 g total) generated 12,000 analyses, and the solvent extraction studies in power reactor fuel reprocessing generated about 6000 analyses.

One unique aspect of fuel reprocessing studies was the testing of a device for nondestructive analysis (NDA) of fuel elements. A cooperative effort among the Chemical Technology, Instrumentation and Controls, and Analytical Chemistry divisions was necessary for testing of the NDA device. The Transuranium Analysis Laboratory was responsible for coordination of the destructive analysis efforts among our laboratory, the Radioactive Materials Analytical Laboratory, and the Mass and Emission Spectrometry Laboratory. After the fuel elements were assayed by NDA, they were dissolved by TRU operations personnel. Samples, with appropriate "spikes," were analyzed for density, uranium, plutonium, and lutetium. A known amount of lutetium had been added to the dissolved fuel solution to enable us to make a check on the total volume of solution. Agreement between the NDA and the chemical determination of uranium and plutonium was within 1%.

During laboratory studies of the behavior of plutonium in fuel reprocessing, we were requested to determine the valence states of plutonium in many samples. By measuring absorption spectra of the plutonium solutions, we were able to determine not only the valency of the plutonium but also the presence of plutonium polymer. This method of analysis is valuable not only because of its nondestructive nature but also because of its short turnaround time. The only sample preparation step required is that of dilution of high-concentration plutonium samples.

The Transuranium Analysis Laboratory is frequently requested to assist in preparation of special materials containing radioactivity. An example of this special activity was our preparation of a solution of ^{241}Am in sodium citrate. The AmO_2 (insoluble in sodium citrate) was dissolved in concentrated nitric acid. The resulting solution was evaporated to remove most of the acid and was adjusted to the proper pH by addition of a saturated solution of sodium citrate. The final solution was diluted to 300 ml and an americium concentration of 3.7×10^7 Bq/ml. In addition to the preparation of this special solution, we often aliquot and dispense many other transuranium elements for shipment.

Updating of equipment is necessary for high-quality analytical results. The Transuranium Analysis Laboratory has procured several items of equipment to help maintain the quality of our analyses. A dielectric constant meter, designed and built in the Analytical Chemistry Division, is now being used for measurement of tributylphosphate concentration in organic diluents. An alpha counter that uses a disposable phosphor is now in use to provide low-level alpha activity measurements in liquid effluents from the Laboratory. We have acquired all components for a gamma spectrometry system that utilizes a Ge(Li) detector and a computer analyzer (ND-6600). Personnel are now being trained in the use of this system. Some hot-cell equipment is being redesigned to give more reliable operation. The prototype of a remote pipettor has been constructed and is being tested. A new titration system is being designed for use in our laboratory. To implement the determination of acidity during design and construction of this system, we have ordered a commercial automatic titrator for use on out-of-cell samples.

REACTOR PROGRAMS

D. A. Costanzo, Group Leader

The primary function of the Reactor Programs Group is to provide analytical support to ongoing reactor technology development programs, which include the Consolidated Fuel Reprocessing Program (CFRP), High-Temperature Gas-Cooled Reactor (HTGR) Program, and the Alternative High-Level Waste Forms Development Program. "Laboratory-oriented" research and development in support of these programs is also performed in other sections (and reported elsewhere). This group also performs methods development to meet the needs of the service laboratories.

Consolidated Fuel Reprocessing Program Studies

Reference sample plan, HEF-modified flow sheet (200 series). A reference sample plan for analytical chemistry and process control requirements of the proposed CFRP Hot Experimental Facility (HEF), a pilot-scale fuel reprocessing demonstration plant, has been issued (1). The plan provides an assessment of the level of analytical support required for the process by describing projected locations, physical characteristics, and frequency of sampling and analysis necessary for plant control and material accountability. With that information, planning for equipment, personnel, and operating costs necessary to meet conceptual design requirements was completed. The plan also shows availability of analytical methods and of sensors for in-line application, as well as the status of research and development of new analytical techniques and new in-line sensors. *(J. L. Marley, E. D. North (2))*

CFRP analytical support laboratory. The analytical support laboratory located in Building 7603 provides technical support to CFRP engineering development tasks by providing onsite analytical service and by carrying out special projects to meet the needs of engineering studies. During 1979, 2280 analyses were performed, primarily in support of the rotary dissolver, iodine absorption, and voloxidizer studies. The following special "laboratory-oriented" projects were completed: (1) collection of data to determine the ferric nitrate-conductivity-density relationships at 45, 70, and 95°C (the information was needed for instrument development), (2) performing a scoping experiment to determine the feasibility of obtaining significant volume reduction (∼40%) for boric acid-borax solutions to aid in the evaluation of waste-handling processes for the Three Mile Island reactor site, (3) comparison of the effectiveness of calcium oxide, magnesium oxide, and calcium sulfate for the absorption of tritium as HTO. *(J. L. Marley)*

Thermal analysis studies. Thermal analysis (TA) and mass spectrometry (MS) have been used to study a variety of uranium compounds in support of CFRP process research and development and product conversion studies. A DuPont 990 thermal analyzer, which includes a thermogravimetric analyzer (TGA), a differential thermal gravimetric analyzer (DTA), a differential scanning calorimeter (DSC), and a Bendix MA-2 time-of-flight mass spectrometer, was used.

A kinetic study was made of the dehydration and denitration of uranyl nitrate hexahydrate (UNH). A stepwise dehydration of UNH followed by nitrate decomposition was observed in TG and DSC analyses. The DSC analyses at different heating rates were the basis of the kinetic determination of activation energies using the method of Sakamoto, et al. (3). Evolved gas analysis (EGA-MS) of UNH by MS at linear programmed heating rates confirmed the following reactions:

$UO_2(NO_3)_2\cdot 6H_2O \rightarrow UO_2(NO_3)_2\cdot 3H_2O + 3H_2O$ 72 kJ/mol

$UO_2(NO_3)_2\cdot 3H_2O \rightarrow UO_2(NO_3)_2\cdot 2H_2O + H_2O$ 85 kJ/mol

$UO_2(NO_3)_2\cdot 2H_2O \rightarrow UO_2(NO_3)_2\cdot H_2O + H_2O$ 128 kJ/mol

$UO_2(NO_3)_2 \cdot H_2O \rightarrow UO_2(NO_3)_2 + H_2O$ 133 kJ/mol

$UO_2(NO_3)_2 \rightarrow UO_3 + NO_x$ 173 kJ/mol

DSC data for the dehydration and thermal decomposition of uranyl nitrate hydrates have been produced for five heating rates. These nonisothermal data are being evaluated using the rate equation proposed by Sestsk and Berggren (4):

$$d\alpha/dt = K(t)\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p ,$$

where

α = the degree of conversion,
$d\alpha/dt$ = the rate of reaction, and
$K(t)$ = the temperature-dependent rate constant.

The m, n, and p parameters are estimated by taking the logarithm of both sides of the Sestak-Berggren equation to make the equation linear and using linear regression to estimate the coefficients, with one value of m, n, and p always being zero. In addition, this method gives estimates of the activation energy and preexponential parameters of the Arrhenius rate constant.

Preliminary analysis of the data indicates that dehydration of uranyl nitrate hydrates is controlled by a nucleation process according to an exponential law; in contrast, the thermal decomposition is a phase-boundary-controlled process. The value of activation energy is very sensitive to the type of process assumed; further investigations are being conducted to determine the correct process.

Several studies have been made on the thermal analysis of other uranium compounds. One study was made on a series of four samples: (1) 25% UO_3-75% $UO_2(NO_3)_2$, (2) NH_4NO_3, (3) $NH_4UO_2(NO_3)_3 \cdot H_2O$, and (4) $(NH_4)_2UO_2(NO_3)_4 \cdot H_2O$. The TA data showed reaction temperatures for dehydration, denitration, and $UO_3 \rightarrow U_3O_8$ reduction processes. The significant masses reported by EGA-MS were N^+, NH^+, NH_2^+, NH_3^+, H_2O^+, N_2^+, NO^+, O_2^+, N_2O^+, and NO_2^+.

Studies were made on acid-deficient uranyl nitrate (ADU) by TA. Differences between ADU samples dried from methanol and samples dried from aqueous solutions were compared. TGA thermograms were distinctly different for ADU obtained by evaporation from methanol and ADU evaporated from aqueous solutions. DSC data for aqueous-evaporated ADU samples exhibited only endotherms; in contrast, each methanol-evaporated sample exhibited a large exotherm at 75°C, which indicated the reduction of nitrate by methanol. The MS data substantiated the TG and DSC data.

Another set of similar analyses was done on a sample of $UO_2(NO_3)_2 \cdot xCH_3COOH$. These analyses show that uranyl nitrate coordinated with acetic acid is more stable than uranyl nitrate coordinated with methanol or water and has thermograms more like $UO_2(NO_3)_2 \cdot xH_2O$ than $UO_2(NO_3)_2 \cdot xCH_3OH$. The major decomposition reaction temperature was 350°C for the acetic acid $UO_2(NO_3)_2$ complex. *(D. A. Lee, C. K. Bayne (5))*

Studies on the reaction of sugar with nitric acid. The reaction of sugar with concentrated nitric acid was closely examined at temperatures of 100 and 110°C and in the presence of low levels of iron [0–0.2 *M* Fe(III)]. These experimental parmeters simulated solution conditions for a proposed process to denitrate highly acidic radioactive nitrate waste.

Under these conditions, the denitration of nitric acid by reaction with sucrose is an extremely complex series of hydrolysis and oxidation reactions, and no simple mechanistic treatment is suitable. However, the overall reaction can be defined (for a 24-hour reaction period) by the following equation:

$$\frac{-d[A]}{dt} = K(t)\,[A][C] \quad ,$$

where

$K(t)$ = time-dependent rate coefficient in $l\text{-}mol^{-1}min^{-1}$,
A = residual hydrogen ion concentration in mol/l, and
C = residual carbon concentration in mol/l.

The rate coefficient $[K(t)]$ mathematically delineates the change from a rapid initial reaction to a slower digestion reaction. For relatively short reaction times, the rate coefficient may be used as a second-order rate constant. Rate constants for this "second-order reaction" are calculated to be from 0.49 $\times 10^{-4}$ to 1.88 $\times 10^{-4}$ $l\text{-}mol^{-1}$ min^{-1}, depending on temperature of the reaction and concentration of iron(III) present in the nitric acid. The relationship of the rate constant, K, with iron(III) at 100°C is

$$K = 0.60 \times 10^{-4} + 5.60 \times 10^{-4}[Fe(III)] \quad .$$

Efficiencies of the acid kill reaction, expressed as moles of nitric acid consumed/mole of carbon added, ranged from 2.56 to 2.93 (or 26 to 35 moles of acid/mole of sucrose). *(C. S. MacDougall)*

Ion chromatography. One disadvantage of the commercial Dionex ion chromatograph is pump-pulse noise encountered at high sensitivity of the conductivity detector [e.g., 1 µS (1 µmho) full scale]. To alleviate this problem, both our model 10 and model 16 ion chromatographs have been equipped with pulse dampers (available from Glenco Scientific, Inc.). The result of the pulse dampers has been an improvement in signal-to-noise ratio by a factor of 15 on the 1-µS full-scale range.

To increase sample throughput and eliminate manual injection of samples, the Waters intelligent sample processor (WISP), model 710A, available from Waters Associates, Inc., was interfaced to our model 16 ion chromatograph. This sample processing unit has a capacity of 48 samples per carriage and permits automatic, unattended, overnight operation of the instrument.

A model 10 ion chromatograph was modified for glove-box use. The columns, injector valve, column switching valves, and conductivity cell were removed from the main instrument and enclosed in a separate stainless steel cabinet. Four feet of air and liquid line comprise the connections of the remote cabinet and instrument controls. A four-wire low-capacitance shielded cable was used to connect the detector cell to the electronics. *(J. M. Keller)*

Determination of Cr(VI) in nuclear fuel reprocessing solutions. Because Cr(VI) accelerates the corrosion of stainless steel process vessels, a method was devised for the determination of Cr(VI) in simulated nuclear fuel element dissolver solutions containing high concentrations of nitric acid, corrosion products, and fission products. The method involves the separation of most cations, including Cr(III), by precipitation as hydroxides from basic solution. Ruthenium, which is not removed by this first separation, is oxidized by argentic oxide and is subsequently removed by fuming the solution with sulfuric acid. The chromium that remains in the residue is then assayed by a standard *s*-diphenylcarbazide spectrophotometric technique. The method is accurate to ±3 µg/ml at the 10 to 100 µg/ml level of Cr(VI) in the test aliquot. *(C. S. MacDougall)*

Alternative High-Level Waste Forms Development Program Studies

Thermal analyses of SYNROC. Thermal analysis studies for the Alternative High-Level Waste Forms Development Program have been made on internal gelation SYNROC microspheres. SYNROC is a mineral-type ceramic being evaluated as a waste form to immobilize radioactive waste for ultimate disposal. Wet and dried samples of washed and unwashed gelled microspheres have been examined by TGA, DSC, DTA, and EGA-MS. Thermograms from each technique were obtained by linear-programmed heating. From profiles of the thermograms, the pyrolysis reactions were proposed. For SYNROC sol-gel samples, the DSC and DTA thermograms were not very definitive. Most of the data were taken from TGA and EGA-MS thermograms.

Water was a major component evolved — even from dried (200°C) microspheres. Each of the DSC and DTA thermograms had a large endotherm for release of water near 100°C. Closer examination of TGA and EGA-MS profiles revealed the release of different sources of water — outer-sphere, inner-sphere, and that formed from the combustion of organic materials and dehydration of metal hydroxides.

For unwashed microspheres there were residual quantities of the original gelation chemicals and their chemical reaction products. These included urea and its decomposition compounds, ammonia, and formaldehyde from the hydrolysis of hexamethylenetetramine (HMTA). After the evolution of outer-sphere water, ammonia was released upon further heating. The EGA-MS thermogram for ammonia had two peaks. This suggests that the first peak was due to ammonia from HMTA hydrolysis and the second from urea decomposition. The release of CO and CO_2 near 300°C indicated the combustion of organic residuals. At this temperature, a large number of organic masses were released for unwashed microspheres. However, for washed microspheres the organic products were practically nil. Washed microspheres released mostly water and small concentrations of NH_3, CO, and CO_2.

A kinetic study of some of the decomposition reactions was conducted by the method of Sakamoto et al. (3) using MS. Mass spectral scans were made at several different heating rates. Arrhenius plots were made of the logarithm of the heating rate against the reciprocal of the absolute temperature for peak ion current intensities of each particular mass. Activation energies were determined from the slope of these plots: outer-sphere water = 36 kJ/mol, CO from urea decomposition = 179 kJ/mol, and CO_2 from organic combustion = 293 kJ/mol. *(D. A. Lee, K. E. Knipschild (6))*

Quasi-isothermal drying of sol-gel SYNROC microspheres. During the drying process, SYNROC microspheres tend to crack due to excessive gas release. To prevent cracking of the microspheres, two quasi-isothermal drying systems were developed to control the rate at which gas is evolved.

The first system uses a DuPont thermogravimetric analyzer interfaced with a Macsym II microcomputer. This system, called the thermogravimetric-constant weight loss (TGA-CWL) system, was used to determine the drying conditions necessary to minimize cracking of the microspheres. The system monitors total weight loss and controls the rate of heating through a feedback loop. Intact microspheres were obtained when they were predried at 100°C for 48 h and then dried at a controlled temperature to maintain a constant weight loss rate of 0.4 wt %/min. The heating cycle obtained from the TGA-CWL system was programmed onto a 3.8-cm Astro furnace. In this furnace, larger (100 g) batches of unwashed spheres were successfully dried and sintered with only minor cracking. However, porosity studies indicated that density of the spheres was low.

To further study the problem, evolved gas from the TGA furnace was fed into a time-of-flight mass spectrometer (TOFMS). The mass spectrometer analyzed the gases and their rates of evolution as they were produced during TGA-CWL drying. Results indicated that the large rate of ammonia evolution was reponsible for most of the weight loss of the sample.

A second system, called the mass spectrometer-constant weight loss (MS-CWL) system, was set up to control heating rate by monitoring the rate at which specific gaseous components were released. Using the TOFMS, the heating cycle was controlled by the rate of ammonia evolved. An argon leak was used to calibrate the instrument and normalize the data. *(K. P. Cross (7), D. A. Lee)*

Baseline-drift compensator for a Perkin-Elmer DSC-1B differential scanning calorimeter. Baseline drift, for an extended temperature range on the DSC-1B, has been a troublesome problem for many years. The source of the drift is probably a combination of electronic drift, thermal instability, and mismatched thermistors. To avoid internal modification of the instrument electronics, a simple drift compensator, connected to the output of the instrument, was proposed. Adjustment of the instrument provides a drift with fairly constant slope. By approximating the drift slope with a ramp generator and taking the difference between the two signals, a constant baseline can be obtained.

The baseline compensating circuit was constructed and connected to the DSC-1B. Initial evaluation of the circuit was successful, and a fairly constant baseline was obtained for a temperature scan of 350 to 700 K. However, a problem that prevents reproducible setting of the constant baseline drift appears to exist with the front panel controls of the DSC-1B. This project is still in progress. A report on the baseline-drift compensator is in preparation and will be submitted to *Analytical Chemistry*. *(J. M. Keller, G. E. Gorder (8), G. R. Mack (9))*

Leaching studies of SYNROC. Leaching studies were undertaken to determine the suitability of SYNROC for disposal of radioactive waste. SYNROC is a solidified waste fixation product formed from a mixture of a number of oxides, principally Al_2O_3, BaO, CaO, TiO_2, and ZrO_2. It is one of several materials recommended for use in immobilizing high-level nuclear waste. One of the most important criteria for a good waste fixation material is low leachability.

Leaching studies of SYNROC pellets spiked with U-238, Pu-239, Am-241, and Cm-244, which were begun in the last quarter of 1979 and reported in the 1979 annual report (10), are continuing. Additional leaching studies on unspiked SYNROC microspheres were carried out during the past year. Deionized water and simulated ground water were used as leachants; leaches were conducted at temperatures of 23, 70, and 90°C. Leachants were analyzed for the main components of SYNROC by atomic absorption, x-ray fluorescence, flame emission, inductively coupled plasma, and activation analyses. *(P. L. Layton)*

High-Temperature Gas-Cooled Reactor Program Studies

Graphite oxidation studies. In a joint effort with the Metals and Ceramics Division and the Chemical Technology Division, laboratory experiments are underway to study the oxidation of reactor-grade graphites by moisture and the effect this oxidation has on structural properties of the graphite. These oxidation studies are carried out in a closed-loop apparatus using helium as a carrier gas. The operating conditions of temperature, gas flow, and moisture in the helium sweep gas are varied to simulate the secondary coolant in an HTGR. Graphite species are to be characterized for density, surface area, and porosity before and after treatment (11).

Construction and evaluation of the automated BET-type surface area apparatus are complete. The system can measure specific surfaces as small as 0.5 m^2 and has an accuracy and precision of better than ± 0.02 m^2. Larger surfaces up to 1000 m^2 can be measured with an accuracy and precision of $\pm 0.5\%$. In addition to oxidation studies, the system has been used to measure a number of special samples, including some highly activated charcoals (>900 m^2/g) and some iridium powders (<0.5 m^2/g). We are also participating in an ASTM round robin to study measurement of surface areas of reactor-grade graphite samples. The apparatus is also used to measure helium densities of the samples. Solids in the range of 1-20 g/cm^3 can be measured with a precision and accuracy of ± 0.005 g/cm^3. *(C. R. Kennedy)*

Special Projects

Thermal analyses. The use of TA to solve process chemistry problems has increased significantly during this period. The number of customers, the variety of materials and reactions, and the number of analytical instruments and accessories used have all increased. More than one technique has been used for each analysis. Comparison of the analyses by TGA, DTA, DSC, and MS has been useful in elucidating chemical and physical reactions.

Thermal analyses were made of mixed (U-Th) nitrate-NH_4NO_3 (solution, slurry, and moist powder) samples. The only difference in the samples was the amount of NH_4^+. The thermograms from DSC analyses became more complex as NH_4^+ concentration increased. From MS data it was determined that NH_3 complexing with U-Th ions was increased as the NH_4^+ concentration increased. In these systems it was found that NH_4NO_3 decomposition was not simply $NH_4NO_3 \rightarrow N_2O + 2H_2O$ because N_2, NH_3, and NO were also released.

Urania gel microspheres from General Atomic (GA) Corporation were compared with ORNL urania microspheres. The GA material contained much more carbonaceous materials and other fragments than the ORNL material. The MS, DSC, and TGA analyses were significantly different for the two materials.

Samples of UO_3 + C from GA were sintered. After sintering, the samples were heated in Ar-0.5% CO, Ar-2% CO, Ar-4% H_2, and Ar. Small differences in peak temperatures of the MS thermograms were noted for masses 12, 16, 18, and 44, but no differences could be detected for the four samples in their TGA and DSC analyses.

Tb_2O_3 prepared in the Chemistry Division from a carbonate solution was analyzed by TGA and MS. From MS data it was concluded that principal decomposition products were CO_2 and H_2O. These data indicate that the composition of the compound was $Tb_2O_3 \cdot 2CO_2 \cdot 2H_2O$, which was described by Sastry, et al. (12).

Preparations of uranium and thorium molybdates, as well as molybdenum oxides for the CFRP, have been studied by TA. TGA, DSC, and EGA-MS thermograms were used to characterize these materials.

TGA and MS studies were made on the decomposition of sodium nitrate for denitration of Savannah River nitrate wastes. Reactions studied were the reduction of $NaNO_3$ by sulfur in Li_2CO_3, the reduction of $NaNO_3$ by carbon in Na_2CO_3, the reduction of $NaNO_3$ with iron powder, and the thermal decomposition of $NaNO_3$ in the presence of freshly precipitated aluminum silicate. Other possible reactions for $NaNO_3$ decomposition were also proposed. *(D. A. Lee)*

A bipolar-pulse conductivity detector for ion chromatography. Ion chromatography employs a background suppressor column to eliminate or decrease background conductivity due to the eluant. There are several disadvantages associated with employing a suppressor column: (1) decrease in efficiency; (2) limited choice of mobile phase; (3) requisite regeneration of the suppressor; and (4) analysis complications due to ion exclusion, oxidation, and insolubilities of sample ions. One approach to elimination of the suppressor column is to employ a bipolar-pulse technique for the measurement of conductivity (13). This technique involves the application of two successive, constant dc voltage pulses of equal but opposite polarity to the conductivity cell and measurement of current flowing through the cell at the end of the second pulse. One of the main advantages of the bipolar-pulse technique over conventional ac techniques is that the duty cycle of dc pulses applied to the cell can be varied to minimize solution heating. With ac methods of conductivity measurement, continuous power is applied to the cell.

The design, construction, and evaluation of a prototype were completed. Athough the prototype produced encouraging data, the amplifiers employed did not have the speed or current capabilities to handle highly conductive solutions (greater than 5 mM salt). A new design, employing high-speed, high-current amplifiers, has been completed. This design has been a joint effort between the Instrumentation and Controls Division and Analytical Chemistry Division. Evaluation of this prototype is still in progress. A report on application of the bipolar-pulse technique to ion chromatography has been accepted for publication in *Analytical Chemistry*. *(J. M. Keller)*

Development of a monitor for spark-induced by-products of sulfur hexafluoride. The 25-MV tandem accelerator of the Holifield Heavy-Ion Research Facility employs sulfur hexafluoride as an insulating gas. When high-voltage corona discharge or electrical arcing occurs in the sulfur hexafluoride atmosphere of the accelerator, degradation of the gas occurs and results in formation of various by-products through dissociation and ionization reactions. Although sulfur hexafluoride is inert and nontoxic, the spark-induced by-products may be highly corrosive and toxic. These by-products are primarily responsible for corrosion of accelerator hardware and electrical instabilities that degrade performance of the accelerator. It is therefore desirable to have a monitor for these spark-induced by-products so that appropriate actions can be taken when there is a buildup of by-products.

Various techniques for qualitative and quantitative analysis of SF_6 by-products have been reported. However, the techniques lack either the sensitivity or selectivity required. Although analysis of each individual by-product might be desirable, a more practical view may be to employ a method that provides a measure of the total contamination of SF_6. To obtain a measurement of total SF_6 contamination, one may take advantage of high reactivity of the by-products. High reactivity can cause considerable problems with instrument techniques, such as IR, GC, and MS. These problems may be due to instrument corrosion and artifacts resulting from the sampling technique.

By allowing the by-products to hydrolyze in an aqueous solution, one may analyze for fluoride and obtain a measurement of the total hydrolyzable fluoride (THF). Our design of a THF monitor, in which by-products are allowed to hydrolyze, employs a Hall electrolytic conductivity detector (HECD) (14).

A Tracor model 700 HECD was used for construction of a THF monitor. The conductivity cell was connected to a flow of helium through an all-Teflon sample loop (200 μl) injector. The cell electrolyte was 50/50 ethanol/water. Trace impurities in SF_6 were generated in the laboratory by discharging a Tesla coil through 50 ml of SF_6 for several minutes. Samples of the contaminated SF_6 were then injected into the helium flow. Sensitivity to the by-products was excellent, less than 0.01 μg/mV hydrolyzable fluoride with a high attenuation of the detector signal. A brief report of our initial studies on monitoring SF_6 by-products is published in the proceedings of a recent EPRI workshop (15). *(J. M. Keller, R. W. Holmberg (16))*

Examination of irradiated brines. Storage of radioactive waste in salt repositories has spurred interest in the products formed by radiolysis of chloride solutions.

Microanalytical techniques for the assay of free Cl_2, H_2O_2, ClO_4^-, and ClO_3^- in irradiated brine solutions were developed in support of Chemical Technology Division radiolysis studies. Concentrations of the species of interest were not expected to exceed 2 μg/ml in saturated brine, which greatly limited the choice of analytical methods.

A spectrophotometric technique utilizing *o*-tolidine was chosen for determination of free chlorine. In neutral solutions, *o*-tolidine reacts with free chlorine to form a green-colored complex. Absorbance of the color-developed solution obeys Beer's law at 625 nm. Quantities of chlorine from 0.1 to 6 μg in the test aliquot were determined with a precision of about ±5%. Normally, a buffer stabilizer would be utilized to minimize low-pH interference or high-pH fading. However, the buffer formed a turbid solution when brine was added. Therefore, no buffer was used, and all color development was carefully timed. Strong oxidizing agents (e.g., Br_2, ClO_2, I_2, O_3, etc.)

interfere, but their reduced forms do not. Chlorate ion up to 10 μg/ml does not interfere. Hydrogen peroxide, also typically present in irradiated brine solutions, does not interfere in the analysis *per se*. However, peroxide does quantitatively react with chlorine. The presence of peroxide signals the absence of free chlorine.

A technique using the oxidation of Fe(II) with H_2O_2, followed by spectrophotometric determination of the Fe(III)-xylenol orange complex, was chosen for the determination of hydrogen peroxide. Hydrogen peroxide, in dilute H_2SO_4 (0.05 *M*), oxidizes Fe(II) to Fe(III). Under these conditions, the Fe(III) forms a complex with xylenol orange (XO), which exhibits an absorption peak at 540 nm. The absorbance is directly proportional to Fe(III) concentration, which is in turn directly related to the original concentration of H_2O_2. Any redox reagent that interacts with the Fe(III)/Fe(II) couple interferes in the technique. Quantities of H_2O_2 from 0.1 to 3 μg in the test aliquot are determined with a precision of about ±5%. Free chlorine and chlorate ion, typically present in irradiated brine solutions, do not interfere in the analysis.

Chlorate ion was also determined spectrophotometrically. In moderately concentrated H_2SO_4 (3 *M*), chlorate ion oxidizes Fe(II) to Fe(III). A few drops of 0.1 *M* OsO_4 in H_2SO_4 are used to catalyze the oxidation. The Fe(III) that is produced forms a complex with thiocyanate, which exhibits an absorption maximum at 480 nm. The absorbance is directly proportional to the Fe(III) concentration, which is in turn directly related to the original concentration of ClO_3^-. Any redox reagent that interacts with the Fe(III)/Fe(II) couple interferes in the technique. Both H_2O_2 and free Cl_2 react with Fe(II) under the described conditions to positively bias the chlorate assay. Since each effect is quantitative, however, that bias may be subtracted and the chlorate assayed. Quantities of ClO_3^- from 0.2 to 10 μg in the test aliquot were determined with a precision of about ±10%.

An ion chromatographic technique was chosen for the determination of perchlorate ion. A Dionex model 10 ion chromatograph was fitted with a low-capacity anion exchange separator column (#20232) and a cation suppressor column in the Ag^+ form. The eluant was 0.005 *M* NaI (2.3 ml/min). Under these conditions, the perchlorate elutes in about 3-4 min and is well separated from chloride. No dilution of the sample is necessary, and 0.2 μg/ml ClO_3^- can be determined with a precision of ±15 percent.

For each of the spectrophotometric methods, a slight enhancement of the absorbance of the colored complex was noted with increasing amounts of chloride ion. Therefore, the total quantity of chloride ion was maintained at 1.09 *M* in the color-developed test solution by addition of saturated $MgCl_2$ solution. *(C. S. MacDougall)*

Determination of SO_2 and SO_3 in gas samples. The Metals and Ceramics Division is studying the stability of various materials in an H_2SO_4 environment. These studies have direct applicability to the H_2 production processes under investigation by General Electric Corporation, General Atomic Company, and Los Alamos Scientific Laboratory. Consequently, we adapted two techniques to assay gases for SO_2 and SO_3.

Sulfur dioxide is measured by collecting the gas in NaOH solution. The mixture is adjusted to a slightly acid pH, and the SO_2 is titrated iodometrically. Quantities of SO_2 up to 1 g may be determined with a precision of ±5%.

To determine total sulfur content (as SO_3) in a gas mixture, the sample is reacted with 3% H_2O_2. This oxidizes the SO_2 to SO_3, and all SO_3 is absorbed in the aqueous solution. If no other acid gases are present in the sample, total sulfur can be determined by titrating the H_2SO_4 with standard base. If, however, other acid gases (such as nitrogen oxides) are present in the sample, total sulfur must be determined by titrating for sulfate. The method recommended for SO_4^{2-} determination is titration with $BaCl_2$ by using tetrahydroxyquinone as an indicator (17). *(C. S. MacDougall)*

Particle size distribution of uranium metal and uranium dioxide powders. A Micromeritics Sedigraph 5000/GB particle size analyzer, which was located in a glove box and used for many years to examine radioactive materials, was upgraded and placed into routine operation for the measurement of particle size distribution of UO_2 and uranium metal powder samples. Particle size is based on the rate of sedimentation. A new sedimentation cell containing small steel balls was installed, and several electronic components replaced. A glass bead standard (NBS SRM 1003) was used to calibrate the instrument over the particle diameter range 5-30 μm.

The instrument was employed to determine particle size distribution of a number of samples of UO_2 and uranium metal. A 40% glycerol solution containing 0.016% Daxad-23, a dispersing agent, was used to disperse the UO_2 samples (density = 10.96 g/cm^3); no problems were encountered. However, dispersion of the uranium metal samples (density = 19.03 g/cm^3) was quite a problem. Even when an 80% glycerol-0.016% Daxad-23 solution was employed, it was noticed that a portion of the sample could not be suspended by magnetic stirring prior to introducing the mixture into the sedimentation cell. A commercial dispersing agent, Sediperse A-12, has been ordered and will be tested with the uranium metal samples as soon as available. *(F. L. Layton)*

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4. BIO/ORGANIC ANALYSIS SECTION

M. R. Guerin, Section Head

Work in the Bio/Organic section can be broadly divided into three classifications: Quantitative Methods and Applications, Isolation and Identification, and Sampling and Special Projects. These are not clear-cut distinctions, however, since methods or techniques developed in one program are often used in another. Close communication between workers in different programs results in synergistic effects on section activities.

Techniques used for quantitative methods include Fourier transform infrared spectroscopy, high-performance liquid chromatography, and resin trapping followed by thermal desorption and capillary column gas chromatography. The first two techniques are primarily investigative tools, while the latter is used more for routine determinations of organovolatiles.

Isolation and identification studies rely heavily on preparative-scale liquid chromatography, nuclear magnetic resonance spectrometry, and gas chromatography-chemical ionization mass spectrometry. A primary goal of this work is to isolate biologically significant compounds and to discriminate between structural isomers. In attempting to distinguish amine isomers, for example, ammonia-chemical ionization mass spectrometry has proved quite effective. Our involvement in these activities has grown, not only because of increasing environmental compliance regulations and expanded ORNL programs using organics, but also because we have developed techniques and acquired equipment to perform the needed analyses. Such preparedness is a result of the synergism mentioned earlier.

The section has also a large and varied program in sampling and special projects. Some of this applied work is in support of environmental, occupational health, and toxicology programs. A new major program is concerned with generating and monitoring military obscurants for animal inhalation toxicology. Instrumentation to generate and deliver a diesel oil aerosol to rodents was developed, as well as methods to characterize the aerosol. Synfuels research has centered on identification and measurement of mutagens. For shale oil we have compiled data on a unique set of shale-derived oils.

Running through these and all our programs is the thread of mutual support and sharing of information. Though we perform a great variety of research for a number of different customers, our ultimate aim is to use knowledge, techniques, and experience gained in each of these efforts in a way to maximize technology transfer throughout all programs.

QUANTITATIVE METHODS AND APPLICATIONS

High-Performance Liquid Chromatographic Isolation and Determination of Mutagens in Natural and Synthetic Fossil Fuels

Polycyclic aromatic hydrocarbons (PAH) and polycyclic aromatic amines (PAA) are two classes of particularly mutagenic compounds that are present in natural and synthetic fossil fuels. Because there are many individual compounds, we are developing methods to quantitate "marker" compounds of both classes. Benzo(*a*)pyrene (BaP) is used as a PAH marker, and the isomers α-naphthylamine (α-NA) and β-naphthylamine (β-NA) appear to be useful markers for the PAAs.

We find high-pressure liquid chromatography (HPLC) to be an effective means of isolating and/or detecting these compounds (1,2). The isolations are achieved using a semipreparative-scale bonded-phase column, whereas the analytical determinations are performed using an analytical-scale, reversed-phase column. Use of a fluorescence detector to monitor the effluent of the analytical column permits a selectivity that cannot be achieved with the more common single-wavelength uv detectors. Recovery of analyte is determined using carbon-14-labeled tracers added to the sample before isolation.

BaP is determined by first injecting a spiked aliquot onto a bonded polar amino-cyano (PAC) column, eluting the sample with 6% (v/v) methylene chloride/pentane, and collecting the BaP-enriched fraction. This isolate is then injected onto an analytical-scale octadecyl silane ODS-HPLC column and eluted with 25% (v/v) water/acetonitrile. The effluent is monitored at excitation and emission wavelengths of 365 and 425 nm, respectively.

BaP is recovered quantitatively (>95%) from all oils studied to date. The BaP concentrations determined by this procedure agree well (absolute results generally within ±20% and sample correlation coefficient of 0.984 for eighteen samples) with those determined by a reference procedure (3). An aliquot may be isolated and analyzed in three hours using the new method.

The α-NA and β-NA may be isolated and detected similarly. The two PAA markers are eluted from a semipreparative-scale aminosilane column with 50% (v/v) pentane/methylene chloride. The final determination is performed using the analytical-scale ODS-HPLC column with a 50/40/10% (v/v) mixture of water/methanol/acetonitrile made to 0.06 *M* in ammonium hydroxide. The recovery of α-NA typically exceeds 90%. Although the aminosilane column resolves these markers by no better than about 50%, they may be distinguished spectroscopically with no mutual interference by choosing an optimized pair of excitation/emission fluorescence wavelengths. The appropriate wavelengths for α-NA are 310/500 nm; those for β-NA are 270/405 nm.

We intend to analyze many of the samples previously examined for BaP content for both α-NA and β-NA and to compare the data so obtained with our "reference" procedure. In addition, we are refining the HPLC procedure so that BaP, α-NA, and β-NA isolates are generated in a single pass. The procedure may be further extended to include the mutagenic aminoanthracenes and a marker species for the neutral polar fraction. *(B. A. Tomkins, V. H. Ostrum (4), R. R. Reagan, J. E. Caton, H. Kubota)*

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy has been applied to several projects including the Fossil Fuels Research Materials Facility, studies of the nature of the sorption characteristics of fly ash, analyses of super low tar cigarettes, characterization of fossil fuel fractions separated by semipreparative liquid chromatography, and numerous miscellaneous efforts.

Our FTIR capability has been greatly enhanced during the past year by addition of a diffuse reflectance attachment. This allows the spectrum of solid samples to be obtained either in its native form or dispersed in, for example, KBr. Because the procedure involves reflection rather than transmission, it can be applied to both opaque and insoluble samples after minimal sample preparation. Another advantage of diffuse reflectance is an enhanced signal-to-noise ratio, which in many cases allows the measurement of spectral bands with peak absorbances of less than 0.001 absorbance unit. This technique has been especially useful in studies of the nature of sorption characteristics of fly ash where careful comparisons have been made for different fly ashes and for a given fly ash after heating (to remove volatile compounds and ultimately to remove all organic carbon) and extraction. Comparisons utilizing spectral subtraction have yielded spectra that are indicative of the types of organic compounds that are "sorbed" on the surface of the fly ash.

Diffuse reflectance has also proved useful for characterizing the fractions of fossil-fuel-derived products from semipreparative liquid chromatography. One separation scheme yields five fractions: (1) aliphatic hydrocarbons, (2) aromatic hydrocarbons, (3) medium polarity compounds such as amines and heterocyclic compounds, (4) highly polar compounds including phenols and cresols, and (5) extremely polar to ionic compounds such as acids. These fractions have unique infrared spectral features that have easily been documented by adding several drops of the fraction to 300 mg of KBr and obtaining the diffuse reflectance spectrum. No further sample preparation is necessary. This work is taken as a practical beginning toward coupling liquid chromatographic separations with wide-range infrared spectral detection. Advantages of the diffuse reflectance technique for analysis of liquid chromatographic eluants include not only good sensitivity (enhanced signal-to-noise ratio) and ease of sample preparation but also ease in eliminating volatile solvents from the less volatile eluted constituents. A fraction can be sampled for diffuse reflectance infrared analysis by adding three drops of the eluted fraction to a diffuse reflectance sample cup containing powdered KBr. The sample cup and its contents are heated for 5 min in an oven at 100°C to volatilize the solvent. The Kubelka-Munk plot (5) of the resulting spectrum (with powdered KBr used for the reference spectrum) showed a background noise of less than 0.0001 absorbance unit. The detection limit for an aromatic hydrocarbon such as benzo(*a*)pyrene was approximately 0.5 μg.

There are two disadvantages to the use of diffuse reflectance for analysis of liquid chromatographic separations: (1) solvent removal (or sample loss) when the eluted sample has a volatility similar to the eluting solvent system and (2) inability to tolerate water in the eluting solvent system. The first disadvantage is minor because other techniques such as gas chromatography-mass spectrometry are more applicable to volatile sample components. The second disadvantage is of much greater concern because reversed-phase separations involving water as part of the eluting solvent mixture are employed quite extensively in analytical liquid chromatography. Water presents a significant interference to any infrared technique, including diffuse reflectance. At present, the most adequate method of thoroughly eliminating the water interference is by lyophilization. The diffuse reflectance technique appears to be the most promising approach to combining liquid chromatography with infrared spectral measurements. The first commercial interface should be available by the time this report is issued.

Requests for services and programmatic applications involving FTIR increased significantly in this reporting period. FTIR is finding quantitative as well as qualitative applicability. Research is to focus on coupled chromatography/FTIR. *(J. E. Caton, W. H. Griest, S. H. Harmon)*

Resin Collection and Gas Chromatographic Analysis of Vapor-Phase Organics

The health and environmental effects of vapor-phase organics are important in such areas as occupational exposure, ambient air pollution, and tobacco smoking. We have developed a particularly useful method for the collection and analysis of these vapor-phase organics by use of the sorbent resin, Tenax®.

Collection of vapor-phase organics from ambient air is accomplished with the Moneyhun sampling system (6), which mounts on the side of a conventional high-volume air sampler. Vapor-phase organics collected by the Tenax® cartridges are efficiently analyzed by our thermal-desorption gas chromatograph (GC) procedure (7). This method involves taking a 100-mg portion of well-mixed Tenax® from the trap, adding an internal standard before thermal desorption of the organics onto a glass capillary GC column, temperature programming the column, and detecting the separated organics by flame ionization.

A wide range of vapor-phase organics is determined by our method. Examination of samples collected near a coal gasifier revealed the presence of benzene, toluene, the xylenes, seven C_3-benzenes including cumene and mesitylene, several diaromatics, phenol, and the cresols, at air concentrations ranging from 0.01 to 9 $\mu g/m^3$ of air. Except for the phenols, (8) most of these same compounds have been observed previously (9) in urban atmospheres. The thirty GC peaks identified comprise 70 to 80% of the total chromatographic peak area of the GC profile. Compounds present in the greatest amount were toluene, *m*-xylene, a C_3-benzene, naphthalene, benzaldehyde, and acetophenone. All were present in concentrations a thousand-fold greater than particulate-phase components, such as the paraffins and PAHs.

Examination of front and backup cartridges from 24-h ambient air sampling indicated that several of the most volatile vapor-phase organics broke through the front cartridge during the sampling period. Breakthrough (percent of analyte in backup trap vs front trap) for benzene and toluene often was 100%, but breakthrough for the xylenes was less than 10%, and for less volatile organics there was essentially no breakthrough. Thus, for extended periods of collection, a backup trap composed of a more efficient sorbent (such as the carbonaceous Ambersorb) for the most volatile constituents is required.

Precision of the analysis was determined by replicate analyses of a single sample. Using an internal standard, we found the average relative standard deviation for all components mentioned above to be ±5%.

An indication of the accuracy of our thermal desorption method was obtained by analyzing Tenax® traps spiked with 2 μg, 8 μg, 40 μg, and 2 mg each of benzene, toluene, *m*-xylene, and naphthalene, which represent the typical range of vapor phase organics. The 2- to 40-μg amounts spanned the range of amounts collected in the field during 24-h sampling. The 2-mg loading represented a hypothetical "worst case" to see if richly laden atmospheres could be sampled and subsequently analyzed accurately. Recoveries ranged from 78 to 123%, with relative standard deviations of ±10%. This suggests that the procedure is accurate as well as precise.

Tenax® trapping is also very useful in the analysis of vapor-phase organics in cigarette smoke. The cigarette is conventionally smoked through a Cambridge filter backed up by a small Tenax® trap (the type used in thermal desorption GC). For extremely low tar delivery cigarettes, gas-phase components can be desorbed directly from the trap and be analyzed with high sensitivity by gas chromatography. In the case of high tar delivery cigarettes, the exposed Tenax® must be diluted and mixed with fresh Tenax® before analysis. Analysis of backup traps indicates that the single Tenax® trap is sufficient for collection of all but the most volatile (e.g., methane-acetone) organics.

This procedure has been successfully applied to the analysis of vapor-phase organics from cigarettes delivering tar in the range of 10 μg to 33 mg/cigarette. For cigarettes delivering <1 mg of tar, it is the only analytical method we have with sufficient sensitivity to measure organic constituents in the smoke of a single cigarette.

Our method is currently being used in support of the ORNL Site Specific Assessment Program and in special studies and internal services dealing with occupational or environmental air contamination. The method is being extended to include element selective detection with first attention being given to organosulfur compounds. *(C. E. Higgins)*

Analytical Chemistry of Cigarette Smoke

Data have been generated in support of several international epidemiology studies. Approximately 120 brands of cigarettes from Germany, Italy, Scotland, India, Hong Kong, Singapore, Malaysia, Indonesia, and the United States have been analyzed for their deliveries of tar, nicotine, carbon monoxide, and carbon dioxide. Deliveries varied sufficiently between products to require adjusting the number of cigarettes smoked per analysis and the analytical procedures themselves. The marketing of "ultralow" tar cigarettes (≤1 mg tar/cigarette) has required the development of improved analytical procedures. Conventional procedures for the determination of tar and nicotine are not applicable to such products. Spectrophotometric procedures appear promising for measuring low-tar deliveries, although there are questions as to exactly what these spectral "tar" measurements are quantifying. Similarly, very low nicotine deliveries may have to be measured by HPLC with uv or fluorescence detection or by GC with thermionic nitrogen-phosphorus detection.

A similar situation exists for gas-phase constituents. The conventional GC method for measuring carbon monoxide and carbon dioxide fails to provide sufficient sensitivity for the ultralow tar cigarettes. However, an environmental monitoring device, the "Ecolyzer," does have sufficient sensitivity with an electrochemical detector. We have recently developed (10) a chemiluminescence method for measuring oxides of nitrogen in smoke gas phase. This new method is more specific and reliable than the older Saltzman colorimetric method and does provide enough sensitivity for the ultralow tar cigarette smoke analyses. A promising method for the determination of gas phase carbonyl compounds is described elsewhere in this report.

We also are refining GC multicomponent analysis methods for profiling the smoke particulate and gas-phase constituents for a more comprehensive analysis of tobacco smoke. Gas-phase organics from even the lowest tar cigarettes can now be determined by resin trapping as described earlier.

Our tar-profiling method involves the gas chromatographic analysis of trimethylsilyl derivatized total particulate matter. Because the total tar delivery is not injected into the GC, this method is not as sensitive as the gas-phase method. However, if 10 to 20 cigarettes are smoked per pad, the method can detect the major particulate-phase organics from even the lowest tar-delivery cigarette. This method will require a small degree of further refinement before it can be placed into routine use. The main problem is that impurities in the derivatization reagent chromatographically interfere with the analysis of phenols.

We are continuing to develop methods of suitable sensitivity and discrimination to provide reliable quantitative results. The methods are being applied to determining the comparative composition of new products and the influence of smoking parameters on smoke composition. *(A. R. Marshall, G. M. Henderson, S. H. Harmon, J. E. Caton, W. H. Griest, R. A. Jenkins, C. E. Higgins)*

Recovery and Quantitation of Organics on Respirable Particles

We have developed more efficient methodology for the extraction, fractionation, and quantitation of particulate-phase organics. The methods involve ultrasonic extraction and HPLC as an alternate to the traditional acid/base fractionation (11) of Soxhlet extracts.

The organics are recovered from the filter pad or bulk particulate sample by ultrasonication with benzene in a water-jacketed sintered-glass funnel. Three extractions, each with 100 ml of benzene, yield quantitative recovery of benzo(*a*)pyrene (BaP) from air particulates, as indicated by liquid scintillation counting of a carbon-14-labeled BaP tracer added to the pad before extraction. More polar solvents (e.g., azeotropic benzene/methanol) are currently being tested for their extraction efficiency for more polar organics, such as carboxylic acids.

After concentrating the extracts to 0.1–0.5 ml, direct GC analysis allows a survey of the major chromatographable organics, such as the paraffins and phthalates. Derivatization of the crude extracts at this point may be useful in GC determination of major polar constituents, such as carboxylic acids or phenols.

Identification and quantitation of specific chemical subclasses is facilitated by fractionation of the particulate extracts using semipreparative-scale HPLC with a bonded cyano/amino silane column. Using hexane as the first solvent, two separate fractions corresponding to alkanes and PAHs (plus some phthalates) are eluted. Analysis of the alkanes is conveniently accomplished by GC with a capillary column, and "clean" profiles are readily generated. The PAH fraction is analyzed by either capillary column GC, or if the PAH concentrations are too low for GC analysis, reversed-phase HPLC using a DuPont Zorbax® octadecyl silane column and fluorescence detection (λ_{ex} = 360 nm, λ_{em} = 425 nm). The latter provides a very sensitive analysis, but it is selective for only a few PAHs, such as benzopyrene and benzofluoranthene isomers. In contrast, the GC method allows a more comprehensive but less sensitive analysis of PAHs.

Using increasing concentrations of methylene chloride in the hexane, increasingly polar chemical class fractions of particulate organics are obtained from the semipreparative normal phase HPLC separation. The 50/50 (v/v) methylene chloride/hexane fraction contains nitrogen heterocyclics and the remainder of the phthalates, and it is readily analyzed by glass capillary column GC. The remaining particulate organic fractions are eluted from the semipreparative HPLC column with 90/10 methylene chloride/hexane and then 80/10/10 isopropanol/methylene chloride/hexane. The former fraction is expected to contain polar organics such as phenols, and the latter, even more polar and possibly macromolecular compounds. These two classes of constituents are not readily analyzed by GC and analytical HPLC is more appropriate.

We find that this combination of HPLC and GC has a wide applicability to the determination of particulate phase organics. The major organics on airborne particles collected near a coal gasifier were found to be *n*-paraffins (from C_{10} to at least C_{36}, each at 0.4–40 ng/m^3 of air) and phthalates (usually butylbenzyl- and bis[2-ethyl hexyl]phthalates at as much as 120 ng/m^3) (12). The *n*-paraffins also are major constituents of the extracts of raw and retorted shale. We have measured them at levels of 3-130 μg/g in the former and 1-30 μg/g in the latter. The major organics from coal fly ash also are dominated by the *n*-paraffins at much lower levels (1 to 800 ng/g in various fly ash samples), but they are more complex and variable in overall composition (13).

The polycyclic aromatic hydrocarbons (PAHs) in ambient air near a coal gasifier are found to be the three- through six-ring parent PAHs (∿0.05-3 ng/m^3); only a few simply alkylated derivatives are present. For coal fly ash, the PAH concentrations are much lower (e.g., ∿1 ng/g in some samples). The high sensitivity of HPLC with fluorescence detection allows the sample to be kept to a manageable size (∿25 g).

Of the more polar constituents, only the fraction containing *n*-heterocyclics has been examined in some detail. An air particulate sample collected downwind of a coal gasifier was enriched (13) in heavily alkylated (C_7-C_{13}) pyridines and alkylated (C_3-C_8) quinolines. The concentrations appear to be at least equal to those of the PAHs (to 3 ng/m^3).

Generally, summation of the levels of these known classes of organics in air particles or fly ash does not account for all the organic carbon present. The final fraction from the semipreparative HPLC apparently consists of "intractables," which comprise a considerable percentage of the particulate organics, but which are relatively undefined as to composition. Research next year will focus on the analytical chemistry of these compounds, particularly those originating in both airborne particles and coal fly ash. *(W. H. Griest, J. E. Caton, R. R. Reagan, J. S. Wike)*

Synfuels Research Sample Management

Research (14) into the potential health and environmental effects of synfuels technologies is supported through the research sample supply and information transfer services of our Fossil Fuels Research Materials Facility. Materials suitable for methods development, comparisons of synfuels versus petroleum, and for informal interlaboratory comparison are made available to qualified researchers. The core aspect of this service is research sample management.

Our repository contains approximately 220 different types of samples. Records must be kept of the current inventory and status of each sample. We have now implemented a computerized system for improved management of such records. The system makes use of the Laboratory's DEC-10 computer and is accessible on the Bio/Organic Analysis Section Lanier word processor and on a Tektronix terminal. The current inventory and all sample transactions to date have been entered into the system and include data on the source, "history," sample number, description, location, and amount of each sample, in addition to sample transaction data on requestor, sample name/number, amount, study, and date shipped. Now, as each new sample transaction is entered into the system and recorded, the inventory for that sample is automatically adjusted to show the new, correct amount. The system also has provisions for providing printouts of the inventory and sample transactions of any desired sample or set of samples. Similarly, printouts can be made of all samples received by a particular investigator. This facile access to current, updated inventory and transactions information has allowed rapid response to requests from the sample suppliers for status reports.

A similar arrangement with an existing laboratory data management system has been made for keeping records of all data reports received from the study of repository materials. Records are kept of the investigator, his address, report title and full citation, keywords for the study, and the repository *samples considered* in the report. Similarly to the inventory/transaction system, computer searches can be made by sample, investigator, or study keyword. The facility is able to issue completely computerized status records to the sample suppliers and funding agencies, showing inventory/sample transaction/data reports received.

Additional information transfer was achieved through a symposium, "Health Effects Investigation of Oil Shale Development," which was held in Gatlinburg, Tennessee, last June. The investigators, sample suppliers, and funding agencies participating in the study of a special sample suite exchanged findings and discussed results. Proceedings (15) of the symposium were published.

Other important aspects of sample management are studies of sample aliquot homogeneity and periodic measurement of sample stability. High-priority samples (those undergoing widespread or detailed study) such as the crude and refined shale oil samples from the Paraho/SOHIO/U. S. Navy suite and the Comparative Research Materials (CRMs) are given special attention. The tests (not all are being applied to each sample) include physical measurements of viscosity; density; pour point; flash point; simulated distillation and heating value; and chemical measurements including ultimate analysis (percent C, H, N, S, and O), direct GC profile, an NAA scan of the elemental composition, and an FTIR spectrum. Specific chemical constituents to be measured include benzo(*a*)pyrene, phenol and the cresols, and α/β-naphthylamines. Headspace volatiles and chemical class distribution also are being determined. These tests were designed to provide extensive characterization of the samples and to allow detection of changes that might accompany degradation, evaporative loss, or contamination during storage.

Thus far, the crude and refined shale oil suite has undergone a stability characterization at one year of storage (16). Of the small-scale sample aliquots stored to meet immediate distribution requests, only the viscosity appears to have increased and by a small amount (10-30%). These samples are kept under an argon blanket in borosilicate glassware, at -30°C in the dark. Other aliquots are being stored under different conditions (e.g., container material and temperature) to test the effects of such storage variables upon apparent stability. After one year, few differences have been detected. The knowledge gained from the stability characterization of these materials helps to indicate the optimum storage conditions for other important sample suites to be obtained in the future. It also will determine whether it is possible to carry out long-term bioassays requiring repeated use of a given sample for a year or more. *(L. B. Yeatts, Jr., W. H. Griest, P. A. Tilson (17))*

The Isolation of Polycyclic Aromatic Hydrocarbons from Aqueous Samples

The general methodology for analyzing aqueous samples for polycyclic aromatic hydrocarbons (PAHs) may be divided into three steps: (1) isolation of the components of interest from the aqueous media, (2) concentration of the isolated sample into the appropriate solvent, and (3) determination of the PAHs of interest in the concentrate. The isolation step usually gives rise to the most problems. Therefore, eight different methods for the isolation of PAHs from aqueous media were compared and evaluated. These included three extraction methods, two methods employing polystyrene adsorbent resins and three different approaches involving C_{18}-silica materials commonly used in reversed-phase liquid chromatography. The extraction methods were applied to synthetic water samples to which known amounts of 16 different PAHs (EPA Priority Pollutants) were added and also to industrial waste water samples received as part of an ASTM round robin analysis concerned with the determination of PAHs in water. The recoveries for each of the PAH Priority Pollutants varied depending on the extraction method but usually ranged between the recoveries shown for ^{14}C-naphthalene and ^{14}C-benzo(*a*)pyrene shown in Table 4.1. This table also incorporates a brief description of the isolation methods that have been described in greater detail in other publications (18,19).

Methods involving extraction (Nos. 1, 2, and 3) were judged superior with Method No. 1 (Table 4.1) generally being preferred because it combines good recoveries with ease of sample manipulation and short analysis time. The resin methods (Nos. 4 and 5) and reversed-phase methods (Nos. 6, 7, and 8) are generally inferior. The reversed-phase methods involving isolation on a guard column (Nos. 7 and 8) may present a convenient approach to quick, relative comparisons of PAHs in water because the concentration step has been eliminated and PAHs isolated onto the reversed-phase guard column can be directly analyzed by HPLC. *(J. E. Caton, Z. K. Barnes (20), H. Kubota, W. H. Griest, M. P. Maskarinec)*

ISOLATION AND IDENTIFICATION

Ammonia Chemical Ionization Mass Spectrometry (CIMS) for the Direct Characterization of Amines

Previous work has shown that the acetone subfraction of the ether-soluble base fraction of several crude fossil fuels possesses very high bacterial mutagenic activity (21,22) Analysis of these subfractions has shown that they are composed principally of primary

Table 4.1. Summary of different methods for isolation of PAHs from aqueous samples

		Percentage recovery[a]	
No.	Description of method	^{14}C-B*a*P[b]	^{14}C-Nap[c]
1	1.0 ml of water extracted three times by vigorous stirring for 10 min with 50 ml of CH_2Cl_2 in 2-l separatory funnel.[d]	96	73
2	3.8 l of water doubly extracted with 100 ml of CH_2Cl_2 by stirring for 24 h in a 4-l Erlenmeyer flask.[d]	91	87
3	0.5 l of water at adjusted pH and fixed ionic strength extracted five times with 100 ml of either CH_2Cl_2 or cyclohexane.[d]	100	100
4	Water drained through glass column (30-cm × 1.7-cm ID) packed with XAD-2. PAHs recovered from XAD-2 in 100 ml tetrahydrofuran (THF) followed by 125 ml ether or by sequential elution with 50 ml methanol, 100 ml THF, 150 ml ether, and 30 ml CH_2Cl_2.	83	ND
5	Water drained through a prepacked XAD-2 column. PAHs backwashed from column with two 10-ml portions of methanol and three 10-ml portions of CH_2Cl_2.[d]	89	50
6	Water drained through Sep-Pak® C_{18} cartridge PAHs recovered in two 10-ml methanol washes and three 10-ml CH_2Cl_2 washes.[d]	81	ND
7	Water sample was pumped through a Rheodyne C_{18} cartridge. Cartridge plumbed into reversed-phase analytical HPLC system as a guard column with PAHs on cartridge being eluted directly onto the analytical column.	43	ND
8	Method same as No. 7 except that a 5-cm × 2-mm ID column packed with Whatman CO:Pell ODS was substituted for the C_{18} cartridge.		

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[a] Percentage recovery indicates the fraction of added activity available at the final quantitating step in the analysis procedure. ND indicates that no recovery determination was made.

[b] ^{14}C-benzo(*a*)pyrene.

[c] ^{14}C-naphthalene.

[d] Samples were concentrated under dry flowing nitrogen at reduced temperature and pressure.

aromatic amines (PAAs) and azaarenes. The electron impact ionization (EI) mass spectra of a PAA and an azaarene that have the same mass are virtually identical because both exhibit strong parent ions at the same mass-to-charge ratio with little additional fragmentation. Because of this, the selectivity of ammonia chemical ionization has been adapted and developed for the direct mass spectral characterization of nitrogen-containing compounds.

The ammonia chemical ionization (NH_3 CI) of the nitrogen-containing compounds is accomplished by reaction with ammonium ions (NH_4^+) formed in the ion source at 0.1–0.2 torr. That is,

$$R_{3-n}NH \xrightarrow{NH_4^+} [R_{3-n}NH_{n+1}]^+$$

where n may be zero, one, or two, corresponding to a tertiary, secondary, or primary amine, respectively (23). If ammonia-d_3 (ND_3) is used as the ionization reagent, not only is the amine ionized by transfer of a deuterium ion, but hydrogen atoms on the nitrogen atom exchange with the deuterium atoms of the ammonia as well:

$$R_{3-n}NH_n \xrightarrow{ND_4^+} [R_{3-n}ND_{n+1}]^+$$

Thus, the resulting deuterated ion exhibits a change in mass from the NH_3 CI spectrum of one, two, or three mass units, indicating that the compound is a tertiary, secondary, or primary amine, respectively. An additional feature of NH_3/ND_3 CIMS is that only the protonated (deuterated) species is observed in the mass resulting spectrum, with no interference from fragmentation.

Previous applications of this technique have been limited to aliphatic amines (23). Experiments using amine-substituted polycyclic aromatic hydrocarbons demonstrated that NH_3/ND_3 CI could be used to characterize these aromatic amines also. Azaarenes, with the nitrogen within the aromatic ring, were found to ionize as well, yielding a change of one mass unit upon going from NH_3 to ND_3. Studies with aminesubstituted azaarenes showed that only the amine group, which is more basic than the ring nitrogen, is ionized. Diamino-substituted aromatic compounds were found to ionize at only one of the amine groups (presumably the more basic site). However, hydrogen atoms attached to the nonionized amine group also exchange with deuterium atoms of the ND_3, allowing characterization of both amine groups.

Ammonia chemical ionization has been successfully applied to the characterization of acetone subfractions of five fossil fuels (24). These subfractions were found to contain primarily PAAs and azaarenes, but a number of secondary amine and secondary amine-substituted azaarenes (i.e., two nitrogen atoms per molecule) were detected in some of the subfractions. Ammonia chemical ionization has also been used in the characterization of nitrogen-containing compounds in the neutral fractions of fossil fuels (25) and in the characterization of a cricket teratogen (described elsewhere in this report).

This technique has proven to be useful in the characterizations of nitrogen-containing compounds, which are difficult to distinguish using other methods. Only compounds more basic than NH_4^+ are ionized; thus, most non-nitrogen-containing compounds, such as alkanes and PAHs, are not observed in the resulting mass chromatogram. This has been shown to be useful in the analysis of nitrogen-containing compounds in complex mixtures without extensive sample preparation. Conjugated aromatic ketones, such as benzanthrone, are the only non-nitrogen-containing compounds that have been found to be ionized by NH_4^+. However, these ketones can usually be distinguished from amines and azaarenes by molecular weight.

One limitation of the technique is the ambiguity in differentiating tertiary aromatic amines and azaarenes. However, in the analysis of synthetic fuels, it has previously been shown (26) that these materials contain little if any tertiary aromatic amines.

Work is continuing in the further development of ammonia chemical ionization mass spectrometry as an analytical tool. *(M. V. Buchanan)*

Identification of Neutral Aromatic-Polar Compounds in Synfuels

The neutral components of coal- and shale-derived petroleum substitutes are thought to contain important carcinogens and mutagens. Sequential Sephadex LH-20 and silicic acid chromatography was found to be an effective means of separating neutral fractions into aliphatics, aromatic hydrocarbons, neutral azaarenes, and neutral aromatic polar constituents. Ames bioassays of the neutral subfractions of all investigated petroleum substitutes have indicated that greater mutagenicities are exhibited by the neutral aromatic polar constituents than by the aromatic hydrocarbons or neutral azaarenes. A notable bioassay result is a decrease in activity with subfractionation; that is, summed activities of subfractions do not equal those of the unfractionated neutral fraction. This suggests either the loss of active components in the subfractionation scheme or a rather important synergism among neutral fraction components.

The reliability of our fractionation procedure was first examined (27) by analyzing each fraction produced from an H-Coal sample. The aliphatic fraction was found to consist of the usual homologous series of straight chain hydrocarbons, ranging from C_{12} to C_{34}, as well as alkyl-substituted dicyclohexanes and saturated perhydrofluorenes, perhydroanthracenes/phenanthrenes, and perhydrofluoranthenes/pyrenes. The mass spectral analysis of gas chromatographable constituents of the polyaromatic fraction showed that this fraction contains aromatic constituents of from two to six rings in size. This fraction is free of saturated compounds, heteroatom-containing, and polar-substituted polycyclic aromatics according to electron impact mass spectrometry. Electron impact and ammonia chemical ionization mass spectrometric analyses of the neutral azaarene subfraction indicate that virtually all chromatographable constituents contain the indole-type secondary amine functionality. Infrared absorption bands at 3410 cm^{-1} confirm the N-H functionality. The aromatic polar subfraction contains primarily oxygenated compounds. These were mostly hydroxyl-substituted or carbonyl-containing polycyclic aromatic compounds. There were some alkyl-substituted primary aromatic amines and azaarenes as well.

Some of the compounds in the neutral aromatic polar fractions of five fossil fuels (three coal oils, one shale oil, and one petroleum) have been identified using a variety of spectroscopic techniques, including both electron impact and chemical ionization GC/MS, and infrared spectroscopy. The three coal oils contain one- to four-ring aromatic hydroxy compounds, whereas the shale and petroleum fractions contain compounds with only one or two aromatic rings. Nitrogen containing compounds, including primary aromatic amines and/or basic azaarenes, are detected in all five fractions by ammonia chemical ionization mass spectrometry. The petroleum fraction contains only substituted anilines and no basic azaarenes. The other four fractions contain small amounts of two- to three-ring primary aromatic amines and two- to four-ring basic azaarenes. However, two of the coal fractions contain >10% azapyrenes. These same two fractions also contain substituted benzanthrones and benzopyrene-ones. *(C.-h. Ho, M. R. Guerin, B. R. Clark, M. V. Buchanan)*

Synthesis of Compounds for Chemical and Biological Analysis

Problems frequently arise in determining the structural detail of a compound or class of compounds isolated from complex organic mixtures. Structural identification is based on measurements of chemical and physical properties. While much can be learned from *ab initio* interpretation of data, subtle structural differences require a reference compound for unequivocal identification. In the complex organic mixtures we frequently deal with, few compounds of any given class are commercially available. Those compounds that are available are mostly low molecular weight, unsubstituted or simply substituted, and poorly representative of real samples, which are usually highly substituted, higher in molecular weight, and often multifunctional. For this reason and because of a basic interest in structure-biological activity relationships, discretionary model compound synthesis has become a part of chemical characterization and bioassay support activities.

Compounds having particularly significant relevance because of their high biological activity and abundance in fossil-derived crude oils are the primary aromatic amines. Isolates of primary aromatic amines are crude and would contain secondary and some tertiary amines if they were present in the original sample. Some amines of the latter two classes were synthesized to determine their biological activites and, hence, their possible importance in aromatic amine isolates. Two secondary amines (N-methyl-2-aminofluorene, methyl-1-aminopyrene) and two tertiary amines (N,N-dimethyl-2-aminofluorene, N,N-dimethyl-1-aminopyrene) were synthesized. Synthesis followed the route of methyl addition to the primary amines by reaction with methyl iodide. Purities of the products were determined using thin layer chromatography (TLC), GC, and MS. This procedure usually produced a mixture of secondary and tertiary amines.

Ames tests of the pure compounds proved important. Results of the 2-aminofluorene (35,000 rev/mg) primary amine exhibited about the same activity as the secondary [N-methyl-2-aminofluorene (30,000 rev/mg)] and tertiary [N,N-dimethyl-2-aminofluorene (35,000 rev/mg)] amines. The same trend was observed for the aminopyrene series. It is therefore essential that analytical chemical methods be available to distinguish the amines since Ames testing does not discriminate between them.

Other compound types have been synthesized to support various aspects of characterization work. Some of these are nitro-substituted polycyclic aromatic hydrocarbons, long-chain alkyl substituted pyridines, and N-heterocyclic homologues of benzo(*a*)pyrene. In addition, monooctadecyl phosphoric acid was synthesized for making the zirconium salt that is to be used as an HPLC reversed-phase column packing. *(C.-h. Ho, B. R. Clark, B. D. Barkenbus)*

Isolation and Identification of a Cricket Teratogen

B. T. Walton of the Environmental Sciences Division has observed gross abnormalities in crickets [*Acheta domesticus (L.)*] resulting from eggs that are incubated in sand treated with an aqueous solution of impurities found in a commercial acridine sample. We have been assisting in identification of the teratogenic compound(s) in the acridine sample and have also extended this work to study the possible presence of similar teratogens in synthetic fuels.

Impurities in the commercial sample of acridine represented less than two percent of the original material. To isolate enough of the teratogenic material for spectroscopic identification, approximately 25 g of the impure acridine was fractionated using a Waters LC-500 preparative-scale high-performance liquid chromatograph. The acridine was eluted first using 23 l of benzene. Then the solvent was switched, first to acetonitrile, then to methanol, to elute the remaining components. Eight cuts were taken in total and each of the eight fractions was tested by B. T. Walton for a positive response from the cricket eggs. The first cut proved to be the only active fraction. Thin layer chromatography (0.25-mm-thick silica gel G plates, eluted with 90:5:5 chloroform/methanol/acetic acid) showed that fraction 1 contained one major compound and about nine other minor constituents. The major compound (R_f = 0.74) was shown to be the active teratogen. When analyzed by ammonia chemical ionization GC/MS, this compound was found to be an azaarene with a molecular weight of 179. Thus, it was thought to be one of the seven isomers of acridine.

Fraction 1 was separated further to isolate the active compound for further spectroscopic analysis using a semipreparative silica HPLC column eluted with a mixture of ethylacetate in methylene chloride. The largest peak was collected, and its ^{13}C NMR spectrum was studied as detailed in a following section. Thus, it was deduced that the isolated compound was 5,6-benzoquinoline. This was verified using a commercial sample of this compound. At the present time, this isolated material is being tested on cricket embryos to check if it is indeed responsible for the teratogenic activity.

A series of three whole oils and their subfractions have also been tested using cricket embryos. These three oils included coal-, shale-, and petroleum-derived liquids. Of the three whole oils, only the coal-derived liquid produced abnormal crickets. Neither the whole petroleum liquid nor any of its seven fractions were active. The whole shale oil was inactive, as were six of its seven fractions. However, the ether-soluble base fraction of the shale oil was active. Likewise, only the ether-soluble base fraction of the coal liquid was found to be active; it was separated further into three subfractions. Of these three subfractions, only the acetone cut was active. This cut, which contains principally primary aromatic amines and azaarenes, has previously been found to exhibit significant bacterial mutagenic activity. Work is continuing in the assessment of synthetic fuels using cricket embryos. *(M. V. Buchanan, A. R. Jones)*

Preparative-Scale Purification and Isolation Methods

Many projects and outside work requests require preparative-scale amounts of substances for a variety of studies. Typical requirements are the separation of trace impurities from "pure" substances; the isolation of a class of compounds for biological and chemical characterization; the fractionation of complex mixtures; and the isolation and concentration of trace substances from gases, waters, biological fluids, and solid particles.

A procedure has been developed for routine fractionation of complex organic mixtures for Ames testing with the intention of finding biologically active components (28). The first steps after a vacuum devolatilization of a 5-g sample are continuous extractions of an ether solution of the devolatilized sample first with hydrochloric acid and then with sodium hydroxide. The bases and acids are recovered by back-extraction into ether from the hydrochloric acid and sodium hydroxide phases, after pH adjustments to 11 and 1 respectively. Neutral components remain in the starting ether solution, are concentrated by evaporation of the ether, and are placed on a Sephadex LH-20 column (5 cm × 1 m). Elution of the neutral components with isopropanol yields four fractions: aliphatics, mono- and di-aromatics, polyaromatics, and a residue. These are defined by elution volumes obtained with ^{14}C-labeled hexadecane, toluene and phenanthrene, used to "calibrate" the column before each separation. A large data base of fractional weight percentages and specific Ames test activities has been built from the application of this procedure to a host of petroleum substitutes and petroleums (28).

Other preparative-scale methods are used less frequently, but add a good deal of breadth to overall capabilities. The acquisition of a Waters LC-500 liquid chromatograph has been useful in performing polar/nonpolar and aliphatic/aromatic separations rapidly with large samples (tens of grams). Also, this instrument is tailored to the separation of impurities into a concentrate suitable for chemical characterization and/or bioassay studies. A teratogenic impurity was separated from a 98.5% pure commercial acridine (reported elsewhere in this section).

Methods for isolation of specific classes of compounds have been developed. Basic fractions are now separated routinely from fossil-derived materials using a two-column chromatographic approach (29). An ether-soluble base isolate (from the "routine fractionation procedure" above) is eluted on basic alumina with benzene, followed by ethanol. The ethanol eluate is further separated on a Sephadex LH-20 column eluted with isopropanol, followed by acetone. It is this acetone fraction that has received much attention because of its extremely high mutagenic activity. The benzene fraction contains most of the azaarenes in the basic fraction.

Neutral fractions are being separated rather routinely to give desired aliphatic, aromatic, neutral-azaarene, and neutral polar fractions (20). This procedure employs a two-column elution on Sephadex LH-20/isopropanol (to separate aliphatics) followed by elution on silicic acid with a benzene/hexane step gradient to give the latter three fractions.

Other purification/isolation methods under continuing development include the removal of organics from aqueous samples (waters, urine, and leachates), the concentration of organics in gas streams on various adsorbants, and the removal and concentration of organics from solid surfaces.

Another category of materials that has required preparative-scale isolation of major components, as well as concentration of impurities, is that of colored dye mixes used in military signal smokes. A set of four smoke mixes was provided by the U.S. Department of Defense. These were red, violet, yellow, and green mixtures, and were composed of anthrone- and anthraquinone-derived dyes. Vacuum sublimation, differential solubility, Soxhlet extraction, column and thin layer chromatography, and combinations of these techniques were used for the separations. The red smoke mix was composed only of 1-methylaminoanthraquinone (MAA) as the colored constituent, but also contained about 20% of a black insoluble, nonvolatile material. This mixture was separated into a fraction enriched in the more volatile impurities, a volatile purified MAA fraction and a nonvolatile fraction by vacuum sublimation. The violet smoke mix was composed of MAA and 1,4-diamino-2,3-dihydroanthraquinone (DDA). These two compounds were separated relatively easily by differential solubility because the MAA is about 70-fold more soluble in chloroform than DDA. A complicating factor in this mixture is the ease with which DDA is oxidized to 1,4-diaminoanthraquinone (DAA), which is substantially more soluble than the DDA. However, DAA could be separated from MAA and DDA by preparative-scale thin layer chromatography on silica layers. The yellow smoke mix is composed of benzanthrone (BZA) and dibenzochrysenedione (DBC). The DBC is insoluble and nonvolatile compared to BZA. Both vacuum sublimation and differential solubility techniques were used with this mixture because it was discovered that a soluble, nonvolatile impurity was present in the original DBC, and this material was concentrated into a separate fraction. The green smoke mix contained 1,4-di-*p*-toluidinoanthraquinone, as well as BZA and DBC in a 70:20:10 ratio. The PTA and BZA have approximately the same solubility in chloroform, and they volatilize together under the conditions used for vacuum sublimation. The bulk of the PTA was separated from the other major components as well as the impurities by column chromatography on basic alumina. In all of the smoke mixes except the red, the chloroform insoluble material was separated by Soxhlet extraction. Fractions prepared by these methods were characterized chemically by a number of analytical techniques and were assayed for their biological activity by the Ames test for mutagenesis. *(B. R. Clark, C.-h. Ho, A. R. Jones, I. B. Rubin)*

Applications of Nuclear Magnetic Resonance Spectrometry

Nuclear magnetic resonance (NMR) has been used in a number of projects since the FX90Q FTNMR was acquired one year ago. A multinuclear probe has been added to the instrument, and now all active nuclei between 6.5 and 90 MHz (at 21.5 KGs) are observable. The major use of the NMR in this first year has been identification of the components of four colored smoke mixes used by the Department of Defense. The smoke mixes were separated into fractions using a combination of differential solubility, vacuum sublimation, and preparative chromatography, as described in the preceding discussion. The dye fractions were first studied by combined gas chromatography/mass spectrometry to establish the compound type.

Both ^{1}H and ^{13}C NMR were used to help elucidate the actual structure of the compounds. All of the compounds studied were derivatives of anthraquinones, and many exhibited low solubility in most common solvents. For this reason, ^{13}C spectra were accumulated for 24 h or even longer. Special pulsing techniques were also used to observe the compound of interest in the presence of a prominent solvent signal. Even so, one compound, dibenzochrysenedione, was sufficiently insoluble that its ^{13}C spectrum was only obtained using a solid sample probe (courtesy of JEOL, Inc.).

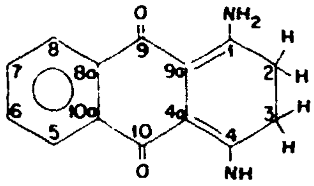
The ^{13}C spectral lines of three of the soluble dye components, 1-methylaminoanthraquinone, 1,4-diamino-2,3-dihydroanthraquinone and 1,4-*p*-toluidinoanthraquinone, have been assigned using proton-decoupled spectra and T_1 measurements. A number of the major impurities present in the dyes have also been identified. For example, a purple compound was isolated in the 1,4-diamino-2-3-dihydroanthraquinone (I in Fig. 4.1), which is yellow-brown. The ^{13}C spectrum of the unknown compound showed that it was similar in structure to I, but the two carbon lines found at 27.5 ppm in I had moved to the aromatic region at 128.6 ppm. The unknown compound was thus identified as 1,4-diaminoanthraquinone (II).

Another project that involved ^{13}C NMR in the structural identification of an unknown was the study of an insect teratogen in a commercial sample of acridine, as discussed earlier. Because both the electron impact and chemical ionization mass spectra of the teratogen were identical to acridine, which has seven isomers, ^{13}C NMR was used to identify the correct isomer. The ^{13}C chemical shift values for acridine are given in Fig. 4.1 (III). Because acridine is symmetric, only seven lines are observed. The unknown compound, however, appeared to be nonsymmetric, with thirteen lines in its ^{13}C spectrum, nine protonated and four nonprotonated. Two of the lines were shifted downfield, suggesting a possible peri-interaction within the molecule, unlike 7,8-benzoquinoline (IV). Two lines, one protonated and one nonprotonated, were shifted downfield, indicating that a nitrogen atom was adjacent to a carbon attached to a hydrogen and a bridging carbon. The molecule was thus identified as 5,6-benzoquinoline (V).

Although most of the work on the instrument involves ^{13}C and ^{1}H spectra, use of the multinuclear probe is increasing. To help distinguish positional isomers of aromatic amines, a number of these compounds have been derivatized with trifluoroacetylimidazole. The ^{1}H and ^{13}C spectra of the underivatized isomeric compounds are very similar. However, ^{19}F spectra of the derivatized amines yield good separation of positional isomers. For example, the spectra of 1- and 2-amino anthracene (which are singlets) are separated by approximately 30 Hz. Further work is continuing in this area of derivatizing compounds to maximize the physical differences among very

ORNL-DWG 80-20722

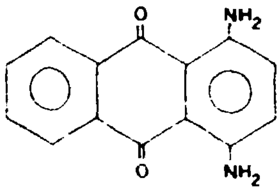
I



1, 4	2, 3	5, 8	6, 7	9, 10
161.9	27.5	125.5	130.1	173.5

10a, 8a	4a, 9a
135.8	100.8

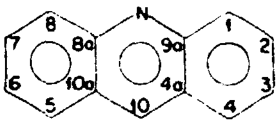
II



1, 4	2, 3	5, 8	6, 7	9, 10
146.8	128.6	125.7	132.1	181.2

10a, 8a	4a, 9a
134.1	107.8

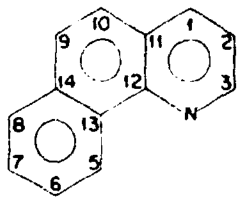
III



1, 8	2, 7	3, 6	4, 5	10
129.7	128.5	125.7	130.5	136.1

8a, 9a	4a, 10a
149.3	126.7

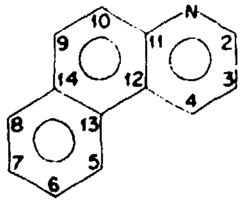
IV



1	2	3	4	5	6	7
135.4	121.5	148.4		127.9[b]	125.1[c]	124.4[c]

8	9	10	11	12	13	14
127.9[b]	126.8	127.6[b]	126.1	146.5	131.5[d]	133.4[d]

V



1	2	3	4	5	6	7
	149.7	121.3	130.8[e]	122.6	127.1[f]	127.3[f]

8	9	10	11	12	13	14
128.2[g]	130.7[e]	128.7[g]	148.3	125.5	129.7[h]	131.7[h]

[a] CHEMICAL SHIFTS ARE QUOTED IN *p.p.m.* FROM INTERNAL Me_4Si

[b] [b] THESE ASSIGNMENTS ARE INTERCHANGEABLE.

Fig. 4.1. Chemical shifts in ^{13}C NMR spectra.[a]

similar materials. *(I. R. Rubin, M. V. Buchanan)*

SAMPLING AND SPECIAL PROJECTS

Field and Inhalation Exposure Sampling

Special emphasis is placed on the collection of samples so as to minimize the chemical and physical impact of the collection process. This is of particular importance where inhalable aerosols are concerned, since the mechanism and magnitude of lung deposition and retention may be dependent on whether the particular constituent is present in the gas or particle phase. Development of analytical methods is usually geared toward compatibility with small, chemically complex samples. Use of monitoring instrumentation is designed to replace the need for frequent chemical sampling.

Our program responsibilities have lead to a number of field sampling expeditions. In the area of solid waste characterization, visits have been made to several municipal and industrial waste disposal sites. Samples of the waste, surrounding soil, groundwater, and leachate have been acquired in order to determine the extent of migration of various organic and inorganic constituents from the waste into the surrounding environment. We make comparisons of the composition of natural leachates with that of those generated in the laboratory from the actual wastes using simulated leaching procedures. Data acquired are used to evaluate the efficacies of these simulation procedures. Generally, we have found that constituent migration is highly site and waste dependent. In all cases, natural leachates have been considerably more dilute than laboratory leachates of the wastes.

We have had a continuing involvement for several years with tobacco smoke inhalation bioassays being sponsored by the National Cancer Institute and the Council for Tobacco Research-USA, Inc. The objective of our research has been to chemically and physically define the inhalation exposure. Laboratories conducting the animal exposures are visited, and smoke samples acquired for chemical analysis at ORNL. Since machine/smoke/animal interactions can alter the apparent chemical composition of the smoke, samples are withdrawn from the exposure systems so as to mimic the animal withdrawal patterns as closely as practical. In the case of the dog exposures, tobacco smoke is withdrawn from the smoking machines through a glass fiber Cambridge filter pad with a large animal respirator. Gaseous constituents are collected in gas sampling bags.

Experiments have indicated that, whereas blood remains an appropriate physiological matrix for measurement of smoke carbon monoxide uptake, 24-h urine samples are more appropriate for measuring the animal's nicotine dose. Data from these experiments have indicated that only slightly more than half of the smoke that would have been estimated from laboratory experiments is actually offered the animals for inhalation. Further, it appears that the animals retain only a third of the smoke particulates offered them. Gaseous components of the smoke may be retained to a greater extent than the particulate phase. Over the course of the bioassay, smoke exposure machine maintenance may contribute as much to relative variability of the exposure as do differences in individual animal inhalation patterns.

The Department of Defense is testing an obscurant aerosol generated by pumping diesel fuel into the exhaust manifold of a tank. In order to assess the chemistry of potential troop exposures, samples of the smoke aerosol emanating from a tank were collected by section staff during the Smoke Week III exercises held at Eglin Air Force Base in August. Because the smoke contains both liquid and gaseous phases, sampling trains designed to collect particulates, volatiles, and "permanent gases" were employed. The samplers consisted of small pumps drawing the smoke through glass fiber pads and cartridges containing Tenax®. Gases were collected in sampling bags. Experiments with laboratory-generated aerosols indicated that particulate collections must be performed at flows of 2 l/min or less. Otherwise, more volatile constituents, originally dissolved in the particulate phase, would be evaporated from the filters during the collection process. Safety hazards on the field sampling grid during actual periods of smoke generation necessitated the remote operation of all of the samplers. Because we expected small chemically complex samples, we used a tiered analytical scheme: samples of aerosol (either laboratory or real-world) are fractionated using analytical-scale high-performance liquid chromatography, followed by high-resolution gas chromatographic analysis.

We find that approximately 70-80% of the aerosol liquid phase is composed of aliphatic hydrocarbons, while most of the remainder consists of alkyl substituted one-, two-, and three-ring aromatic compounds. When comparing the chemistry of the real-world aerosol with that of the aerosol generated in the laboratory, most of the differences between the two can be ascribed to differences in the diesel fuels employed or the sample acquisition conditions.

Instrumentation for remote sampling and monitoring are an important adjunct to on-site experimentation. During the past year, we constructed a set of vapor-phase sampling units for the Environmental Sciences Division, similar to those built for the EPA Kosovo Gasifier study (31). Laminar flow measurement/integration systems, originally constructed to measure sampling rates in a pigeon tobacco smoke inhalation exposure, are now used throughout the group and section. A most recent application is the highly accurate measurement of puff duration on the Phipps and Bird analytical smoking machine. We have recently placed an instrumental exposure system monitor (ESM) at the beagle dog tobacco smoke inhalation bioassay at the Veteran's Administration Hospital (VAH), East Orange, New Jersey. The device, based on the optical particulate sensor used in many of our tobacco smoke studies (32), is designed to measure the smoke output of the exposure systems. Smoke is withdrawn past a sensor with a built-in pump. Instantaneous smoke concentration is integrated to provide a determination of the total particulate matter weight offered the animal. Data are recorded for individual exposure systems by VAH staff and returned to ORNL for evaluation. In place since October, the ESM is already providing a measure of the daily variability in exposure smoke levels, which would otherwise not have been obtained. *(R. A. Jenkins)*

Methodology for the Analysis of Hazardous Solid Wastes

Pollution associated with the disposal of hazardous solid wastes has become a major environmental problem. Analytical chemistry of the solid wastes is confounded by the great diversity of physical matrices encountered. Samples range from aqueous sludges to semisolid oily liquids. Furthermore, the means of entry of the individual pollutants into the environment tends to be either by leaching into groundwater or by volatilization into the atmosphere. The analytical challenge becomes, first, the qualitative and quantitative determination of individual compounds in the solid waste and, second, determination of the compounds in environmental media. Our initial work focused on developing procedures to recover organics from solid wastes.

Historically, the primary method for extracting organics from solids involved Soxhlet extraction with methylene chloride. With solid wastes, significant water content is common. Results obtained using a Soxhlet extractor are difficult to interpret because of channeling of the solvent through the solid, which results in incomplete solvent-sample contact. Therefore, we developed an extraction method that utilizes acid and base equilibrations with the solid, followed by equilibration of the solid with an organic solvent. This methodology results in three fractions for subsequent analysis: acids, bases, and neutrals.

A gravimetric comparison of our method versus Soxhlet extraction was carried out using six solid wastes. The wastes represented a variety of physical states. In every case, the amount and number of organic constituents extracted by the sequential scheme was considerably greater than that extracted by the Soxhlet. The magnitude of the difference ranged from factors of 2 to 50. In every case, the content of the "neutral" fraction alone exceeded the total extracted by the Soxhlet, on the basis of total mass, as well as the quantity of individual constituents. In addition, this system provides a convenient fractionation, which greatly simplifies the final analysis.

A second extraction technique, aqueous/organic co-distillation, has been studied as a means of extracting and analyzing organic materials in solid wastes without contacting the waste with organic solvent. The extraction is conducted as follows: the solid waste is added to a flask containing water, the flask is connected to a dual reflux column with the opposite flask containing an immiscible organic solvent; both flasks are heated, and the vapors co-condense and are returned to their respective vessels.

The solid waste samples described above were extracted using this technique. These extracts were compared with Soxhlet extracts, as well as with laboratory-generated aqueous leachates. In general, the distillation method extracted a higher level of organic material than the aqueous leaching, although chemical compositions were qualitatively similar. The extracts did not contain as much organic matter as did the Soxhlet extract. Thus, the distillation approach is a convenient means of screening solid wastes for potentially leachable materials.

Future studies will involve the comparison of more environmentally relevant extraction techniques with the total content studies in an attempt to determine that constituents are likely to be released into the environment. We are currently pursuing methods for the visualization of constituents which may be volatilized and lost during evaporative concentration. Also under development are techniques for the measurement of the "intractable" or higher molecular weight constituents of the organic extract. These materials are apparently a significant percentage of the total mass and have not been adequately characterized. *(M. P. Maskarinec, R. W. Harvey)*

Determination of Low Molecular Weight Carbonyls in Tobacco Smoke by HPLC

Current procedures for determining gas-phase carbonyl compounds in tobacco smoke involve cryothermal trapping of the sample on the head of a GC column and subsequent elution by programming the column temperature. The method permits analysis of only one brand of cigarettes per day and requires empirical standardization against a reference cigarette for calibration. We have found HPLC separation and determination of the carbonyls as their dinitrophenylhydrazones (DNPH) to be a much improved procedure.

Early studies showed that DNPH derivatives of acetaldehyde, acrolein, propionaldehyde, acetone, and formaldehyde could be easily resolved by reverse-phase HPLC, eluting with 70:30 methanol:water from an n-C_{18} bonded phase column. However, quantitative results were variable and consistently low relative to those obtained using the cryothermal GC method. The difficulty was traced to incomplete and variable trapping of the gas phase carbonyls in the smoke being sampled. Initially, trapping was accomplished by bubbling the diluted gas phase through dinitrophenylhydrazine solution. To improve the collection efficiency, a procedure was devised whereby the gas phase of the smoke was introduced, puff-by-puff, into a partially evacuated flask containing both the aqueous DNPH derivatizing solution and the chloroform extractant. Vigorous agitation of the trapping solution increases contact between the gas and liquid phases. This enhances the rate of conversion of the carbonyls to their DNPH analogs and prevents side reactions with other gas-phase constituents.

Deliveries of acetaldehyde and acrolein, as determined by the new procedure, compare favorably with those measured by cryothermal GC. For example, the HPLC method yielded values for the Kentucky Reference 1R1 cigarette of 1360 and 118 µg per cigarette for acetaldehyde and acrolein, respectively, compared with 1220 and 123 µg by gas chromatography. Relative standard deviations for the HPLC-based method are ±12%. The new procedure offers several advantages. Most important, authentic standard compounds can be employed for calibration. Since the trapping/derivatization and analysis are separate procedures, multiple analyses can be run on the same cigarette. Automated sample injection provides for greater sample throughput. Also, by reevacuating the flask and smoking several cigarettes into the same derivatizing solution, sensitivity can be improved to the point where carbonyl deliveries can be determined for ultra-low "tar" cigarettes. In addition, the method offers the promise of more efficient trapping — and thus more accurate determination — of gas phase carbonyls in other concentrated organic aerosols, including military obscurant smokes and woodburning stove effluents. *(D. L. Manning, M. P. Maskarinec, A. H. Marshall, R. A. Jenkins)*

Advances in High-Resolution Liquid Chromatography

There has been increasing interest in nonvolatile (polar or high molecular weight) compounds because of their apparent contribution to the biological activity of complex mixtures. These properties preclude the use of gas chromatography as an analytical method. Liquid chromatography (LC) offers a better approach to the resolution of these constituents but suffers from two fundamental limitations: lack of total resolving power and lack of universal detection systems. The problem of detection conceivably could be overcome by the use of a mass spectrometer, although there are practical problems. This work has focused on the development of column technology for LC that would result in higher separation power, as well as increased compatibility with mass spectrometric detection.

Several approaches to increased resolution with LC columns exist; each has its advantages and disadvantages. The most straightforward of these is to increase the length of the column. This approach has the advantage that materials and instrumentation are readily available. However, increasing the length of the column extracts a high price in terms of pressure drop, and currently utilized packing techniques must be reconsidered. A study was made to determine the suitability of several packing techniques for producing packed columns greater than 1 m in length. A Teflon® tube was inserted into a stainless steel jacket, and the column was packed under a variety of conditions of flow, solvent, and pressure. The tube was then removed, and the packing uniformity examined. It was found that a slow, upward packing resulted in the highest degree of packing uniformity. This is the opposite of the packing system generally used in analytical LC. The columns produced had fairly high efficiency (approaching twice the mean particle diameter), but very high pressure drops. The total efficiency possible with such columns is limited to $\sim$200,000 theoretical plates. In addition, long analysis times result.

The more promising approach seems to be the use of open-tubular columns. Such columns are now widely used in GC. This technology has the potential to provide very high ($>10^6$ plates) efficiency, without inordinately long analysis times. However, diffusion rates of solutes in liquids are much slower than those in gases. In order to compensate for lower diffusion rate in the liquid mobile phase, the internal diameter of an open tubular LC column must be on the order of 10-50 μm or about one-tenth that of an open tubular GC column. This reduces the loading capacity and means that extra-column dead volume must be minimized. Detection must be highly sensitive, yet must not produce band-broadening. We have developed open tubular columns with porous silica interior surfaces, which have exhibited superior efficiency with moderate loading capacity, in the normal phase (nonpolar organic mobile phase) mode. These columns are produced by deposition of a layer of sodium silicate on the interior surface of capillary tubing. The water is driven off by heating, and the capillary is drawn by a technique analogous to that used in open-tubular GC. The plate heights measured on such columns are approximately four times the column diameter.

The best hope for a "universal" low-volume detector appears to be the electrochemical cell. However, this system requires the use of aqueous mobile phases. These are only compatible with so-called reverse-phase columns. Attempts to produce reverse-phase columns with the porous silica technology were unsuccessful. We have therefore begun to investigate the use of bis(octadecylphospho)-zirconium(IV), a crystalline solid, for producing a reverse-phase surface on the open-tubular columns. This material has been synthesized at ORNL (33). Results to date indicate that the material can be deposited on microparticulate silica and that the resulting HPLC columns have very high capacity. Thus, the material offers an attractive alternative to conventional bonded-phase silicas, as well as potential for the production of reverse-phase open tubular LC columns. *(M. P. Maskarinec)*

An Aerosol Generator for the Production of Concentrated Oil Aerosols

The military has shown a renewed interest in the use of smokes and obscurants for screening purposes in warfare. This, coupled with present day concerns for environmental and occupational exposure safety, has prompted the Army to investigate the risks associated with passive and/or accidental exposures to these smokes. As part of this program, we have undertaken jointly with the Biology Division an investigation of the inhalation toxicology of one of these obscurants. This smoke is produced from diesel-powered tanks from diesel oil. The same oil that powers the tank is pumped into the hot manifold directly after the engine, where it vaporizes. Vapors are carried through the exhaust system and forcibly ejected, along with normal exhaust gases, into the air. The vapors immediately condense to form a dense aerosol used for military screening purposes. It should be emphasized that this smoke is primarily droplets of diesel oil in the micron and submicron size range. The black sooty particles of normal diesel exhausts make up only a minor fraction of it.

This report describes our efforts to develop a generator that adequately simulates this generation process in a laboratory environment and to physically characterize the aerosol produced. The aerosol is produced by an evaporation-condensation process in a generator simulating the manifold of a tank, albeit on a much reduced scale. The generator is constructed from a one-meter-long section of 2.5-cm OD of stainless steel tubing. A one-kilowatt Vycor immersion heater is mounted inside the tubing to simulate the "manifold" heating. A carrier gas to simulate the exhaust gases passes along the heater where it is heated to 600°C. (Presently we are using nitrogen as the carrier gas.) The temperature is controlled by means of a thermocouple controller. Diesel oil is pumped into the manifold, impinges on the end of the heater where it is volatilized, and is carried down the tube. A thermostatically controlled heater surrounding the last two-thirds of the manifold is used to keep the exiting vapors at 350°C to prevent premature condensation. The hot gases and vapors exit countercurrently into the downflowing air supply, where they mix turbulently and cool rapidly to form a dense aerosol. The aerosol concentration is regulated either by varying the injection rate of the diesel oil using low-volume metering pumps or by varying the flow of the condensing air. Typically, aerosol concentrations from less than one milligram per liter to greater than 30 can be produced.

Particle size distributions have been estimated using a cascade impactor operating at one liter per minute flow rate. Direct weighing of the impactor stages was found to be unreliable. Consequently we have used a computer assisted, low-resolution gas chromatographic technique for estimating the amount of oil collected on each stage. The glass stage plates are immersed in carbon disulfide to dissolve the oil. An aliquot is injected into a GC, operating isothermally with a short column so that the entire band is eluted in 2.5 min. The output signal of the GC is amplified and fed into an analog-to-digital converter of a MINC-11 computer. BASIC programs have been written to facilitate analysis of the chromatogram. The spectrum is displayed on a graphic terminal with sufficient resolution to separate the solvent peak from the oil band. The solvent peak is discarded and the contribution from the oil peaks is numerically integrated and quantitated by comparing this area with that from standardized solutions of the same oil type. Particle size distributions were found to be approximately logarithmic normal, with low polydispersity (geometric standard deviations of ∿1.5). Mass median aerodynamic diameters vary considerably, primarily depending on aerosol age and concentration. In the flowing stream immediately after the condensation region, median diameters of 0.4 μm were found. In a static chamber, particle growth to approximately 2 μm was observed in one-half hour. This growth at high-aerosol concentrations, 5 mg/l, is in semiquantitative agreement with that predicted from simple second order theory. *(R. W. Holmberg, J. H. Moneyhun)*

An Inhalation Exposure System for Toxicological Studies of Diesel Oil Aerosols

Existing exposure facilities in the Biology Division have been modified in order to study the toxicological effects of a diesel oil aerosol. Rochester-type exposure chambers of approximately one cubic meter volume presently installed in Building 9211 at Y-12 were chosen for this study. Generators have been installed at the top of each chamber to supply the diesel oil aerosol. The chamber system operates at a constant air flow of 420 liters per minute. The aerosol concentration is regulated using low-volume metering pumps to supply oil to the generators. Oil flow rates from 0.5 to 10 ml per minute produce aerosol concentrations from 1 to 20 mg/l.

It was found that the existing chamber design was not adequate to distribute the aerosol uniformly throughout the exposure volume. The aerosol stream did not follow or spread out in the tapered top section. Rather, it entered as a discrete plume, flowing to the bottom, where the chamber only slowly approached a uniform concentration by turbulence. This of course posed a serious threat of nonuniform exposure of animals. To correct this problem, an assembly consisting of a dispersing cone and two laminarizing screens was designed and installed in the upper section of the chamber. With this addition, aerosol concentrations were found to be uniform throughout the chamber within 10%. These aerosol concentration profiles were monitored both photographically and with an array of six Gayle/ORNL particle sensors mounted in the chamber. With this laminar flow, some particle size growth has been seen in the aerosol as it progresses from top (inlet) to bottom. For example, at 3 mg/l mass median aerodynamic diameters of 0.6 μm were found at the top, growing to 0.9 μm near the bottom.

The exposure facility has been designed to accommodate the lengthy exposures to highly concentrated diesel oil aerosols that may occur during these chronic exposure studies. The spent aerosol — that which passes through the chambers — must be properly disposed of. Under some realistic exposure conditions, over one liter of liquid diesel oil will be consumed in a single chamber during a six-hour exposure. We have found that the absolute filters of the existing facility will plug in a fraction of that time. Further, it would be unacceptable to directly vent these fumes in the crowded laboratory environment. We have found that coalescing filters (Baltson Company) are ideally suited for this use. We have installed somewhat oversized arrays of these filters just after each chamber to keep the pressure drop through them within acceptable bounds. To date they have performed better than anticipated. They remove greater than 99.5% of the aerosol and have yet shown no deterioration with use.

A monitoring/safety system has been designed for use during the chronic exposures. Gayle/ORNL particle sensors will be used as on-line monitors of aerosol concentration. For redundancy, two will be installed in each chamber, and their signals recorded on dual pen recorders to provide a permanent analog record of each exposure. The physical arrangement of the exposure facility, each chamber located in a separate room, makes supervision during lengthy exposures difficult and labor intensive. To alleviate some of this difficulty, signals will be fed to a central station (a nearby office) where panel meters and alarms will be provided for convenient monitoring of all four exposure rooms. Alarm monitors will signal and shut down the exposure system in the event of the following faults: (1) high aerosol concentration (2) low carrier gas manifold pressure, (3) loss of negative pressure in a chamber, or (4) an open door on the chambers. *(J. H. Moneyhun, R. W. Holmberg, T. M. Gayle)*

PROGRAMS

Synfuels Program

Several activities highlight the synfuels component of our work during this period. A major effort continues to be the identification of biologically active constituents in a variety of synfuel-related materials (34). Crude coal-derived oils, a suite of refined and crude shale oil products from the Paraho operation, and a number of natural petroleum crudes are receiving special attention. The importance of aromatic amines (35) has been demonstrated further by examining additional oils and synthesizing and testing model compounds. Recent work has focused on determining the relative importance of primary aromatic amines compared with secondary and tertiary aromatic amines in the basic fraction (36) and on the importance of nitrogen-containing aromatic compounds in the neutral fraction (37). In addition, we have found that the neutral polar materials have a special significance in terms of activity (38). The importance of this class of compounds may exceed that of the alkaline mutagens (39).

The application and development of chemical class fractionation methods also continue as major activities in the synfuels area. Examples of applied studies include the following: (1) a suite of shale oil samples from the Paraho site was fractionated as part of a multilaboratory activity in the characterization (both chemical and biological) of raw and refined products being tested by the Navy for their suitability as fuels; (2) several samples of feed waters and waste waters from coal conversion sites were fractionated in cooperation with the Chemical Technology Division for their evaluation in the Ames test system; (3) a suite of samples from the bench-scale H-Coal Plant was analyzed and biologically characterized in order to provide a preliminary indication of what the materials, produced at the 600 ton/day pilot plant in Catlettsburg, Kentucky, might look like; (4) a variety of samples from the Wilsonville SRC plant were fractionated in support of corrosion studies in the Metals and Ceramics Division; and (5) a variety of other materials were fractionated in this period in order to establish a broader data base of weight yields vs chemical class and biological activity vs chemical class. In seeking answers to the broad question of the validity of biological assays, we maintain a continuing interest in the problems of dosimetry, in particular with the Ames plate assay. Synfuels are composed of a variety of compounds having different physical and chemical properties; therefore, we expect that the uptake of these materials in any bioassay system will be a function of the physical-chemical nature of the sample. Pilot studies have shown that oils are dispensed inhomogeneously in the bioassay media used for Ames testing. In addition to looking at the problems related to the dosimetry involved in bioassays, we are also developing methods by which synfuel-related materials can be simply prepared for bioassay, circumventing the tedious and lengthy fractionation procedures, which have been applied for most of the crude materials we have assayed up to this time.

The repository function remains an important part of our program. We have obtained an additional large number of samples in the past year, and a serious effort has begun to characterize the more important samples with regard to their chemical and physical stabilities. A number of requests, both in-house and out-of-house, have been made for samples, and a significant data base is being accumulated on some of the more important samples. We have been, through the repository function, a focal point in the study of the Paraho suite of oil shale related samples. A symposium was held this past summer to bring together the various investigators who have been studying the Paraho samples, and a proceedings volume is being issued which summarizes the results to date.

A major portion of the work now involves site-specific related assessment research and services. A very large amount of analytical work is to be carried out both in this section and in other sections of the Analytical Chemistry Division. At the present time, ORNL is responsible for carrying out the health and environmental assessment programs at the University of Minnesota-Duluth (UMD) low-Btu gasifier (40) and at the 600 ton/day pilot plant of the H-Coal process in Catlettsburg, Kentucky. The assessment program at the UMD site has proceeded spasmodically over the past two years. Although the periods of operation have been short and intermittent, we have accumulated a large amount of data on the various samples that we have obtained in those past periods. In the next year the focus of effort will be on characterization of the gas phase streams, both the process streams and the flue gases at that facility. Activities in support of the H-Coal pilot plant facility have concentrated on implementing the plan and preparing for a large activity in sampling and analysis. This is expected to be a very significant activity in the coming year. *(B. R. Clark, M. R. Guerin)*

Inhalation Bioassay Chemistry Program

Inhalation bioassay chemistry deals with the generation, monitoring, and characterization of exposure atmospheres for inhalation toxicology. Concepts and methods for determining the actual dosages achieved during exposure are also developed and applied in support of the biological experimentation. Cigarette smoke continues to be studied in our program. Military obscurants have received increasing attention in this reporting period. Discussions are in progress to extend studies to a consideration of fugitive emissions and other inhalation hazards associated with fossil fuels conversion processes. Research is carried out in collaboration with inhalation toxicologists in the ORNL Biology Division and at other institutions. Our responsibility is to ensure that the material tested is relevant to the human situation.

Systems have been constructed and installed to supply inhalation exposure chambers in the ORNL Biology Division with uniform diesel oil aerosols. The systems include aerosol generators, instrumental monitors of aerosol concentration, and spent aerosol collection traps. Three systems are currently in use to acquire baseline biological data. The uniformity of the aerosols throughout the chamber, the physical and chemical properties of the aerosol, and changes in aerosol composition with time are under investigation. The aerosol consists of liquid droplets composed primarily of unchanged diesel oil suspended in the air. Some of the more volatile components, depleted from the particles, are found in the vapor phase. Particle size as determined by cascade impaction is well within the respirable range.

The need to determine the relevance of the test material to actual exposure environments led to two field sampling efforts. The first experiment involved sampling a diesel oil smoke introduced into a wind tunnel from an M-60 battle tank at the Edgewood Arsenal, Aberdeen Proving Ground, Maryland. An additional sample was obtained from a 40-m^3 static exposure chamber filled with smoke from the same tank during the same visit. The second experiment involved ambient air sampling and instrumental monitoring of the diesel oil smoke produced during Army-sponsored field trials of a variety of obscurants at the Eglin Air Force Base, Ft. Walton Beach, Florida. Particle and vapor-phase samples were collected for analysis at both sites. Carbon monoxide and nitrogen oxide concentrations were monitored continuously at the Eglin site. Results were disappointing at both sites because sampling time was very limited. Results suggest, however, that field aerosols are similar to our experimental aerosol in that they consist mostly of unaltered diesel oil. Differences due to the presence of diesel exhaust in the field aerosols could not be addressed because of the small samples available for analysis.

We continue to develop dosimetry methods for both the diesel oil aerosol and tobacco smokes. Decachlorobiphenyl (DCBP) is being studied as a diesel oil particle tracer. The DCBP is added to the oil and transfers to the oil particles upon aerosolization. Methods are being developed to quantitatively determine DCBP in animal tissues and body fluids and to demonstrate its presence in only the particle phase of the aerosol. Dosimetry accompanying the exposure of dogs to cigarette smoke is being addressed through methods for the determination of blood and urine concentrations of nicotine alkaloids, blood levels of carboxyhemoglobin, and concentrations of carbon monoxide in exhaled air. We find that as little as 30% of the smoke offered the animals is actually retained. We also find that the degree of retention depends on the nature of the cigarette smoke; low tar/nicotine smokes appear to be more readily tolerated and therefore are retained to a greater degree than are higher tar/nicotine smokes.

Studies of human dosimetry continued to receive some attention as part of the program. Chromatographic profiles of urinary volatiles from a small group of pooled smoker/nonsmoker urine samples showed no major differences in composition. Methods are currently being developed for a more detailed analysis of urinary components related to smoke exposure. An especially interesting experiment carried out in this period involved the isolation, acid-base-neutral separation, and Ames testing of organics concentrated from pooled smoker/nonsmoker urine samples. Mutagenicity was found only in the basic fraction and only in the samples from smokers. This observation suggests causative agents and analytical methods in need of development to identify the actual mutagens.

Our major accomplishment in bioassay monitoring research is the successful field trial of our instrumental particle monitor for the continuous measurement of cigarette smoke. The instrument, based on back-scattered infrared light, produced excellent approximations of "tar" delivery in laboratory trials and operated reliably at the inhalation exposure testing laboratory.

Our long-standing interaction with Microbiological Associates (MBA) for the Council for Tobacco Research-USA, Inc., is coming to a close. MBA has been asked to terminate its studies. We are assisting in the final phases of the project by preparing operating manuals for the instrumentation we have developed and by quality assuring final experiments.

The inhalation bioassay chemistry program is being strengthened by the addition of personnel and special facilities. Major new initiatives are underway for the Department of the Army in studies of phosphorous smokes. It also appears likely that the inhalation toxicology of synthetic fossil fuels materials will be receiving considerable attention. *(M. R. Guerin, R. W. Holmberg, R. A. Jenkins)*

Environmental Analytical Chemistry Program

Our program addresses analytical research and special services required to determine organic compounds in ambient and occupational environments. Current projects address the analytical chemistry of cigarette smoke, air contaminants, solid wastes, and to a lesser extent, water pollution.

Our cigarette smoke project has changed in response to the changing needs of the Smoking and Health Program (S&HP). The S&HP now requires analytical chemistry in support of its international epidemiology studies, to provide early and reliable results on the characteristics of newly introduced cigarettes, and to address the issue of smoker compensation to ultra-low delivery cigarettes. The ultra-low delivery (< 1 mg tar/cigarette) cigarettes challenge the sensitivity of many standard analytical procedures. Cigarette engineering (mostly physical manipulations) used to produce such products challenge the relevance of current experimental smoking methods.

Epidemiological studies are supported by the semiroutine analysis of commercial cigarettes from throughout the world using standard smoking and analyses methods. Newly introduced cigarettes are characterized by their deliveries of tar, nicotine, carbon monoxide, hydrogen cyanide, oxides of nitrogen, and acrolein using standard methods. Methods for the determination of each of these constituents in the smokes of ultra-low delivery cigarettes are currently being developed as part of this project, as are methods for the chromatographic visualization of total organic matter. Smoker compensation is being investigated by analyzing cigarette smokes produced using a variety of smoking conditions. Major accomplishments in the past year include developing methods for the quantitation of acrolein and other gas-phase carbonyls in low-delivery cigarette smoke (41,42), validating the utility of chemiluminescent determinations of nitrogen oxides in low delivery products (43), developing spectroscopic methods for the estimation of tar deliveries, and finding that subtle changes in smoking conditions can yield greatly increased quantities of toxic constituents per cigarette.

A systematic approach to the determination of organic air contaminants is evolving (44) as a result of several studies. A sampling device (45) designed and constructed here to collect vapor-phase organic pollutants was used by an EPA contractor to sample the air in the vicinity of a foreign commercial coal-gasification plant. Samples of the particulate matter (collected on standard hi-vol filter pads) and vapor-phase organics were forwarded to us for analysis. Our results (44) agreed well with those determined by an EPA contractor and our method allowed improved sensitivity, precision, and resolution. Particulate organic matter is now removed with good recovery, class separated by HPLC, and quantitatively analyzed by high resolution GC or LC. We have also demonstrated (45,46) the ability to carry out replicate thermal desorption analyses of vapor phase constituents and have developed a calibration method allowing high-precision quantitative determinations of selected compounds. The approach is expected to be equally applicable to respirable contaminants in workplace environments.

Research into the characteristics of solid wastes has emphasized the development of methods to recover organics for subsequent analysis. Diffuse reflectance infrared spectroscopy has been found especially useful for characterizing organics adsorbed on fly ash (47). Applying the technique to fly ash from various sources and after various solvent or heat treatments shows the sorptivity of the ash to be directly related to the quantity and kind of carbonaceous matter on the surface. Traditional Soxhlet extraction, ultrasonic-assisted solvent extraction, thermal desorption, and pressure-assisted column extraction have been found suitable for the removal of selected compound types from the ash. Industrial and municipal solid wastes pose special problems because of their diversity and inhomogeneity. Aqueous/organic solvent partition and combined steam distillation-solvent partition have been found effective (48) for removing many of the organic contaminants for further analysis. The relationship of such extraction procedures to both experimental aqueous leachates and to natural leaching is being examined (49).

Problems associated with the analysis of aqueous samples for organic contaminants are also being systematically addressed (50). Studies are driven by the need for trace analyses of natural waters and treated process effluents and the need to recover organics from aqueous leachates of solid wastes. Aqueous-organic partition remains the most generally useful method for recovering organics; recoveries are high and the method is applicable to acidic, alkaline, and neutral contaminants. Concentration onto a small reversed-phase liquid chromatographic packing cartridge is found especially useful for neutral contaminants. The approach is somewhat selective for neutrals and allows direct coupling of the trap to an analytical liquid chromatograph. These methods and polymeric resin adsorption are also being compared for their general effectiveness in preparing concentrates for biological testing.

A general observation of importance is that larger masses of organics are removed from many environmental samples than can be accounted for by the individual constituents ultimately determined. In extreme cases, less than 20% of the material is visualized (51). We suspect that much of this discrepancy is due to the presence of polar, macromolecular, or other compounds insufficiently volatile to be seen upon gas chromatography and not containing chromophores required to be detected using common liquid chromatography methods. Methods for the determination of such compounds are scheduled to receive increased attention in the next reporting period. *(M. R. Guerin, W. H. Griest, M. P. Maskarinec, R. A. Jenkins)*

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5. NUCLEAR AND RADIOCHEMICAL ANALYSIS

J. R. Stokely, Section Head

The Nuclear and Radiochemical Analysis section continues to provide general radioanalytical and activation analysis support for a number of ORNL and Nuclear Division programs. This support ranges from routine analysis of samples to long-term development projects. The section has three groups: Radiochemical and Activation Analysis, Low-Level Radiochemical Analysis, and Special Projects. Over the past three years, the section has emphasized upgrading and diversification of general support analysis capabilities. Much progress has been made in these areas, and the section has evolved into a highly productive unit, which handles most routine radiochemical analyses and short-term development work in an efficient, competent manner. With the basic radioanalytical capabilities well in-hand, present endeavors are to strengthen the long-term research capabilities and programmatic aspects of the section's work.

A continuing activity is to improve the laboratory facilities and instrumentation used by the section. A concerted effort is now underway to automate the handling of routine analysis data generated by various laboratories in the section. Three additional computer terminals have been procured for use with the DEC-10 computer to process and store analytical data. The ND-6620 data acquisition system located in the Radiochemical and Activation Analysis group is being developed into a general data-processing system for most counting instrumentation located at our laboratory at Building 3019. Future plans call for connection of the ND-6620 to the DEC-10 computer for direct transfer of analytical data to the division's Data Management System. In the Low-Level Radiochemical Analysis group, a new sample preparation laboratory and sample receiving room were put into operation this year. These new facilities have increased the overall efficiency and capabilities of the low-level group. Also, an automated, high-sample-capacity liquid scintillation counter was procured for use in the low-level group, replacing an old manually operated unit.

Development activities have continued to support a number of projects within the Laboratory, UCC-ND, and other organizations where our special capabilities or expertise is applicable. We are supplying radioanalytical development support for the DOE-sponsored health and environmental assessment of the coal gasifier plant at the University of Minnesota. This work consists of activation analysis of trace elements and low-level radiochemical analysis of important naturally occurring radionuclides in feed materials, tars, and discharges from the plant. A collaborative project with IBM Corporation is underway to determine ultratrace levels of uranium and thorium in semiconductor components. Sensitivities for these elements have been extended to about 0.01 ng/g by neutron activation analysis at the High Flux Isotope Reactor. Development support for the Consolidated Fuels Recycle Program has resulted in improved methods for analysis of carbon-14 and iodine-129 in dissolved reactor fuel solutions. Interest in analysis of technetium-99 in environmental materials has continued. Methods for analysis of technetium-99 in soils and vegetation have become fully developed and are in routine use; efforts are being made to extend analysis methodology to animal tissues. A project to develop techniques for determination of gamma-emitting radionuclides in small animals is nearing completion. This project is directed at determination of the biological radionuclide assimilation of wild animals living on the Oak Ridge reservation. A new method for electrolytic enrichment of tritium was developed this year. This method extends our sensitivity to the sub-picocurie level and has been used for analysis of well water from Three Mile Island (TMI).

RADIOCHEMICAL AND ACTIVATION ANALYSIS

Sample Analysis Program

The Radiochemical and Activation Analysis group continues to provide support to several Laboratory and Nuclear Division programs in the areas of gamma-ray spectrometry, radiochemical measurements, and neutron activation analysis. Over the past year, the group performed approximately 54,000 analyses on 34,000 samples. Special development studies were also carried out by the group in support of sample analysis efforts. Development studies consisted of gamma-ray spectrometry and radiochemical analyses for the TMI facility, uranium and thorium analyses for IBM Corporation, and multielement neutron activation analysis of coal, ash, and tars from several coal gasification facilities. Over 31,000 neutron activation analyses were performed this year, an increase of 28% over last year.

The National Uranium Resources Evaluation (NURE) program submitted 21,000 sediment samples for the determination of uranium by the delayed neutron counting method. Radioisotope products analyzed by gamma-ray spectrometry this year were ^{33}P, ^{37}Ar, ^{43}K, ^{47}Ca, ^{55}Fe, ^{60}Co, ^{57}Co, ^{60}Co, ^{67}Ga, ^{75}Se, ^{85}Kr, ^{89}Sr, ^{91}Y, ^{95}Zr-Nb, ^{103}Ru, ^{106}Ru, ^{109}Cd, ^{113}Sn, ^{119m}Sn, ^{113}Xe, ^{144}Ce, ^{153}Gd, ^{237}U, ^{237}Pu, ^{244}Cm, and ^{253}Es. In addition, gamma-ray spectrometry was performed on samples of SiC, paper, flux monitors, air filters, charcoal traps, V_3Si, and Oak Ridge Research Reactor (ORR) and TMI reactor waters.

Tritium separations and analyses were performed on TMI reactor water, fuel dissolver solutions, pump parts, creek water, silica gels, and ethylene glycol. In addition, gross alpha, gross beta, gross gamma, and alpha spectrometric analyses were made on these materials. Multielement neutron activation analyses were performed on coal, tars, fly ash, zeolite, flux monitors, soils, sediments, vegetable ash, MgO, GeO_2, SYNROC materials, Pt, and TiC. *(J. P. Emery, L. C. Bate, A. R. Crook, P. P. Dyer, H. A. Parker, L. M. Roseberry, J. W. Wade, L. R. Hall, J. W. Hanna, K. J. Northcutt, and S. H. Prestwood)*

Analytical Methods for the Coal Gasification Program

An effort is underway to determine by neutron activation analysis (NAA) the trace elements in samples of coal distillates obtained from the coal gasification plant of the University of Minnesota at Duluth, Minnesota. The samples being analyzed are tar materials of high viscosity. At temperatures of 200–300°C, the materials have a very small component (a few percent) that is volatile. The materials contain particulates which we suppose may vary in size and amount from sample to sample and which may contain major fractions of the trace elements. Initially, attempts were made to irradiate the materials in polyethylene rabbits in the pneumatic tube facility of the ORR. Irradiations longer than a few seconds were found to be infeasible because the tars attacked the rabbits and tended to escape during irradiation. Some attempts were made to evaporate more volatile components of the tars in an effort to obtain samples that would not become fluid during irradiation and thus prevent attack of the plastic containers. This approach was found to be too time-consuming and was also believed to be undesirable because of the possibility of loss of some trace elements. The method that was finally adopted was to irradiate samples of 50–100 mg in the plastic rabbits for 10 s in the pneumatic tube at the ORR and to irradiate samples of about 2 g in sealed quartz vials for 5 h in the Bulk Shielding Reactor (BSR). The thermal neutron flux in the BSR is about 7×10^{11} neutrons cm^{-2} s^{-1}. Each quartz vial is wrapped with a flux monitor. No significant epithermal flux is present. After samples are removed from their irradiation containers, radionuclides are measured nondestructively by Ge(Li) gamma spectroscopy, and trace element concentrations are determined by absolute NAA.

Irradiations in the quartz vials have proven to be effective for measuring elements that yield radionuclides with half lives of a few hours or more. Thus far, we have allowed decay to take place 6–7 h before attempting to retrieve and open the vials. This time might be reduced to about 1–2 h. No buildup of gas pressure in the vials has been detected. We are presently making replicate measurements with quartz vial irradiations to determine the variability obtained among 2-g samples.

Irradiations of the small samples in plastic rabbits are usually satisfactory, but replicate measurements often yield greatly different trace element concentrations due to the large inhomogenity of the samples. We therefore do not yet have a satisfactory procedure for neutron activation analysis of those trace elements that yield short-lived products. *(P. P. Dyer, L. M. Roseberry, K. J. Northcutt)*

Uranium and Thorium Determinations in Semiconductor Materials

The collaborative effort with the IBM Corporation to determine uranium and thorium in computer memory materials has continued. Nearly 200 samples of aluminum, silicon, and a few other materials have been analyzed. Levels of uranium and thorium in silicon as low as about 0.01 ng/g have been measured. Most analyses have been made on aluminum samples in which the uranium and thorium content lies between 2 and 300 ng/g.

To effect these analyses, we first attempt to determine uranium by delayed neutron counting following irradiations in the pneumatic tube of the ORR in which the thermal neutron flux is nominally 5 × 10^{13} neutrons cm^{-2} s^{-1}. The detection limit is approximately 20 ng/g. An irradiation is then made in the pneumatic tube of the High Flux Isotope Reactor (HFIR) for a period of 10-60 m. After a decay period of 2-10 d, the samples are placed very near a large Ge(Li) detector (20% relative counting efficiency), and a gamma spectrum is acquired for a period of 2-16 h. If the photopeaks of ^{239}Np and ^{233}Pa can be measured, uranium and thorium are determined by absolute neutron activation methods.

Barring interferences from other radionuclides, this method of analysis is extremely sensitive for uranium and thorium. The neutron flux in the HFIR facility is nominally 5 × 10^{14} neutrons cm^{-2} s^{-1}, and photopeak counting efficiencies for source-to-detector distances of a few millimeters are nominally 10% for the 278-keV and 312-keV lines of ^{239}Np and ^{233}Pa. It can thus be easily shown that after 1 h irradiation, 10 d decay, and 15 h counting interval, about 4000 and 15,000 counts would be acquired in the respective photopeaks listed above per nanogram of uranium and thorium. Irradiations are made in graphite rabbits and could, if needed, be extended significantly.

Some of the samples contained trace elements, principally gold and chromium, that interfered with the nondestructive analyses. In addition, the uranium level may be too low to permit its measurement by delayed neutron counting. To analyze these samples, we dissolve them and employ a combination of precipitations and solvent extractions to separate the ^{239}Np and ^{233}Pa to obtain reliable analyses. *(F. F. Dyer, J. F. Emery, K. J. Northcutt)*

An Evaluation of Facilities for Neutron-Capture Prompt Gamma-Ray Analysis at ORNL

An effort is being pursued to evaluate the facilities of ORNL for possible applications in neutron-capture prompt gamma-ray measurements that would extend our capabilities in neutron activation analysis. Definite needs exist in determining light elements such as H, B, C, and N and certain heavier elements such as S, Fe, and Cd to which conventional NAA is either not amenable or only marginally useful. Studies by others (1) indicate that prompt gamma analysis (PGA) is applicable to these elements and has, in addition, other desirable features that complement conventional NAA. Interferences by macroconstituents such as sodium or chlorine on trace components can often be significantly decreased, and certain types of samples such as volatile or large nonhomogeneous specimens can be analyzed that otherwise are difficult to irradiate.

In our present study, we are comparing the possible merits of irradiations in (1) the horizontal beam holes of the ORR and HFIR, (2) facilities that might be installed in the BSR, (3) neutron flight tubes of the Oak Ridge Electron Linear Accelerator and (4) facilities that might be established with a ^{252}Cf neutron source. Neutron flux magnitude (i.e., analytical sensitivities), general availability, and cost of equipment needed are criteria being used in the comparisons. The possibility of selecting neutron energies that would enhance analytical sensitivities of certain elements over others is also being studied. *(J. F. Emery, F. F. Dyer)*

New Programs and System Software for the ND-6620 Data Acquisition System

A new version of the control operating system, Midas Version D, was implemented on the ND-6620 during the past year. The new software has better input-output control and expanded magnetic tape capabilities. The user now has a choice of activity units in the final report by giving the computer a factor to convert microcuries to the desirable unit. The software also enables the user to set up echoes to and from any terminal to suit his needs and terminal capabilities. The system has been set to reassign ADC memory for each detector in the event of a power or system failure.

We have made major strides during the year toward utilizing full power of the ND-6620 as a data acquisition system. A series of programs has been written that accept paper tape output from a Packard model 2405 liquid scintillation counter for processing on the ND-6620. The computer performs all calculations, prints a summary report, and punches tape for direct submission to the Sample Transaction System (STS) on the DEC-10 computer. The programs have greatly reduced user-created errors. Future plans call for links among the Packard 2405, ND-6620, and the DEC-10, which will further simplify the acquisition procedure.

Several Fortran programs have been written to process data from various gross counting systems. The ND-6620 generates a hard-copy report with sample and report numbers for direct submission to the STS. Limits of detection are indicated where appropriate and help in reducing input time to the STS.

Current work includes evaluation of a user-written NAA software package. The package works interactively with the ND software and generates a report with units in parts per million. Preparation of a NAA nuclide library will complete the package. A large volume of samples for multielement analysis is expected from the NURE program, and the new software will greatly simplify the analysis procedure. *(J. W. Wade J. F. Emery)*

Bench Manual Procedures

Several bench-manual procedures have been written to aid technical personnel in the Radiochemical and Activation Analysis group. Procedures for the setup and operation of the gross alpha, beta, and gamma counters aid personnel in error checking for system failure. A procedure for counting and processing a sample on the ND-6620 has been written also. Job streams (command files) enable a user who is unfamiliar with the system to follow the bench-manual procedure with confidence. Procedures have been written for delayed neutron counting and multielement analysis at the ORR. Personnel who use the procedures must be familiar with operation of the pneumatic tube facility and the Fortran program MONFTR, which runs on the PDP-15. Documentation on the operation of any instrument or machine is essential. Verbal instructions are often misconstrued resulting in poor performance and quality assurance problems. These procedures have helped in filling this need. *(J. W. Wade)*

Data Management Program

An immediate need for the simplification of handling customer charges each month produced two computer programs for use on the PDP-10 that are capable of handling data management from beginning to end. MANAGE is a conversational Fortran program that accepts data from the user and outputs the data to a file on the user's disk. The file name is generated when the month and year of the data are given to the computer by the user. The file extension is the abbreviated name of the user's group. The user may obtain listings of the file on the terminal or hard copies on the printer upon command. These listings may contain all of the data pertinent to a customer and his samples or just the charge code, samples, analysis, and hours charged. In the latter case, the listing will contain the combined and totaled charges of a customer according to the charge code. The totaled listings are sorted in numerical order with alphanumerics placed last. These listings are used by Program PCARD to generate punched cards for direct submission to the computer. Future plans call for a routine that will check charge codes against a master ORNL file for validity. If a bad code is found, it can be flagged for correction. MANAGE has an editor to correct and change any invalid entries. *(J. W. Wade, J. F. Emery)*

Improved Methodology for ^{14}C Analysis of Reactor Fuel Solutions

Apparatus has been redesigned to improve the carbon-14 analysis of reactor fuel solutions. The changes include incorporation of smaller hyamine traps, alteration of the method for transfer of $^{14}CO_2$ to the traps, and incremental addition of the carbonate carrier to insure complete $^{14}CO_2$ removal from the sample. Addition of small amounts of carbonate carrier also increases the liquid scintillation counting efficiency by several percent. These improvements in the apparatus and method have doubled the overall counting efficiency for ^{14}C measurement. A bench-manual procedure has been written, and the improved method is in routine use. *(L. C. Bate)*

Stability of Iodine in Acidic Reactor Fuel Solutions

Previous observations with samples containing ^{129}I in nitric acid have suggested that the solutions were not stable and that iodine was being lost from solutions by precipitation or volatilization, leading to low analytical results. A study has been conducted to verify these observations, to establish conditions under which losses are significant and troublesome, and to devise means for stabilizing the solutions.

Stability experiments were performed in neutral and 0.5 to 5 *N* HNO_3 solutions, with iodide concentrations from 1 to 50 μg/ml. Iodine-131 tracer was added to the solutions in order to monitor the iodide concentration over a 10-d period. These experiments showed that losses of iodine from nitric acid solution were rapid (1-3 d) and significant (>70% loss in some cases). No appreciable losses were observed from neutral solutions. Apparently the losses resulted from oxidation of iodide to iodine by nitric acid and either volatilization of iodine from the solution or precipitation of iodine on the walls of the sample container. Similar experiments with iodate, tagged with ^{131}I, showed no instability in all nitric acid solutions tested (0.5-5 *N*).

The valence state of iodine in several samples (6 *N* HNO_3) submitted for ^{129}I analysis was established. The iodide content of these samples average about 33% (range: 16-47%). The remaining iodine was present as iodine or iodate. One basic sample had 92% of the iodine present as iodide.

This study has shown that there definitely are instability problems with nitric acid samples containing iodide. It is recommended that a holding reductant, such as sodium metabisulfate, be added to all nitric acid samples to prevent iodine losses from solution and erroneous analytical results. *(L. C. Bate)*

An Integrity Study of Type 347 Stainless Steel Tubes after a Five-Year Service in the High Flux Nuclear Reactor

The High Flux Isotope Reactor (HFIR) is used by our group for neutron activation analyses. Samples are pneumatically routed in and out of the reactor by means of a type 347 stainless steel tube assembly. The design life for this tube assembly is five years. This life expectancy is based on a calculated 50% loss in ductility due to radiation damage to the stainless steel. The present pneumatic tube has been in service for nearly five years, and its replacement is being considered for the near future. However, the replacement cost is high, and an extension of its service life would be attractive. A tube assembly that had been used for nearly five years was removed several years ago. The portion of the tube that was in the reactor core was subjected to a thermal fluence of approximately 7 × 10^{22} neutrons/cm^2 and a fast fluence of approximately 2 × 10^{21} neutrons/cm^2. The upper portion of the tube assembly was not subjected to any irradiation and therefore provided material from which the as-received properties of the type 347 stainless steel could be determined. A comparison of irradiated and unirradiated sections of the tube assembly was made. This study included tensile, microhardness, and bend tests, which were correlated with microstructures observed with optical and scanning electron microscopy.

The study showed an expected increase in hardness, which was reflected in a loss of ductility in both the tensile and bend tests. The embrittlement of the type 347 stainless steel, however, was less than anticipated. Additional evaluation of the radiation damage is being done by comparing internal structure of irradiated specimens with nonirradiated specimens by transmission electron microscopy. *(R. J. Gray (2), D. A. Canonico (2), L. C. Bate)*

Elemental Analysis of Human Lung Tissues by Neutron Activation Analysis

A comparative study of trace element concentrations in autopsied lung tissue of workers and nonworkers in the rubber industry has been made made. Analyses have been carried out on 124 samples of ashed human lung tissue. These analyses were done following two irradiations of each sample at the neutron activation analysis pneumatic facility at the HFIR. The first irradiation (3 s) permitted identification of short-lived radioisotopes. These samples were permitted to decay before the second irradiation (200 s) was done. Radioactivity measurements were made approximately one and three weeks following the second irradiation. Computer program MONSTR was used to reduce the spectral data to concentration values of the elements measured.

Although 36 trace elements were detectable in the lung tissue, only 30 yielded definite results. Ag, Mo, W, Sm, Eu, and Ni were found in a very limited number of cases.

Statistical analyses of the data are continuing in an attempt to correlate concentrations of the trace elements with factors such as age, sex, race, smoking history, and lung pathology. A paper that summarizes this work is in preparation. *(G. R. Norris (3), L. C. Bate)*

Quality Assurance and Assessments

In the Radiochemistry and Activation Analysis group, quality control samples are provided for gamma- and x-ray spectrometry; liquid scintillation counting; radiochemical separations of ^{3}H, ^{14}C, and ^{129}I; and neutron activation analysis (multielement and uranium determination). In addition, quality assurance assessments were prepared for the pneumatic tubes at the ORR and the HFIR and the gamma-ray spectrometers at Building 3019, ORR, and HFIR.

The Ge(Li) spectrometer systems in the 3019 and ORR laboratories are monitored for efficiency changes at intervals of two to three days. Sources of ^{60}Co and ^{232}U plus daughters are used at the ORR, and ^{133}Ba, ^{94}Nb, and ^{60}Co are used in Building 3019. NBS SRMs ^{94}Nb, ^{207}Bi, and ^{55}Fe were used to recalibrate the x-ray spectrometer in the ORR laboratory. Results showed a slight negative bias, up to 4% for ^{55}Fe. The spectrometer had not been calibrated in the ^{55}Fe energy range (∿6 keV) for five years. This recalibration was timely because of an ORNL increase in production of ^{55}Fe radioisotope products.

Performance of the automatic liquid scintillation counter in Building 3019 is monitored with a set of sealed standards. This set is counted with each tray of samples. Also, approximately once each quarter Instrumentation and Controls Division personnel calibrate the counter by setting the "windows" so that interferences are minimized. These adjustments may change the efficiency slightly for a given window. For quality control of determinations of ^{3}H, ^{14}C, and ^{99}Tc, a large batch of slightly alkaline solution was prepared from standard materials, and many portions were stored in separate bottles. Each month one bottle is analyzed by the usual methods. Precision and accuracy of the results for eleven months have been satisfactory.

Quality control of our multielement analysis by neutron activation is accomplished by periodically analyzing NBS standard reference materials. The ORR lab analyzed approximately 20,000 uranium samples this past year. Besides analyzing our own quality control samples with each series of samples irradiated, NURE program personnel also submitted blind quality control samples with their sediment samples. Each quarter the results are tabulated and distributed to everyone involved. *(S. A. Reynolds, J. W. Wade, J. F. Emery)*

LOW-LEVEL RADIOCHEMICAL ANALYSIS

Radiochemical Analysis for Laboratory Programs

The Low-Level Radiochemical Analysis group (LLRAG) provides radioanalytical support to Laboratory programs concerned with the determination of environmental levels of both man-made and natural radionuclides in a variety of materials.

General descriptions of our participation in the Waste Management Program, the Environmental Impact Statement Program, and plant monitoring programs have been given previously (4). Our involvement in the Waste Management Program was curtailed at the end of FY-1980, and the impact and monitoring programs were reduced in April of this year. Other programs in which we have participated deal largely with the determination of beta- and alpha-emitting radionuclides.

The Formerly Used Sites, Remedial Action Program (FUSRAP), continues to produce samples of unusual interest. One of the latest groups of samples is from an area in North Dakota at which a coal-burning operation has been conducted. The primary purpose of burning of the coal was to recover uranium from the coal ash. Vegetation samples from the area were analyzed for uranium, ^{226}Ra, ^{230}Th, and ^{210}Pb in our laboratory and for traces of arsenic, selenium, copper, and molybdenum by other laboratories in the division. Concentrations of ^{210}Pb ranged from 100 to 2000 Bq kg^{-1}, ^{226}Ra ranged from 20 to 1000 Bq kg^{-1}, and ^{230}Th ranged from 40 to 3000 Bq kg^{-1}. Uranium, molybdenum, selenium, copper, and arsenic ranged in concentrations from a few μg/g to 200 μg/g, with molybdenum being the dominant constituent.

A team of investigators in the Environmental Sciences Division continued a study of radionuclide concentrations in the water, sediment, and biota of the 3513 Retention Pond. Results from analyses of filtered and unfiltered water from the pond indicate that plutonium and americium are associated with particulates larger than 0.2 μm in size, whereas curium is essentially in total solution and is not associated significantly with the particulates. More details of the results of this study are forthcoming in a report entitled, "Comparative Uptake and Distribution of Plutonium, Americium and Curium in an Equilibrium Freshwater Ecosystem."

Investigators studying the use of SYNROC (a synthetic rock material) as a means of immobilizing nuclear waste expanded their list of leaching solutions to include NaCl and fluoride. The presence of these components necessitated chemical separations and alpha spectrometry to determine ^{238}Pu, ^{239}Pu, ^{241}Am, ^{244}Cm, ^{234}U, and ^{238}U. When less complex solutions (water and acids) were analyzed, determinations were made by simply drying a portion of the solution on a plate, counting, and performing alpha spectrometry. Concentrations of these nuclides in the various solutions varied from the detection limits to approximately 14,000 Bq ℓ^{-1}. *(T. G. Scott, G. I. Gleason (5), A. J. Weinberger, P. S. Gouge, C. C. Granger, C. V. Holmes, W. C. Massey, R. A. Teasley)*

Developments in the Low-Level Nuclear Measurements Laboratory

During 1980, sample throughput for gamma-ray analysis was increased to about 200 per month. This was in part due to the establishment of a gross activity screening procedure, which permits more efficient utilization of counting time of the three Ge(Li) spectrometry systems. In addition, sample turnaround time has been improved by use of several TI-59 programs developed for hand data reduction. The option of computer data reduction by the ND-6620 system is utilized on samples exhibiting complex spectra.

Extensive background studies of the Ge(Li) spectrometer systems have led to improved assignment of photopeak counting rates of the natural radionuclide lines. This has made possible the measurement of very low-level samples containing ^{226}Ra, ^{228}Th, and ^{40}K. Comparisons of results obtained by NAA for uranium and thorium have been favorable for samples known to be in secular equilibrium.

Development of a method for predicting the efficiency of a Ge(Li) detector for extended sources was initiated in 1979. Further refinements have been made to improve the method, and on several occasions it was applied to samples contained in other than routine configurations where a calibration exists. This procedure greatly expands this laboratory's capability to cope with a variety of measurement requirements.

A simple, nondestructive method has been devised for the determination of uranium isotopic ratios by Ge(Li) spectrometry. Uranium-235 emits a gamma ray at 186 keV, whereas protactinium-234m, a daughter of ^{238}U, emits a gamma ray at 1001 keV. The relative intensities of these two lines provide a means for estimating the ^{235}U/^{238}U isotopic ratio. On samples containing high concentrations of uranium, it is necessary to apply self-absorption corrections. Even here the method provides an assay within 1-2% of the results obtained by mass spectrometry. *(G. I. Gleason, W. C. Massey)*

Development of Sequential, Low-Level Radiochemical Analysis for Lead, Radium, and Polonium in Coal Gasifier Samples

Analytical evaluation of coal gasifier materials in support of the health and environmental assessment of the University of Minnesota at Duluth (UMD) coal gasifier began in June of this year. Methods for sequential radiochemical analysis of the longer-lived uranium daughters in coals and gasifier wastes are being developed. Half-lives and primary modes of decay for the major daughters of uranium are shown in Table 5.1.

Table 5.1 Half-lives and primary modes of decay for the major uranium daughters

Nuclide	Half-life	Mode of decay
^{226}Ra	1600 y	Alpha
^{210}Pb	22.3 y	Beta (0.06 MeV)
^{210}Bi	5.01 d	Beta (1.2 MeV)
^{210}Po	138.4 d	Alpha

During gasification, uranium and its daughters are fractionated into different physical phases. Activation analysis indicates that uranium is concentrated in the ash, while little, if any, collects in the electrostatic precipitator tar. The fate of the radioactive daughters from gasifier operations will have to be determined to assess their impact upon the public.

Considerable attention has been given to dissolution of the various sample materials and the design of sequential radiochemical separations since we became involved in the program. Large samples are needed to acquire the desired detection limits. Low-temperature ashing for removal of carbon proved to be impractically slow for the chosen sample size. The volatility of polonium precluded the use of high-temperature ashing. Wet acid digestion readily solubilized unashed coal and tar. A method developed by Sill (6) for soils and ores solubilized the highly refractory coal ash and cyclone fines. A sequential separation scheme is currently being tested on spiked coal, ash, and tar. Polonium is extracted into trilaurylamine in xylene, stripped with acid, and plated on silver discs for alpha pulse height analysis. Bismuth is separated from lead and radium on an anion exchange column, eluted, and precipitated as the oxychloride for beta counting. Lead is determined indirectly by evaluating its bismuth daughter. Radium is separated from lead by selective precipitation of radium with barium sulfate from an ammoniacal EDTA solution. The sulfate is dried on a disc and alpha counted.

Polonium analysis of the spiked coal, ash, and tar gave chemical yields of 91%, 74%, and 85%, respectively. Ninety-seven percent of the spiked ^{210}Po was recovered, when corrected for chemical yield. Analysis will begin on the gasifier samples after tests on the spiked materials are complete. *(L. M. Roseberry, T. G. Scott)*

Nuclear Analysis for the Health and Environmental Assessment of Coal Gasification Facilities

Neutron activation analysis and low-level radiochemical methods are being applied to coal and gasification wastes for the measurement of uranium, thorium, lead, radium, polonium, and trace elements.

A number of samples of several different types were received from the gasifier plant at the University of Minnesota (Duluth). Neutron activation analysis work on these samples is described in an earlier section of this report. Development of radiochemical methods for the longer-lived uranium daughters, ^{226}Ra (1600 y), ^{210}Pb (22.3 y), and ^{210}Po (138 d) is near completion. Sample digestion procedures that retain polonium and lead have been adopted. A scheme for the sequential separation of the radionuclides is being tested on spiked samples.

The UMD gasifier is expected to resume operation in early 1981 following repairs to its fire grate. Achievement of a steady-state operating status will permit the final and definitive sampling of the gasifier.

By early 1981, samples should be forthcoming from the H-Coal gasifier process being demonstrated at Catlettsburg, Kentucky. The emphasis in this program will then shift to the analysis of H-Coal wastes for U, Th, Ra, Pb, and Po. *(L. M. Roseberry, P. F. Dyer, T. G. Scott)*

Special Projects in Low-Level Radiochemical Analysis

Many samples that we receive are unusual and require special techniques or the development of procedures for analysis.

Alpha spectrometry has been applied to the measurement of small quantities of thorium and uranium on glass plates from an impactor used for particle-size studies. The limits of detection are about 0.03 μg for ^{232}Th and 0.01 μg for ^{238}U. This technique has advantages over others in that it is nondestructive, isotopic compositions can be given, and daughter radioactivities can be measured if desired. Furthermore, thorium or uranium in the substrate material does not cause serious interference, since their alpha radiations are degraded in energy while those from surface deposits are not.

A project conducted by a team of researchers at Y-12 to study the feasibility of using bacteria to decontaminate uranium mill ponds produces complex samples that require radium analysis. The bacteria remain active in many of the liquid samples and cause a continuous change in the sample properties. Separated bacteria samples are processed prior to our receiving the sample. The processing introduces interfering reagents such as sulfates and EDTA. Treatment with carbonates, used either for a metathesis or as precipitating agents, facilitates analysis of radium in these materials.

Experiments on genetic effects and dosimetry of plutonium in mice are carried out in a collaborative effort by the Mammalian Genetics group of the Biology Division of ORNL and the Biomedical Sciences Division of Argonne National Laboratory. Samples of bedding material containing excretions from mice that have been injected with ^{239}Pu (approximately 10 kBq per mouse) are submitted to the Low-Level Radiochemistry Laboratories for ^{239}Pu analysis. Since the samples are bulky and poorly mixed, it is necessary to process the total material in order to acquire a representative portion for analysis. Monitoring of activity levels in the material prior to processing is difficult; therefore, extreme care is taken in sample preparation (ashing, dissolving, etc.) to avoid destroying the integrity of the low-level facilities.

Rubber stoppers that were used as plugs in an off-gas duct system were analyzed for gross alpha, gross beta, and ^{90}Sr activities. Only exposed surfaces of the stoppers were leached with hot nitric acid and evaluated so as to estimate contamination levels on inside surfaces of the ducts. Gross alpha activities were determined by alpha-counting mounts prepared from hexone extractions made on portions of the leach solutions; gross beta-activities were determined by low-background beta counting sources made from dried portions of the leachates; and ^{90}Sr activities were determined by normal radiochemical separations. The purpose of this project was to inventory the radioactivity on the ducts prior to disposal. *(T. G. Scott, S. A. Reynolds, W. A. Teasley)*

Progress in ^{99}Tc Analysis

Considerable interest in the evaluation of ^{99}Tc in environmental materials (vegetation, soil, and animal tissue) still exists, particularly with analytical groups of UCC-ND. A special session on the status of technetium was held at the Twenty-Fourth Conference on Analytical Chemistry in Energy Technology, October 1980. Those attending the session expressed interests in methodology, the acquisition of standard materials containing ^{99}Tc, and implementing an intercomparison program to evaluate methods, sensitivities, etc. Arrangements for the production of a soil standard by the Environmental Measurements Laboratory (EML), which had been initiated in 1979, are at a standstill because of confusion over the quantity of material needed. However, arrangements are presently being made for the production of a vegetation standard. Grass harvested at the Paducah Gaseous Diffusion Plant will be prepared and distributed by EML. No date has been stated for the distribution of this material.

A major portion of our recent low-level analyses for ^{99}Tc has been related to studies conducted to estimate soil-to-vegetation concentration factors for samples collected near three operating gaseous diffusion facilities. Results obtained for the ^{99}Tc concentration factors for these samples are comparable to field experiments that involved the use of ^{95m}Tc (7).

Technetium-95*m*, a gamma-ray emitter, is frequently used in our lab as a tracer to check chemical recovery in the analysis for ^{99}Tc. Since ^{95m}Tc can be measured nondestructively by gamma-ray spectrometry, the technetium losses at each step of the procedure are monitored in one test portion of a sample, while a second test portion is processed through the same chemistry and finally measured by low-background or liquid scintillation beta counting to determine the ^{99}Tc content. The beta-counting technique is limited to decay counting, which primarily detects short-lived contaminants, and absorber counting, in the case of low-background counting, as means of validating the results.

Methods for determining ^{99}Tc in both soil and vegetation are reasonably well established (7), whereas methods for analyzing animal tissue are not. Requests for the determination of low levels of ^{99}Tc in animal samples are increasing to the point that there is a real need for the development of a reliable method. Also needed are standard materials as nearly like real samples as possible for testing the methods once developed. *(T. G. Scott, P. S. Gouge, C. V. Holmes)*

Electrolytic Enrichment of Tritium

Factors that influence the minimum detectable concentration (MDC) of tritium in water are counter background, counter efficiency, count time, and sample size. Our normal procedure for determining tritium will achieve an MDC of approximately 0.1 Bq/ml when all of the above-mentioned factors except sample size are optimized. Normally, 2 ml of sample is about the maximum volume of sample that can be added to a liquid scintillation fluor without causing complications; thus, the volume tends to be the limiting factor.

As a result of a request to determine tritium near the ambient level (0.015 Bq/ml for natural water) in a suite of well water samples from Three Mile Island, we implemented a method to concentrate tritium by acid electrolytic enrichment.

To analyze the required number of samples in the allotted time by this method, we found it was necessary to construct a system with multiple cells from readily available equipment. Glass cells and platinum electrodes were fabricated locally, a power supply was already on hand, and cooling baths were made by modifying ice chests purchased locally. An automatic cutoff circuit was installed to eliminate the possibility of the cells going dry when unattended. The finished system has eight cells, each one capable of concentrating tritium in a sample by a factor of ten in 36–40 h.

The overall procedure involves two distillations, electrolytic concentration, and data acquisition by the normal counting technique. The first distillation precedes the electrolysis and is necessary to eliminate interferences from other radionuclides and organic matter. The second distillation follows the electrolysis and is needed to separate the water (containing the tritium) from H_2SO_4, which is added as an electrolyte in the electrolysis. Temperature of the cells is maintained at 0–4°C by the ice bath(s) to minimize evaporation. Volume reduction is determined by comparing the acid normality after electrolysis with the acid normality before electrolysis. Finally, the concentration for a sample is read from a curve that is established from known tritium standards and relates to the volume reduction.

Typical results for the samples analyzed by this method were 40 to 70 mBq/ml with uncertainties of ±7 to ±14 mBq/ml. Table 5.2 lists the results for controls, blanks, and intercomparison standards. *(T. G. Scott, S. A. Reynolds, C. V. Holmes)*

Table 5.2 Tritium concentrations in water, mBq/ml (95% confidence level)

Sample code	^3H as determined	Known value
Control #1	85 ± 11	96 ± 11
Control #2	89 ± 11	96 ± 11
Control #3	100 ± 11	96 ± 11
Control #4	104 ± 15	96 ± 11
Blank #1	16 ± 7	
Blank #2	18 ± 8	
Blank #3	20 ± 8	
Blank #4	9.6 ± 7	
EML 8004WA	370 ± 37	381 ± 22
EMSL-LV "A"	70 ± 10	
EMSL-LV "B"	6.7 ± 10	

Quality Assurance of Low-Level Radiochemical Analyses

The compilation and revision of procedures for both the UCC-ND four-plant *Environmental and Effluent Analysis Manual* and our bench manual continue to be of interest to the Low-Level Radiochemical Analysis group. A comprehensive procedure for the start-up of the ND-6603 data acquisition system and the configuration of the memory has been completed. This procedure differs from an operating procedure in that it provides for resuming operation of the system after power failure or surge and/or improper response of the system. The operating procedure for the ND-6603 as a multiuser system provides instructions for collecting data from several detectors [NaI, Ge(Li), and Si surface-barrier] simultaneously without conflict.

The three Ge(Li) gamma systems are checked for gain calibration, resolution, and efficiency on a weekly basis by use of a ^{226}Ra standard. The silicon surface-barrier alpha detector systems are monitored for the same factors by use of secondary alpha standards that contain ^{236}U, ^{239}Pu, and ^{244}Cm and have been calibrated by comparison to an NBS standard on a proportional counter. New efficiencies for low-background beta counting of ^{99}Tc (with a variation of geometry) and ^{39}Sr have been determined. Beta-counting efficiencies on the liquid scintillation counter are routinely checked for ^{99}Tc (Amersham standard) and ^{3}H (NBS standard).

Programs for low-level radioanalytical intercomparisons conducted by several agencies are used to supplement our in-house quality assurance analysis programs. We have continued to participate in the QA program of the DOE-EML.

On eleven sets of samples covering almost three years, our range of agreement with means of other participants' values has been 84 to 100%, and with EML, 61 to 89%. Frequency of distribution of samples has been cut from quarterly to semiannual, beginning in 1980. The lack of quality assurance samples due to this cutback has been offset by samples coming from EPA-Las Vegas on a quarterly basis. The EPA samples are submitted to us blindly through customers from the Environmental Sciences Division. These customers have also submitted materials from IAEA. Materials from these programs are synthetic environmental samples of biota, soil, and water and are analyzed for such nuclides as ^{240}Pu, ^{239}Pu, ^{238}Pu, ^{238}U, ^{234}U, ^{241}Am, ^{90}Sr, ^{266}Ra, ^{228}Th, ^{3}H, and numerous gamma emitters.

Gamma measurements for the determination of ^{131}I on charcoal air monitors are made each week on 19 samples from the Industrial Safety and Applied Health Physics Division. Routine measurements of a ^{133}Ba (10.7y - 356 keV γ) standard (sorbed on resin to simulate iodine on charcoal) are made to assure the quality of the ^{131}I determinations. In June, an ^{131}I standard solution from Amersham Corporation was obtained and used as a source to verify the validity of ^{131}I determinations. *(S. A. Reynolds, T. G. Scott, G. I. Gleason (5))*

SPECIAL PROJECTS

Insects as Bioindicators for Radionuclides

Insect collectors near various facilities at ORNL have yielded samples that serve as indicators for the presence of radionuclides. Collectors operate for 1-7 d, yielding insect sample weights of 5 to 100 grams. The mass of collected insects is dependent upon the location of the collector as well as the season of the year.

The average radionuclide content of a collection is determined by means of high-resolution gamma-ray spectroscopy. The spectroscopy system contains a lithium-drifted germanium detector with an efficiency of 23% relative to a 7.6 × 7.6 cm NaI(Tl) detector at 25 cm. The spectroscopy system is part of a low-level environmental surveillance laboratory. Detection limits of 0.1 Bq/g are attained for common radionuclides with this measurement device.

Following the gamma-ray spectrometry, individual insects from the collection are spread upon a thin plastic film covered with a sticky surface. The film is placed in contact with Eastman Kodak Blue Band x-ray film for 24 h in the dark. After development of the x-ray film, dark spots indicate the presence of those insects containing radionuclides.

Results of studies conducted during the past summer showed radionuclide concentrations as high as 80 Bq/g in some bulk samples. Radionuclides detected in these studies have included ^{60}Co, ^{75}Se, and ^{137}Cs. These same nuclides are present as the most common radionuclides in streams and ponds near the collectors. Autoradiographic studies showed that most radioactive insects were species that spend part of their early lives in water.

Detection of ^{75}Se as an environmental contaminant was first observed in the analysis of an insect sample. Later measurements of water and air filter surveillance samples verified the presence of this radionuclide. The releases were due to processing losses from a radioisotope production facility preparing this nuclide for nuclear medicine studies. *(J. S. Eldridge, T. W. Oakes (8))*

In Vivo Determination of Radionuclides in Small Animals

White Oak Lake basin is the habitat of several animal species that are important or potentially important to a biological transport mechanism for radionuclides in the basin. A program has been established to assess the magnitude of biological radionuclide assimilation. Several species of small animals have been counted in a special facility in the C-4 low-level counting room. The animal counting chamber is constructed of 1-cm thick plastic sheet as an enclosure for support during a period of anesthesia. The center of the chamber is placed over a 15- × 15-cm NaI(Tl) detector housed in a shield of 12.5-cm wall thickness.

Animals counted in the *in vivo* facility have included 12 racoons, 25 ducks (mallard, black, and wood), 5 snakes (green, black, and corn), 5 ground hogs, and several smaller animals such as white-foot mice, cotton rats, rabbits, and moles. A road-killed bobcat and an American alligator (dead) were also examined.

Most of the animals surveyed to date were inhabitants of one of the ORNL solid or liquid waste disposal areas. All the ducks were trapped on White Oak Lake. In general, ^{137}Cs and/or ^{60}Co are found in varying concentrations in the animals. With the exception of those few that had expired before capture (bobcat, alligator, two ducks), animals were either sedated or constrained during the counting interval. Larger animals are sedated for the measurement with a tranquilizer, and returned to their habitat after the counting intervals. Ducks are not sedated - they are simply constrained with a soft cotton sleeve that prevents wing flapping.

From studies with two ducks, we found that a significant amount of radionuclide contamination was present on the feathers and feet of the ducks. This was determined by counting the feathers and feet of the ducks after removal from the carcass.

Further efforts in this project will be concerned with detailed standard construction for the myriad shapes required to calibrate program ALPHA-M data reduction techniques. *(J. S. Eldridge, T. W. Oakes (8), D. W. Parsons (8))*

Nuclear Safeguards Application of Nondestructive Gamma-Ray Spectrometry

Changes in the requirements for safeguards measurements in support of special nuclear materials accountability has resulted in a need for additional analytical support measurements and for development of specialized nondestructive techniques. For this reason, a new cooperative program with the Safeguards and Special Nuclear Materials Management Department has been established.

Initial efforts in this program have involved the use of a portable gamma-ray spectrometer system in support of balance area audits. The first exercise in this program was fairly simple, but it demonstrated one of the unique features of the portable γ-ray spectrometer system: the ability to determine γ-ray spectra from emitters in large enclosures. The portable system was used in a qualitative identification of the contents of a drum that had resided in a vault for a long period with no documentation. The portable γ-ray spectrometer verified that ^{137}Cs γ rays contributed essentially all of the external dose from the drum.

Other field audits have occurred at many other "balance areas," and γ-ray spectral determinations have been performed on a variety of nuclear materials including ^{235}U at varying enrichments, ^{239}Pu, ^{239}Pu-Be neutron sources, ^{241}Am, and ^{235}U in fission chambers. All of the site audits have been successful as far as gamma spectroscopic assistance was concerned. Several cases of inaccurate labeling have been uncovered as a result of these measurements. Information gleaned from site audits has been valuable in establishing the sampling protocols at additional balance areas. *(J. S. Eldridge, S. A. Reynolds, L. R. Hall, L. M. Gray (9))*

Low-Level Gamma-Ray Spectroscopy - Sodium Iodide Methodology

Calibration procedures and data reduction techniques have been implemented for samples counted in a 15- × 15-cm well-type sodium iodide detector. To determine the applicability for environmental surveillance samples, a series of counting experiments were performed with mixtures of ^{60}Co, ^{85}Sr, and ^{137}Cs. Libraries were prepared by separately counting 40 ml aliquots of solutions containing these three radionuclides. Test samples of each radionuclide solution at concentrations of 0.4 Bq/ml were analyzed with program ALPHA-M after counting for 3000 s. In all cases, values agreed within $\pm 1\%$ of the amount added. A second experiment was performed like the first with the exception that the concentration level of test samples was of the order of 4×10^{-2} Bq/ml. For the latter experiment, the ^{60}Co and ^{137}Cs values agreed within $\pm 5\%$ of the added value; however, the ^{85}Sr value was in error by +30% due to an error in statistical weighting of the background value.

From these studies, we concluded that radioactive solutions containing several radionuclides be conveniently assayed with minimum detectable activity levels of 4×10^{-4} Bq/ml. Such a detection level to suitable for most environmental samples. *(Belen Balboa (10), J. S. Eldridge)*

Computer Applications: Adjunct Usage for Rapid Analysis and Quality Assurance

Three useful programs have been written in Fortran and are now running in an interactive mode on the PDP-10 system. The first program, EFFCAL, uses pairs of data to solve coefficients of the general calibration equation:

$$\ln(\mathrm{eff})_{\gamma} = \alpha_1 + \alpha_2 \ln \bar{E}_{\gamma} + \alpha_3 (\ln \bar{E}_{\gamma})^2 + \alpha_4 (\ln E_{\gamma})^3 ,$$

where E = energy of gamma-ray in keV.

This equation relates the efficiency of a high-resolution germanium detector to the energy (keV) of the photopeaks of interacting gamma rays. The coefficients α_1, α_2, α_3, and α_4 are stored in a way that they can be used in a second interactive program, GAMDAT. This second program calculates radioactivity values from input parameters such as net area, counting time, weight or volume, branching ratio, etc. From the input parameters and the efficiency coefficient previously determined by the EFFCAL routine, the total activity or activity concentration is calculated and automatically stored in an accessible output file. The output files are ordered as to sample types (i.e., water, deer, insect, etc.).

The final program, RECORD, is a simple program useful for improving QA procedures. It replaces or supplements the sample log notebooks previously used for individual sample types. By means of the interactive mode, all input data are read back for final verification before being stored in a master file. Use of a text editor permits rapid search of the master file for any one or a group of samples of a specific type. Such record keeping will reduce several error types that have resulted in lost data or lost samples.

The RECORD file and the result files from GAMDAT are accessible from terminals in the Environmental Surveillance Section of the Industrial Safety and Applied Health Physics Division. Overall improvement in QA procedures are expected from these innovations. *(T. A. Rhea (11), Belen Balboa (10), J. S. Eldridge)*

Study of Ion Exchange Procedures for Concentrating Radionuclides from Large Volumes of River Water

An experiment was undertaken to provide quantitative information concerning the behavior of three important radionuclides in the system used for concentrating those nuclides from large-volume river water samples. Tracer levels of ^{60}Co, ^{137}Cs, and ^{85}Sr were added to 50-liter samples of Clinch River water that had been acidified to pH 1-2 by the addition of 250 ml of concentrated hydrochloric acid. The water samples were filtered through Whatman #42 filter paper before passing them through the two ion exchange columns (Dowex 50-W and Dowex 1 in a series).

Periodic sampling of effluent from the columns, followed by analysis of the fractions by high-resolution gamma-ray spectroscopy, provided a temporal history of the column effectiveness in concentrating the radionuclides. Analysis of the filter papers and the resin columns provided complete material balance information for this concentration study. Results of this experiment are summarized in Table 5.3.

Table 5.3. Material balance of ion-exchange study

	Percent activity			
Tracer	Recovery in Strip	In Effluent	On Filter	On Resin
^{60}Co	35.1	67.9	0.1	0
^{85}Sr	98.7	8.2	0	0.01
^{137}Cs	7.3	89.8	8.5	0

Results from this experiment show that the current method for concentration of radionuclides from large volumes of river water is not suitable for ^{60}Co and ^{137}Cs. However, the method appears adequate for ^{90}Sr as is evident from data for the ^{85}Sr tracer. *(Belen Balboa (10), J. S. Eldridge, K. E. Shank (8))*

Application of Cerenkov Counting Techniques

Use of Cerenkov counting of energetic beta radiation has continued. Samples up to 20 ml can be counted directly, or concentration of the sample can be performed beforehand, if needed. The "channels ratio" (relative count rates in selected pulse height ranges) is used to detect quenching or the presence of electrons of energy different from that expected. Quenching is compensated by "spiking" with a small volume of solution containing a known activity of the desired radionuclide(s).

Most applications have involved ^{90}Sr determinations through its daughter ^{90}Y. High-priority samples of water were screened for approximate levels of ^{90}Sr and were also analyzed using radiochemical separation techniques. A by-product of this comparison was the finding of a few spurious radiochemical results caused by contamination of SrC_2O_4 mounts by daughters of ^{222}Rn. An interference in the liquid scintillation counting of ^3H in water samples appeared to be due to the presence of energetic beta radiation, but this idea was not supported by Cerenkov counting. Further study showed the unexpected presence of alpha activity.

Some samples require concentration of strontium and yttrium by coprecipitation with calcium oxalate. Reasonable recoveries have been obtained with sample volumes up to 800 ml. In certain samples, decontamination from other activities may be inadequate. In that case, strontium carrier can be added, and a more elaborate separation carried out, with measurement of ^{90}Sr by low-background counters or ^{90}Y by Cerenkov counting (after regrowth).

Cerenkov counting has been applied to the measurement of ^{32}P at a level of less than 1% in ^{33}P radioisotope products. The liquid scintillation counter in Building 3019 was used with a counting efficiency of 43%. A recently received liquid scintillation counter is being evaluated for use for Cerenkov counting by the Low-Level Radiochemical Analysis group. Results indicate good performance. The arrangement of the photomultiplier tubes at an acute angle would be expected to lower Cerenkov backgrounds. A detailed report of the project is being prepared. *(S. A. Reynolds, J. S. Eldridge)*

Literature Reviews on Uranium and Technetium

A program to evaluate the occurrence of uranium in drinking water throughout the United States is being carried out by ORNL for the Environmental Protection Agency in connection with the establishment of a national drinking water standard for uranium. The Information Division has primary responsibility for the program, which involves tabulation of uranium concentrations in ground and surface waters that might serve as supplies for drinking. We have prepared an extensive survey on methodology for uranium analysis. This summary contains information on chemical behavior of uranium in water, variations in isotopic compositions, principles of analysis, methods for total uranium analysis, radioactivity methods, and analytical quality control. Typical uranium concentrations are in the range of micrograms per liter or less; consequently, methods must be sensitive, or effective concentration techniques must be available. The first draft of the analytical summary was submitted in September, and the complete document is due early in 1981.

We have agreed to revise the monograph on technetium for the National Research Council Subcommittee on Nuclear and Radiochemistry. A literature search has been initiated, with emphasis on radiochemical behavior and analysis. Exact content and format will be decided in consultation with subcommittee representatives. *(S. A. Reynolds)*

Development of Improved Liquid Scintillation Counting Techniques

We frequently must develop or modify liquid scintillation counting procedures for samples of unusual types or test performance of established techniques. A "screening" method (.2) was first used here in 1978 to measure simultaneously ^3H and hard-beta-plus-alpha activities of water samples. The method was recently used to monitor lake water samples and other low-level wastes. A "channels ratio" criterion was established to determine for a given sample whether ^3H could be determined directly or decontamination would be required. Background in ^3H counting is believed to be due largely to "cross-talk" between the photomultipliers. The conventional face-to-face arrangement maximizes this effect. An experimental study that would evaluate backgrounds with tubes at an acute angle is being considered. Tritium in waste oil was determined using 1-ml samples, with subsequent additions of a standard to evaluate efficiencies of the quenched samples. Phosphorescence required storage in the dark for at least an hour before counting.

It is known that ^3H escapes from scintillation mixtures contained in plastic vials. With our present equipment and the refrigerator at 3°C, the half-period for escape was found to be about one year. A gradual increase in "blank" count has been observed by us and others. The hypothesis that the increase was caused by transfer of ^{3}H from stored samples was tested by placing blanks and active samples in closed containers at room temperature and at 3°C for six to seven weeks. No significant transfer was observed.

Technetium-99 beta in concentrated $(NH_4)_2CO_3$ solution was determined by use of 1-ml samples in an emulsion "cocktail." Efficiency was about 80%, and the minimum detectable activity was about 0.03 Bq/ml. Polonium-210 alpha radiation was counted with about 100% efficiency in various media. *(S. A. Reynolds, J. S. Eldridge)*

Quality Assurance for the Special Projects Group

Two Ge(Li) spectrometer systems are now in routine service in the G-4 low-level spectrometer facility. A New Brunswick Laboratory uranium standard serves as the primary quality control check source for both detectors. The source was measured on the older detector a total of 25 times in a twelve-month period and in the newer system 21 times during its ten-month operational history. For the older detector the mean value and 95% confidence level was 64.7 ± 0.7 Bq/g, yielding a relative error of 1.1% (indicating suitable quality control for the period). Corresponding results for the newer system were 65.9 ± 0.8 Bq/g with a relative error of 1.2%. A malfunctioning amplifier (long-term drift) was detected by a single erroneous value from the check source.

Quality assurance procedures have been devised and implemented in the sample collection and preservation strategies in a program for *in vivo* radioactivity measurements in small animals.

A paper (13), "Quality Assurance Applied to Environmental Radiological Surveillance," which describes some of the procedures used in the ORNL environmental surveillance program, was published. *(S. A. Reynolds, J. S. Eldridge)*

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4. T. G. Scott, p. 84, ORNL-5619, *ACD Ann. Rep.* (1979).

5. Guest scientist on loan from Oak Ridge Associated Universities.

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8. Industrial Safety and Applied Health Physics Division.

9. Laboratory Protection Division.

10. IAEA Fellow from National Power Corporation, Manila, Philippines.

11. Summer employee from Western Kentucky University, Bowling Green, KY.

12. J. S. Eldridge, T. W. Oakes, and L. D. Eyman, p. 84, ORNL-5518, *ACD Ann. Rep.* (1978).

13. T. W. Oakes, K. E. Shank, and J. S. Eldridge, *Nuclear Safety* 21, 217 (1980).

6. QUALITY ASSURANCE, SAFETY, AND TABULATION OF ANALYSES

L. T. Corbin, Quality Assurance Officer
G. R. Wilson, Quality Control Officer, Division Safety Officer,
and Radiation Control Officer

QUALITY ASSURANCE

The Analytical Chemistry Division semiannual quality assurance (QA) report has been changed to an annual basis; however, the Analytical Technical Support Section has continued its control program with monthly internal reports and with quarterly summaries of the statistical data. Several internal QA audits are held each year, and each section of the division has been audited at least once.

Quality assurance/control operations were incorporated into our computer-based Data Management System last year. It is now possible to do the quarterly statistical calculations, obtain the plots, print the quarterly report, remove and store all old data files to a computer-readable medium, and enter the new control codes, known values, etc. into the system in one day.

In April a weighted average of the "found" limits of error for the previous two years was calculated for each of the control programs. This computation resulted in increasing the expected limit of error for five programs and decreasing it for six other programs.

Table 6.1 shows the quality level for each of the service laboratories and compares the results with those from the previous year. Lists of the different control programs and the number of results reported for each program are given in Table 6.2. During the past year there has been a 13% decrease in the number of control determinations reported and a 5% decrease in the number of control programs.

Quality assurance for the Nuclear and Radiochemical Analysis section is reported in Section 5 of this report.

SAFETY

During the past year, the Analytical Chemistry Division had two recordable injuries and fourteen first aid cases. None of the cases was serious; most of them were lacerations from glass or contusions from striking objects. The Safety Committee has made unannounced inspections of the division laboratories each quarter and has noticed considerable improvement in the housekeeping. Thirty-nine and a half percent of the members of the division attended a training course during the year. The courses included defensive driving, first aid, and the handling of hazardous materials in the laboratory.

Table 6.1. Distribution by laboratory of control tests for October 1979 through September 1980

Laboratory	Number of control results: Total	Number of control results: Outside fixed limits	Quality level (%)[a]: 1979	Quality level (%)[a]: 1980
General Analytical	755	29	96.33	96.16
Environmental Analysis	996	67	94.13	93.27
Radioactive Matls Analytical	298	8	90.12	97.32
Transuranium	369	17	97.52	95.39
Total	2418	121	94.95	95.00

[a] Quality level (%) = [(No. determinations inside fixed limits)/(total No. determinations)] × 100.

Table 6.2. Distribution of control results (by method) for October 1979 through September 1980

Method	Constituent	Number of programs	Number of results	Total
Atomic absorption spectrometry	Aluminum	1	44	
	Calcium	2	53	
	Cadmium	2	2	
	Chromium	1	16	
	Copper	2	9	
	Iron	1	42	
	Lithium	2	10	
	Magnesium	2	40	
	Manganese	1	2	
	Nickel	1	15	
	Potassium	2	34	
	Ruthenium	2	10	
	Sodium	2	105	
	Zinc	2	5	387
Colorimetry	Chloride	1	38	
	Molybdenum	1	101	
	Nitrogen	2	327	
	Phosphorus	1	51	
	Sulfate	2	84	
	Thorium	1	11	
	Uranium (NH_4SCN)	2	166	
	Uranium (DBM)	1	176	
	Zirconium	1	8	912
Coulometry	Uranium	2	32	32
Fluorometry	Uranium	3	422	422
Gravimetry (Leco)	Carbon	1	74	74
Infrared absorption spectrophotometry	Carbon	1	92	92
Ion selective electrode	Fluoride	2	26	26
Volumetric titrimetry	Acid	3	149	
	Chloride	1	6	
	Nitrate	1	20	
	Sulfur	1	103	
	Thorium	2	6	
	Uranium	3	189	473
Total		55		2418

SUMMARY OF ANALYSES RENDERED

Table 6.3 contains a tabulation of support analyses performed by the various laboratories and/or groups within the division during this reporting period.

Table 6.3 Summary of analytical work

	Number of results reported by						
Organization	Mass Spectrometry Laboratory	General Analytical Laboratory	Transuranium Analysis Laboratory	Radioactive Materials Analytical Laboratory	Physico-Chemical Laboratory	Nuclear and Radiochemical Analysis	Total
ORNL divisions							
Analytical Chemistry	1,197	2,251		33	130	1,784	5,395
Biology	157	66		12		3	238
Central Management[a]		419				568	987
Chemical Technology	14,323	24,874	25,887	14,516	1,102	11,340	92,042
Chemistry	1,804	2,230	97	59	1,621	838	6,649
Engineering		11,371				7	11,378
Engineering Physics	158						158
Engineering Technology	472				331	454	1,257
Environmental Sciences		19,884		420	137	7,351	27,792
Finance and Materials		31					31
Fusion Energy	124	6					130
Health	954	62					1,016
Health and Safety Research		185				1,762	1,947
Industrial Safety and Applied Health Physics	242	9,539				4,907	14,688
Information		44				4	48
Instrumentation and Controls	12,972	24	14	117	22		13,149
Metals and Ceramics	886	5,262	26	2,639	1,325	1,375	11,513
Neutron Physics		115					115
Operations		735	9,019	422		10,688	20,864
Physics	58		73	15		11	157
Plant and Equipment	222	46					268
Quality Assurance and Inspection	154						154
Solid State	1,330	123	38	104	659	236	2,490
Others							
Protective Coating Testing				725			725
NURE[b]						19,561	19,561
K-25 and Y-12	1,175	173		278		5,291	6,917
Miscellaneous	12,185	753		256	119	1,554	14,867
Savannah River Laboratory	310						310
TOTAL	48,726	78,193	35,154	19,596	5,446	67,734	254,849

[a] Not a division.

[b] National Uranium Resource Evaluation.

7. SUPPLEMENTARY ACTIVITIES

The division continues to maintain liaison with the academic community through the assistance of its Advisory Committee and consultants. We also make facilities and supervision available for student and faculty research and training programs.

ADVISORY COMMITTEE

This year the division Advisory Committee was composed of

P. F. Kane, National Science Foundation, Chemistry Division, Chemical Synthesis and Analysis Section, Chemical Instrumentation Program, Washington, DC.

L. L. Lewis, Head, Analytical Chemistry Department, Research Laboratories, General Motors Corporation, 12 Mile, Mounds Road, Warren, MI.

H. B. Mark, Jr., Chairman, Chemistry Department, University of Cincinnati, Cincinnati, OH.

H. L. Pardue, Chemistry Department, Purdue University, West Lafayette, IN.

CONSULTANTS

A. E. Cameron advises the Mass and Emission Spectrometry section of the division.

M. T. Kelley advises the Analytical Methodology section, with particular emphasis on computer applications.

The following specialists were brought to ORNL on short-term consulting bases this past year as part of our Seminar Program. Details of seminars are listed in Chap. 8.

K. Ogan, Perkin-Elmer Corporation, Norwalk, CT.
A. Harper, University of Georgia, Atlanta, GA.
H. M. M. Hibbering, University of Amsterdam, The Netherlands.
C. H. Lochmüller, Duke University, Durham, NC.
P. T. Kissinger, Purdue University, West Lafayette, IN.
J. Wright, University of Wisconsin, Madison, WI.
R. L. Watson, Texas A&M University, College Station, TX.
H. Schaap, Electricity Commission of Victoria, Australia.
D. M. Hercules, University of California, Irvine, CA.
W. Ratynski, Institute of Nuclear Research, Swierk, Poland.
C. Burtis, Oak Ridge National Laboratory, Oak Ridge, TN.
C. Fenselau, The Johns Hopkins University School of Medicine, Baltimore, MD.
J. W. Taylor, University of Wisconsin, Madison, WI.

PARTICIPATION IN ORNL IN-HOURS PROGRAM

The following divisional people completed courses during the 1980 winter term of the Continuing Education Program for Scientific and Technical Personnel:

M-310B. Introduction to the DECsystem-10: J. M. Dale, J. S. Eldridge, and T. G. Scott.
M-800A. Practical Solution of Differential Equations: A. R. Crook.
S-202C. Design and Structure of Technical Writing: L. M. Roseberry
S-450B. Russian I: J. E. Strain.

The following courses were completed during the spring 1980 term:

M-100C. *Fortran I: R. D. Brooksbank and T. G. Scott.*
M-300B. Fortran II: R. D. Brooksbank and T. G. Scott.
S-400B. Searching the Technical Literature: B. D. Barkenbus, J. D. Kintigh, and C. S. MacDougall.
S-455B. Russian II: J. E. Strain.

Courses completed during the fall 1980 term were:

G-600. Topics in Geology: J. S. Eldridge and W. S. Lyon.
M-310D. Introduction to the DECsystem-10: J. W. Hanna.
S-201K. Grammar and Mechanics of Technical Writing: B. D. Barkenbus.

IAEA FELLOWSHIP PROGRAM

Belen C. Balboa, Supervising Radiochemist, National Power Corporation, Morong, Bataan, Phillipines, was assigned to the division as an IAEA fellow until April, at which time she was placed on a six-month assignment at ORNL. She worked in the Nuclear and Radiochemical Analysis Section.

The Analytical Technical Support section was host to another IAEA fellow, Mahfuzur Rahman, Atomic Energy Center, Bangladesh. He received a six-month on-the-job training in fluorometric analysis of uranium, atomic absorption, and spectrophotometry.

GUEST ASSIGNMENTS

Geoffrey Gleason, Senior Scientist from ORAU, is working as a consultant on the staff of the Nuclear and Radiochemical Analyses section. His assignment is to develop and implement nuclear measurement instrumentation for low-level radiochemical analysis. He has developed computer programs for the calculation of the minimum detectable activity of low-level samples and for processing of gamma spectral information to give analysis results.

The University of Tennessee is funding Brisco L. Harward and Vincent E. Norvell to work in the Analytical Methodology section on the study of rapid scan spectrometry. Also funded is Huston E. Howell, Jr., who is studying matrix isolation photoacoustic spectroscopy.

Analytical Chemistry initiated a subcontract with The University of Tennessee to provide the technical services of advanced graduate students in environmental analytical chemistry to the division. John Vargo was assigned to the Analytical Technical Support section for a three-month period on this subcontract.

Spencer Lemons, Rollins College, worked for two-three weeks as part of an independent study program.

Gail R. Norris completed his one-year assignment with the Nuclear and Radiochemical Analysis Section. His research was in the study of trace elements in human lungs.

SUMMER PROGRAM

During the summer, the division was host to representatives of the ORAU Undergraduate Research Program, which has been developed to offer laboratory experience to college students as well as to promising high school graduates. R. W. Holmberg served as "Dean" for those guests during their visit.

T. L. Chapman, Angelo State University, worked in the Bio-Organic Analysis section with the NCI smoke program on multicomponent methods for smoke constituents in physiological materials.

K. E. Knipschild, Central Methodist College, was involved in work with the CFRP in the Analytical Technical Support section.

P. B. Liescheski, University of St. Thomas, worked on the DOD smoke project in the Bio-Organic Analysis section.

The Analytical Methodology section was host to D. M. Taylor, Wells College, who worked on trace uranium detection by laser-excited fluorescence.

The division was also involved in the ORAU Faculty Research Program during the summer. Subrahmanyam Pendyala, SUNY College, was assigned to the Analytical Methodology section and worked with advanced spectroscopic methods of analysis.

Two people were assigned to the division as part of the Summer Research Internship Program.

Z. K. Barnes, Michigan State University, was assigned to the Bio-Organic Adalysis section to work on the application of high-performance liquid chromatography to the collection, fractionation, and multicomponent analysis of organics in environmental and fossil fuel materials.

T. A. Rhea, Western Kentucky University, worked on applications of gamma-ray spectrometry with a dual-coincidence spectrometer system in the Nuclear and Radiochemical Analysis section.

GLCA PROGRAM

During the fall semester, K. P. Cross, Lawrence University, was assigned to the Analytical Technical Support section to perform thermal analysis of inorganic materials by mass spectrometry, thermogravimetric analysis, differential scanning colorimetry, and differential thermal analysis.

ORNL CO-OP PROGRAM

Vanessa H. Ostrum, University of Tennessee, worked spring and fall quarters in the Bio-Organic Analysis section on the semipreparative fractionation and analysis of fossil fuel derived products.

SPECIAL AWARDS

W. S. Lyon, Jr., section head for the Analytical Methodology section received the 1980 Radiation Industry Award of the American Nuclear Society. The award, presented November 18 at the International Conference of the American and European Nuclear Societies, recognizes outstanding contributions to industrial applications of radiation technology. It consists of an engraved certificate and a $1000 honorarium.

Lyon was cited for "pioneering research in developing methods for assay and identification of radionuclides for industrial applications, the extension of nuclear analytical methods to studies of fossil energy production, and his leadership in developing and publicizing industrial use of such methods."

23rd ANNUAL ORNL CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

This year's conference was held at the Riverside Motor Lodge in Gatlinburg, Tennessee, October 7-9, 1980. The theme of the conference was "Analytical Chemistry in Environmental Regulation and Control." Attendance was 173, including 16 exhibitors. Topics covered during the meeting included Organic Pollutants, Mass Spectrometry, Trace Element Analyses, and Radiochemical Analyses.

A. L. Harrod was General Chairman, W. S. Lyon was Technical Program Chairman, and M. L. Emery was Treasurer. Gail Vineyard and Donna Watson were Conference Secretaries. Other conference committee members included J. S. Eldridge, C. M. Ferguson, W. H. Griest, W. T. Rainey, W. D. Shults, and J. H. Stewart.

ADDITIONAL PROFESSIONAL ACTIVITIES

BALL, F. L.	
Secretary:	Electron Microscopy Society of America
Representative from EMSA:	Section Committee, AAAS Section on Physics (B)
Member:	Analytical Chemistry Division Seminar Committee
BUCHANAN, M. V.	
Chairman:	Analytical Chemistry Division Seminar Committee
CARTER, J. A.	
Secretary:	Subcommittee C-5:05, Analytical Task Group (Reactor Grade Graphite), Committee C-5, Manufacture of Carbon and Graphite Products, ASTM
Member:	Committee C-26, Nuclear Fuel Cycle, and C-26:05, Test Methods, Task Group Leader, Micro Analytical Techniques, ASTM
	ORNL Management and Supervisory Development Program Advisory Committee
	ORNL Personnel Development Chemistry Course
Laboratory Coordinator:	ISPO Programs
Invited Speaker:	Seventh Annual Meeting FACSS, Philadelphia, Pennsylvania September 28-October 3, 1980
	10th Annual Symposium on the Analytical Chemistry of Pollutants, Dortmund University, Dortmund, FRG, May 27-30, 1980
CHRISTIE, W. H.	
Session Chairman and Invited Speaker:	22nd Rocky Mountain Conference on Mass Spectrometry, Denver, Colorado, August 10-14, 1980
Member:	ASTM Committee E-42, Surface Analysis
CORBIN, L. T.	
Fellow:	American Society for Testing and Materials
Member:	Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM
	Subcommittee E-10:01, Fuel Burnup
	Subcommittee E-10:02, Radiation-Induced Changes in Metallic Materials
Chairman:	Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM

Coordinator: Analytical Chemistry Division Nontechnical Recruiting
Analytical Chemistry Division Quality Assurance Program
Analytical Chemistry Division Energy Conservation Program
Division Representative: ORNL Job Opportunity System
ORNL Labor Relations

COSTANZO, D. A.
Member: Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, and Subcommittee C-26:05, Methods of Test, ASTM

DALE, J. M.
Invited Speaker: American Vacuum Society, Knoxville, Tennessee, October 28–30, 1980

DYER, F. F.
Lecturer: ORAU Traveling Lecture Program
Member: Analytical Chemistry Division Seminar Committee

ELDRIDGE, J. S.
Member: Subcommittee No. 9 (Environmental Radiological Surveillance: Mechanisms for Information Exchange), Health Physics Society

EMERY, J. F.
Consultant: Tennessee Valley Authority

FELDMAN, C.
Fellow: American Society for Testing and Materials
Scientific Editor: *Optics and Spectroscopy* (English translation of Russian journal, *Optika i Spektroskopiya*)
Member: Committee E-2 on Emission Spectroscopy, ASTM; Subcommittees on Fundamental Methods, Editorial Practices, and Nomenclature
Atomic Absorption and Emission Spectroscopy Subgroup, Union Carbide Corporation

GRIEST, W. H.
Consultant: National Cancer Institute
Member: DOE Oil Shale Working Group

GUERIN, M. R.
Consultant: National Cancer Institute
Working Meeting on Research Needs on Low-Yield Cigarettes, Bethesda, Maryland, June 9–11, 1980
National Institute on Drug Abuse, RFP Planning Group, Rockville, Maryland, April 10, 1980
Member: EPRI Source Assessment Subcommittee
Chairman: DOE/OHER Workshop on the Preparation of Complex Mixtures for Bioassay, Oak Ridge, Tennessee, November 12–13, 1980
Invited Speaker: 2nd Symposium on Process Measurements for Environmental Assessment, Atlanta, Georgia, February 25–27, 1980
10th Annual Symposium on the Analytical Chemistry of Pollutants, Dortmund, FRG, May 28–30, 1980
2nd Symposium on Environmental Analytical Chemistry, Brigham Young University, Provo, Utah, June 18–20, 1980
1980 Gordon Research Conference on Analytical Chemistry New Hampton, New Hampshire, August 11–15, 1980

HIGGINS, C. E.	
Coordinator:	Analytical Chemistry Division Affirmative Action Program
HOLMBERG, R. W.	
Coordinator:	Analytical Chemistry Division University Relations
Invited Speaker:	Workshop on Arc By-Products in Gas Insulated Equipment, Chicago, Illinois, June 4-6, 1980
HULETT, L. D.	
Session Chairman:	American Vacuum Society, Knoxville, Tennessee, October 28-30, 1980
JENKINS, R. A.	
Invited Participant:	NIH Program-Project Review, University of Illinois, Chicago, Illinois, December 3-5, 1980
Invited Speaker:	Washington, DC, Chromatography Discussion Group, Gaithersburg, Maryland, May 21, 1980
KLATT, L. N.	
Member:	Program Advisory Committee, Division of Analytical Chemistry Division, ACS
Associate Editor:	*Chemical, Biomedical, and Environmental Instrumentation*
Member:	Fellowship Committee of Analytical Chemistry Division of American Chemical Society
LAING, W. R.	
Chairman:	Subcommittee C-26:05, Test Methods, Nuclear Fuel Cycle, ASTM
	UCCND Analytical Committee
Division Representative:	UCCND Environmental Analysis Committee
LYON, W. S.	
Member:	Committee D-5, Coal and Coke, Subcommittee on Methodology, Task Group on Trace Elements, ASTM
	Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM
	Subcommittee E-10:01, Fuel Burnup
	Subcommittee E-10:05, Dosimetry
	Organizing Committee, 6th International Conference on Modern Trends in Activation Analysis
	Executive Committee, Isotopes and Radiation Division, ANS
	Scientific Committee 25 on Radiation Protection in the Use of Small Neutron Generators, NCRP
Plenary Lecturer:	Fourth International Conference Nuclear Methods in Environmental and Energy Research, Columbia, Missouri, April 17, 1980
Regional Editor:	*Journal of Radioanalytical Chemistry*
Associate Editor:	*Radiochemical and Radioanalytical Letters*
Program Chairman:	Isotopes and Radiation Division, ANS
MASKARINEC, M. P.	
Chairman-Elect:	UCC-ND Gas Chromatography Specialists' Group
Member:	Analytical Chemistry Division Seminar Committee
	ASTM E-19 Committee on Chromatography
	UCCND Liquid Chromatography Specialists' Group
Lecturer:	ORAU Traveling Lecture Program

RAMSEY, J. M.	
Member:	Analytical Chemistry Division Seminar Committee
REYNOLDS, S. A.	
Member:	Committee D-19, Water, ASTM
	Committee E-10, Nuclear Technology and Applications, ASTM
	Standards Subcommittee ANS-16, Isotopes and Radiation Division, ANS
	Technical Advisory Group, ISO Technical Committee 147 on Water Quality
Secretary:	D-19 Subcommittee 4, Methods of Radiochemical Analysis, ASTM
Chairman:	Working Group 1, Subcommittee 3, ISO Technical Committee 147 on Water Quality
ROSS, H. H.	
Chairman:	ORNL Graduate Student Selection Panel
	Education Committee, ORNL Credit Union
Member:	ORNL Technology Utilization Committee
	Editorial Advisory Board, *Journal of Radioanalytical Chemistry*
	Board of Directors, ORNL Credit Union
RUBIN, I. B.	
Invited Speaker:	1980 American Chemical Society Summer Symposium on Analytical Chemistry, Durham, North Carolina, June 4-6, 1980.
SCOTT, T. G.	
Member:	Committee D-19, Water, ASTM, and Subcommittee 4, Methods of Radiochemical Analysis
SHULTS, W. D.	
Chairman:	Division of Analytical Chemistry, ACS
	Analytical Specialist Group, UCC
Member:	ORNL In-House Continuing Education Committee
	Technical Services Committee, UCCND
	Editorial Board, *Analytica Chimica Acta*
	Advisory Committee, "Analytical Approach," *Analytical Chemistry*
Program Chairman:	San Francisco National ACS Meeting, 1980.
SMITH, D. H.	
Coordinator:	Analytical Chemistry Division PhD Recruiting
STEWART, J. H., Jr.	
Member:	ASTM C-26 Nuclear Fuel Cycle Task: Group Leader for X-Ray Fluorescence Methods
Invited Speaker:	1980 Summer Meeting of ASTM C26, Denver, Colorado, July 21, 1980
STOKELY, J. R.	
Coordinator:	Analytical Chemistry Division MS/BS Recruiting
TODD, P. J.	
Member:	Analytical Chemistry Division Seminar Committee

8. PRESENTATION OF RESEARCH RESULTS

As in past years, the division has actively responded to the changing priorities of the ORNL research effort by changing the emphasis of some of its own programs or instituting new studies. The increasing concern with energy - nuclear as well as non-nuclear - is reflected in the research results listed below. The multidisciplinary approach required in many such problems is indicated by the number of papers and talks coauthored by members of other ORNL divisions. Such persons are designated by an asterisk.

PUBLICATIONS

Contributions to Books, Proceedings, and Reports

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Bate, L. C.	Bate, L. C. "Determination of Technetium-99 in Mixed Fission Products by Neutral Activation Analysis"	*Radioelement Analysis - Progress and Problems*, Proc. 23rd Conf. on Anal. Chem. in Energy Techn., Gatlinburg, Tenn., W. S. Lyon, Ed., 1980, pp. 125-190
Bostick, D. T.	Bostick, D. T. "Acid-Componensate Multiwavelength Determination of Uranium in Process Streams"	*Proc., Am. Nucl. Soc. Topical Meet. on Measurement Techn. for Safeguards and Mater. Control*, NBS SP-582, June 1980, p. 121.
Buchanan, M. V.	Walton, B. T.;* Buchanan, M. V. "Teratogenic Effects of Fuel Oils on Insects Developing in Contaminated Substrates"	*ACS, Div. Environ. Chem. Prepr. 20(2)*, 1980, pp. 100-101
Carter, J. A.	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. "A SSMS Surface Analysis of B in Irradiated Zircaloy-2: Ion Implantation Standard as a Calibration Technique"	*Proc., 28th Annu. Conf. on Mass Spectrom. and Allied Topics*, New York, N.Y., May 25-30, 1980, pp. 678-689
Caton, J. E.	Dalbey, W. E.;* Nettesheim, P.;* Griesemer, R.;* Caton, J. E.; Guerin, M. R. "Chronic Inhalation of Cigarette Tobacco Smoke by Rats"	*Proc., 19th Annu. Hanford Life Sci. Symp., Pulmonary Toxicol. of Respirable Particles*, Richland, Wash., Oct. 22-24, 1979, DOE Symp. Ser. 53, CONF-791002, TIC, USDOE, 1980, pp. 522-535
	Henry, C. J.;* Whitmire, C. E.;* Lopez, A.;* Dansie, D. R.;* Avery, M. D.;* Caton, J. E.; Stokely, J. R.; Holmberg, R. W.; Guerin, M. R.; Kouri, R. E.* "The Dosimetry and Distribution of Whole Cigarette Smoke Particles in Inbred Strains of Mice: Comparison of a large Smoke Exposure Machine (SEM) with a Small-Capacity Smoke-Exposure Machine (Walton)"	*Proc., 19th Annu. Hanford Life Sci. Symp., Pulmonary Toxicol. of Respirable Particles*, Richland, Wash., Oct. 22-24, 1979, DOE Symp. Ser. 53, CONF-791002, TIC, USDOE, 1980, pp. 177-192

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Christie, W. H.	Narayan, J.;* Larson, B. C.;* Christie, W. H. "Effect of Thermal Annealing in Boron Implanted, Laser Annealed Silicon"	*Laser-Solid Interactions and Laser Processing-1978*, S. D. Ferris, H. J. Leamy, J. M. Poate, Eds., AIP Conf. Proc. No. 50, New York, N.Y., 1979, p. 440
	Wang, J. C.;* Wood, R. F.;* White, C. W.;* Appleton, B. R.;* Pronko, P. P.;* Wilson, S. R.;* Christie, W. H. "Dopant Profile Changes Induced by Laser Irradiation of Silicon: Comparison of Theory and Experiment"	*Laser-Solid Interactions and Laser Processing-1978*, S. D. Ferris, H. J. Leamy, J. M. Poate, Eds., AIP Conf. Proc. No. 50, New York, N.Y., 1979, p. 123
	White, C. W.;* Christie, W. H.; Pronko, P. P.;* Appleton, B. R.;* Wilson, S. R.;* Young, R. T.;* Wang, J. C.;* Wood, R. F.;* Narayan, J.;* Magee, C. W.* "Dopant Profile Changes Induced by Pulsed Laser Annealing"	*Proc., Int. Conf. on Ion Beam Modification of Mater.*, Vol. II, J. Gyulai, T. Lohner, E. Pasztor, Eds., Central Inst. for Phys., Budapest, Hungary, 1979, p. 839
	Young, R. T.;* Wood, R. F.;* Narayan, J.;* Christie, W. H. "Laser Techniques in Photovoltaic Applications"	*Laser Applications in Mater. Processing*, Vol. 198, J. F. Ready, Ed., Soc. of Photo-Optical Instrumentation Engineers, Bellingham, Wash., 1980, p. 36
	Zehner, D. M.;* White, C. W.;* Ownby, G. W.;* Christie, W. H. "Silicon Surface Structure and Surface Impurities After Pulsed Laser Annealing"	*Laser and Electron Beam Processing of Mater.*, C. W. White, P. S. Peercy, Eds., Academic Press, New York, N.Y., 1980, p. 201
	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. "A SIMS Surface Analysis of B in Irradiated Zircaloy-2: Ion Implantation Standard as a Calibration Technique"	*Proc., 28th Annu. Conf. on Mass Spectrom. and Allied Topics*, New York, N.Y., May 25-30, 1980, pp. 678-689

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Clark, B. R.	Rubin, I. B.; Goeckner, N. A.;* Clark, B. R. "Polar Constituents of a Shale Oil: Comparative Composition with Other Fossil-Derived Liquids"	*Proc., Oil Shale Symp.: Sampling, Analysis, and Quality Assurance*, Denver, Colo., Mar. 26-28, 1979, EPA-600/9-80-022, June 1980, pp. 390-401
	Holland, J. M.;* Rahn, R. O.;* Smith, L. H.;* Clark, B. R. ; Change, S. S.;* Stephens, T. J.* "Dosimetry of Coal and Shale Derived Crude Liquids as Mouse Skin Carcinogens"	*Proc., Oil Shale Symp.: Sampling, Analysis, and Quality Assurance*, Denver, Colo., Mar. 26-28, 1979, EPA-600/9-80-022, June 1980, pp. 443-454
	Griest, W. H.; Guerin, M. R.; Yeatts, L. B.; Clark, B. R. "Sample Management and Chemical Characterization of the Paraho/SOHIO/U.S. Navy Crude and Refined Shale Oil Suite"	*Proc., Symp. on the Health Effects Investi. of Oil Shale Dev.*, Gatlinburg, Tenn., June 23-24, 1980, Ann Arbor Sci. Pub., pp. 27-44
	Rao, T. K.;* Epler, J. L.;* Guerin, M. R.; Clark, B. R. "Short-Term Microbial Testing of Shale Oil Materials"	*Proc., Symp. on the Health Effects Investi. of Oil Shale Dev.*, Gatlinburg, Tenn., June 23-24, 1980, pp. 161-172
Corbin, L. T.	Laing, W. R.; Corbin, L. T. "Radioactive Materials Analytical Laboratory"	*Proc., 27th Conf. on Remote Systems Techn.*, 1979, p. 86
Eby, R. E.	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. "A SSMS Surface Analysis of B in Irradiated Zircaloy-2: Ion Implantation Standard as a Calibration Technique"	*Proc., 28th Annu. Conf. on Mass Spectrom. and Allied Topics*, New York, N.Y., May 25-30, 1980, pp. 678-689
Eldridge, J. S.	Reynolds, S. A.; Eldridge, J. S. "Investigation of Cerenkov Counting of Environmental Strontium-90"	*Liquid Scintillation Counting Recent Applications and Dev.*, Academic Press, New York, Vol. 1, 1980, pp. 397-405
	Oakes, T. W.;* Shank, K. E.;* Auxier, J. A.;* Eldridge, J. S.; Jenkins, F.;* Love, G. L.;* Oberg, S. G.;* Panesko, V.;* Selby, B.;* Travers, W. D.;* Strodl, W. R.* "Environmental Radiological Surveillance: Mechanisms for Information Exchange"	*Upgrading Environ. Radiation Data*, J. E. Watson, ed., EPA 520/1-80-012, Aug. 1980, pp. 9-1 to 9-11
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	Rao, T. K.;* Epler, J. L.;* Schmidt-Collerus, J. J.;* Leffler, L.;* Guerin, M. R. "Biological Monitoring of Oil Shale Products and Effluents Using Short-Term Genetic Analyses"	*Proc., Oil Shale Symp.: Sampling, Analysis, and Quality Assurance*, Denver, Colo., Mar. 26-28, 1979, EPA-600/9-80-022, June 1980, pp. 431-442
	Haschek, W. M.;* Boling, M. E.;* Guerin, M. R.; Witschi, H. P.* "Pulmonary Toxicity of a Coal Liquefaction Distillate Product"	*Proc., 19th Annu. Hanford Life Sci. Symp., Pulmonary Toxicol. of Respirable Particles*, Richland, Wash., Oct. 22-24, 1979, DOE Symp. Ser. 53, CONF-791002, TIC, USDOE, 1980, pp. 338-356

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Laing, W. R.	Laing, W. R.; Corbin, L. T. "Radioactive Materials Analytical Laboratory"	*Proc., 27th Conf. on Remote Systems Techn.*, 1979, p. 86
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Lyon, W. S.	Lyon, W. S., "Radioelement Analysis - Progress and Problems"	*Proc., 23rd Conf. on Anal. Chem. in Energy Techn.*, Oct. 9-11, 1979, W. S. Lyon, Ed., 1980, Ann Arbor Sci. Pub.
Maskarinec, M. P.	Herbes, S. E.;* Southworth, G. R.;* Shaeffer, D. L.;* Griest, W. H.; Maskarinec, M. P. "Critical Pathways of Polycyclic Aromatic Hydrocarbons in Aquatic Environments"	*The Scientific Basis of Toxicity Assessment*, H. Witschi, Ed., Elsevier/North Holland Biomedical Press, 1980, pp. 113-128
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AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Yeatts, L. B.	Griest, W. H.; Guerin, M. R.; Yeatts, L. B.; Clark, B. R. "Sample Management and Chemical Characterization of the Paraho/SOHIO/U.S. Navy Crude and Refined Shale Oil Suite"	*Proc., Symp. on the Health Effects Investi. of Oil Shale Dev.*, Gatlinburg, Tenn., June 23-24, 1980, Ann Arbor Sci. Pub., pp. 27-44
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Young, J. P.	Haire, R. G.;* Young, J. P.; Bourges, J. Y.* "Absorption Spectrophotometric and X-Ray Diffraction Studies of NdI_3 and SmI_3"	*Proc., 14th Rare Earth Res. Conf.*, North Dakota Univ., Fargo, N.D., June 25-28, 1979, Vol. 2, G. J. McCarthy, J. J. Rhyne, and H. B. Silber, eds., Plenum Press, New York, N.Y., 1980, pp. 159-164

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Carter, J. A.	Smith, D. H.; Walker, R. L.; Carter, J. A. *Progress Report for the Office of Safeguards and Security*	ORNL/TM-7218 (Jan. 1980)
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Smith, D. H.	Smith, D. H.; Walker, R. L.; Carter, J. A. *Progress Report for the Office of Safeguards and Security*	ORNL/TM-7218 (Jan. 1980)
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	Smith, D. H.; Walker, R. L.; Carter, J. A. *TASTEX Task J: Resin Bead Mass Spectrometry for Safeguards*	ORNL/TM-7429 (ISPO-105)

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Weinberger, A. J.	Costanzo, D. A.; Weinberger, A. J.; Marley, J. L. *A Solvent Extraction Study of the Thorium Nitrate, Nitric Acids, and Tributyl Phosphate-Dodecane System: Density and Acidity Relationships*	ORNL/TM-7240 (May 1980)

ORAL PRESENTATIONS

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

At Meetings of Professional Societies, Conferences, and the Like

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Beall, G. W.*	Beall, G. W.;* Kelley, K. L.;* Beall, G. W.;* Young, J. P.; Boatner, L. A.* "Volume States of Actinides in Synthetic Monozites"	Mat. Res. Soc. Annu. Meet., Boston, Mass., Nov. 16-20, 1980
Beene, J. R.*	Young, J. P.; Beene, J. R.;* Bemis, C. E.,Jr.;* Kramer, S. D.* "Study of the Fission Isomer ^{240m}Am (S.F.) Using Laser Induced Nuclear Polarization"	Am. Phys. Soc., Washington, D.C., Apr. 21, 1980
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Bemis, C. E.*	Bemis, C. E.;* Beene, J. R.;* Young, J. P.; Kramer, S. D.* "Laser-Induced Nuclear Polarization (Linup): Application to the Study of Short-Lived Nuclide"	11th Int. Quantum Electronic Conf., Boston, Mass., June 23-26, 1980
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Buchanan, A. C.*	Buchanan, A. C.*; Buchanan, M. V.; Dworkin, A. S.;* Smith, G. P.* "Low Temperature Catalytic Hydrocracking of Naphthalene in Molten SbCl$_3$-AlCl$_3$"	3rd Int. Symp. on Molten Salts, Hollywood, Fla., Oct. 5-10, 1980
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Carter, J. A.	Carter, J. A.; Walker, R. L.; Smith, D. H. "Isotope Dilution Resin Bead Mass Spectrometry - An Ultra Trace Technique for Measuring Nuclides in Three-Mile Island Water"	Invited, 10th Annu. Symp. Anal. Chem. of Pollut., Fed. Repub. of Germany, May 28-30, 1980
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	Caton, J. E. "Use of FTIR in the Quality Control of the EPA/DOE Fossil Fuel Sample Repository at ORNL"	UCC Anal. Specialists' Meet., Tarrytown, N.Y., Oct. 16-17, 1980
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Christie, W. H.	Christie, W. H.; Carter, J. A.; Eby, R. E.; Landau, L.; Musick, W. R. "A SSMS Surface Analysis of B in Irradiated Zircaloy-2: Ion Implantation Standards as Calibration Techniques"	28th Annu. Conf. on Mass Spectrom. and Allied Topics, New York, N.Y., May 25-30, 1980
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Christie, W. H.	Christie, W. H. "Secondary Ion Mass Spectrometry: Quantification Techniques and Their Application"	1st Annu. Symp. of the Tenn. Valley Chap. of the Am. Vacuum Soc., Knoxville, Tenn., Oct. 28-30, 1980
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Compere, A. L.*	Compere, A. L.;* Griffith, W. L.;* Rao, T. K.;* Griest, W. H. "Potential Use of Organosolv Underflow Tar Lignin as a Petrochemical Refinery Feed"	TAPPI Papermakers Conf., Atlanta, Ga., Apr. 15-16, 1980
Costanzo, D. A.	Costanzo, D. A. "CRFP Analytical Chemistry Development"	USDOE/UKAERE Breeder Info. Exchange Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., May 1, 1980
	Costanzo, D. A. "Analytical Chemistry in Support of Reactor Programs"	UCCND Anal. Meet. at Oak Ridge Nat. Lab., Oak Ridge, Tenn., June 11, 1980
	Costanzo, D. A. "Nuclear Activities - Progress and Prognosis"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21, 1980
	Costanzo, D. A. "Analytical Chemistry for Reactor Fuel Reprocessing"	CFRP Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Mar. 11, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Costanzo, D. A.	Costanzo, D. A. "Analytical Chemistry Development: CFRP Semiannual Technical Program Review of Process R&D Tasks"	Oak Ridge Nat. Lab., Oak Ridge, Tenn., Mar. 19, 1980
Cross, K. P.*	Cross, K. P.;* Lee, D. A. "Quasi-Isothermal Drying of Sol-Gel Synroc Microspheres"	Nat. Academy of Sci., Oak Ridge Am. Museum of Sci. and Energy, Nov. 22, 1980
Dalbey, W. E.*	Dalbey, W. E.;* Holmberg, R. W.; Moneyhun, J. H.; Lock, S.;* Guerin, M. R. "Toxicological Evaluation of an Aerosol of Diesel Fuel #2"	11th Conf. on Environ. Toxic., Dayton, Ohio, Nov. 18-20, 1980
	Dalbey, W. E.;* Nettesheim, P.;* Griesemer, R.;* Caton, J. E.; Guerin, M. R. "Chronic Inhalation of Cigarette Tobacco Smoke by Fischer Rats"	19th Annu. Meet. of the Soc. of Toxic., Washington, D.C., Mar. 9-13, 1980
Dale, J. M.	Dale, J. M.; Hulett, L. D.; Pendyala, S.* "Low Energy Positron Spectroscopy of Solid Surfaces"	Gordon Res. Conf. on Electron Spectros., Wolfboro, N.H., July 14-18, 1980
	Dale, J. M.; Hulett, L. D.; Pendyala, S.* "Low Energy Positron Spectroscopy of Solid Surfaces"	Am. Vacuum Soc. Conf., Knoxville, Tenn., Oct. 27-29, 1980
Dunn, H. W.	Dunn, H. W.; Stewart, J. H. "Quantitative Determination of the Asbestos Content of Building Materials"	24th Conf. on Anal. Chem. in Energy Techn., Gatlinburg, Tenn., Oct. 7-9, 1980
	Dunn, H. W. "The Quantitative Analysis of Asbestos in Building Materials"	INTER/MICRO-80 Meet., McCrone Res. Inst., Chicago, Ill., July 21-25, 1980
Eldridge, J. S.	Eldridge, J. S.; Oakes, T. W.* "Radionuclide Transport in a Liquid Waste System"	179th Nat. Anal. Chem. Soc. Meet., Houston, Tex., Mar. 23-28, 1980
	Eldridge, J. S.; Oakes, T. W.;* Shank, K. E.* "Radionuclide Concentrations in White-Tailed Deer on the Department of Energy's Oak Ridge Reservation"	Health Phys. Soc. Annu. Meet., Seattle, Wash., July 20-25, 1980
Feldman, C.	Feldman, C. "The Determination of Traces of Fluoride in Natural Waters and Residues"	24th Conf. on Anal. Chem. in Energy Techn., Gatlinburg, Tenn., Oct. 7-9, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Ferguson, N. M.	Ferguson, N. M.; Lund, J. R. "The Determination of Mercury in Environmental Samples - A Constant Challenge"	1980 Pittsburgh Conf. on Anal. Chem. and Appl. Spectros., Atlantic City, N.J., Mar. 10-14, 1980
Francis, C. W.*	Francis, C. W.;* Maskarinec, M. P.; Epler, J. L.;* Brown, D. K.* "The Utility of Extraction Procedures nad Toxicity Testing with Solid Wastes"	Solid and Hazardous Wastes Res. Div. Symp., Mar. 3-5, 1980
Glish, G. L.	Glish, G. L.; Zakett, D.;* Hemberger, P. H.;* Cooks, R. G.* "New Instrumentation for MS/MS"	285th Annu. Conf. on Mass Spectrom. and Allied Topics, New York, N.Y., May 25-30, 1980
Gray, R. J.*	Gray, R. J.;* Canonico, D. A.;* Bate, L. C. "An Integrity Study of Type 347 Stainless Steel Tubes After a Five-Year Service in a High Flux Nuclear Reactor"	13th Annu. Techn. Meet. of the Int. Metallographic Soc., Brighton, England, Aug. 18-20, 1980
Griest, W. H.	Griest, W. H.; Higgins, C. E.; Caton, J. E.; Wike, J. S. "Characterization of Ambient Vapor and Particulate Phase Organics Collected Near the Kosovo Coal Gasifier"	180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 24-29, 1980
	Griest, W. H.; Caton, J. E. "Interaction of Polycyclic Aromatic Hydrocarbons with Fly Ash"	5th Int. Symp. on Polynucl. Aromat. Hydrocarbons, Battelle Columbus Lab, Columbus, Ohio, Oct. 28-30, 1980
	Griest, W. H.; Caton, J. E.; Yeatts, L. B.; Maskarinec, M. P. "Methods for Analysis of Trace Organic Constituents on Fly Ash"	2nd Conf. on Air Quality Manage. in the Electric Power Industry, Austin, Tex., Jan. 22-25, 1980
	Griest, W. H.; Guerin, M. R.; Yeatts, L. B.; Clark, B. R. "Sample Management and Chemical Characterization of the Paraho/SOHIO/U.S. Navy Crude and Refined Shale Oil Suite"	Invited, Symp. on the Health Effects Invest. of Oil Shale Develop., Gatlinburg, Tenn., June 23-24, 1980
Guerin, M. R.	Guerin, M. R. "'Bioassay Chemistry' and the Characterization of Polycyclic Aromatic Organonitrogen Compounds - New Environmental Analytical Problems"	Invited, 2nd Symp. on Environ. Anal. Chem., Brigham Young Univ., Provo, Utah, June 18-20, 1980
	Guerin, M. R.; Ho, C.-h.; Buchanan, M. V.; Rubin, I. B.; Griest, W. H.; Clark, B. R.; Epler, J. L.;* Rao, T. K.* "Separation and Identification of Mutagens in Synthetic Crude Oils and Related Products"	Invited, 10th Annu. Symp. Anal. Chem. of Pollut. Fed. Republ. Germany, May 28-30, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Guerin, M. R.	Guerin, M. R. "Inhalation Bioassay Chemistry and Instrumentation"	Invited, Nat. Inst. on Drug Abuse Meet. on Cannabis Inhalation Bioassay, Rockville, Md., Apr. 10, 1980
	Guerin, M. R. "Smoking and Health Issues Related to Low Tar Cigarettes"	Invited, Working Meet. on Res. Needs on Low-Yield Cigarettes, Bethesda, Md., June 9-11, 1980
	Guerin, M. R. "The Integrated Approach to Chemical-Biological Analysis"	Invited, 2nd Symp. on Process Measure. for Environ. Assessment, Atlanta, Ga., Feb. 25-27, 1980
	Guerin, M. R. "'Bioassay Chemistry', Analytical Chemistry in Biological Testing"	Invited, 1980 Gordon Res. Conf. on Anal. Chem., New Hampton, N.H., Aug. 11-15, 1980
	Ho, C.-h.; Buchanan, M. V.; Clark, B. R.; Guerin, M. R. "Chemical Characterization of the Neutral Fraction of Synfuels"	Proc., 20th Hanford Life Sci. Symp., Richland, Wash., Oct. 20-24, 1980
Haire, R. G.*	Haire, R. G.;* Young, J. P.; Peterson, J. R.;* Ensor, D. D.* "Chemical and Structural Consequences of Radioactive Decay in Transplutonium Oxides"	180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 25-29, 1980
	Haire, R. G.;* Young, J. P.; Ensor, D. D.;* Peterson, J. R.* "Solid State Spectroscopic Studies of CfF$_3$ and CfF$_4$"	Southeast-Southwest Reg. Am. Chem. Soc. Meet., New Orleans, La., Dec. 10-13, 1980
	Haire, R. G.;* Young, J. P.; Bourges, J. Y.* "Absorption Spectrophotometric and X-Ray Diffraction Studies of NdI$_3$ and SmI$_3$"	Proc., 14th Rare Earth Res. Conf., North Dakota State Univ., Fargo, N.D., June 25-28, 1980
Higgins, C. E.	Higgins, C. E.; Holmberg, R. W.; Moneyhun, J. H.; Griest, W. H. "Sampling and Analysis of Vapor Phase Organics in Ambient Air"	24th Conf. on Anal. Chem. in Energy Techn., Gatlinburg, Tenn., Oct. 7-9, 1980
Ho, C.-h.	Ho, C.-h. "Separation of Aromatic Nitrogen Compounds from Synthetic Crude Oils for Biological Testing"	Invited, Pittsburgh Energy Techn. Ctr., Pittsburgh, Pa., May 15-16, 1980
	Ho, C.-h.; Buchanan, M. V., Clark, B. R.; Guerin, M. R. "Chemical and Biological Evaluation of Synthetic Fuels"	CONFAB '80 on Fossil Fuel Chem. and Energy, Laramie, Wyo., July 22-25, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Holmberg, R. W.	Holmberg, R. W., Keller, J. M.; Jones, C. M.* "The Problems of Sulfur Hexafluoride Impurities on the Operation of Large Electrostatic Accelerators"	Invited, Workshop on Arc By-Products in Gas Insulated Equip., Chicago, Ill., June 4-6, 1980
	Holmberg, R. W.; Moneyhun, J. H. "An Inhalation Exposure System for Toxicology Studies of Diesel Oil Aerosols"	2nd Symp. on Phys. and Chem. Charac. of Army Smokes/Obscurant Aerosols, Frederick, Md., Nov. 13-14, 1980
	Holmberg, R. W.; Moneyhun, J. H.; Dalbey, W. E.* "Modification of Rochester Chambers for Studies with High Concentrations of Oil Aerosols"	Symp. on Inhalation Toxic. and Techn., Kalamazoo, Mich., Oct. 23-24, 1980
Jenkins, R. A.	Jenkins, R. A. "Tobacco Smoke from an Analyst's Standpoint: Pigeon Feathers and Chromatography Really Do Mix"	Invited, Washington, D.C., Chromatog. Discussion Grp., May 21, 1980
	Jenkins, R. A.; Wike, J. S. "Chemical Characterization of Diesel Fuel Obscurants"	2nd Symp. on Phys. and Chem. Charac. of Army Smokes/Obscurant Aerosols, Frederick, Md., Nov. 13-14, 1980
Johnson, J. M.*	Johnson, J. M.;* Lemberger, L.;* Novotny, M.;* Forney, R. B.;* Maskarinec, M. P. "Pharmacological Activity of the Basic Fraction of Marihuana Whole Smoke Condensate in Mice"	19th Annu. Meet. of the Soc. of Toxicol., Washington, D.C., Mar. 9-13, 1980
Keller, J. M.	Keller, J. M. "Application of Ion Chromatography to Nuclear Technology Development"	22nd Rocky Mount. Conf., Denver, Colo., Aug. 11-14, 1980
	Keller, J. M. "Ion Chromatography"	Anal. Chem. Div. Techn. Sup. Sec. Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Jan. 24, 1980
	Keller, J. M. "Ion Chromatography"	USDOE/UKAERE Breeder Info. Exchange Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., May 1, 1980
	Keller, J. M. "Ion Chromatography"	UCCND Anal. Meet., Oak Ridge Nat. Lab., Oak Ridge. Tenn., June 11, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Keller, J. M.	Keller, J. M. "Ion Chromatography"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 22, 1980
Kintigh, J. D.	Kintigh, J. D. "BET Surface Area Measurements"	Anal. Chem. Div. Techn. Sup. Sec. Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Feb. 28, 1980
Klatt, L. N.	Klatt, L. N. "Simultaneous Multiwavelength Measurements in HPLC and Spectroelectrochemical Studies"	Invited, Wayne State Univ., Detroit, Mich., Feb., 1980
	Klatt, L. N.; Goeringer, D. E. "Advanced Instrumentation for Analytical Hot Cells"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-22, 1980
Lackey, W. J.*	Lackey, W. J.;* Layton, F. L.; Angelini, D. P.;* Stinton, D. P.;* Vavruska, J. S.* "Sol-Gel Technology Applied to Glass and Crystalline Ceramics"	Waste Manage. 1980 Symp. Tuscon, Ariz., Mar. 13, 1980
Laing, W. R.	Laing, W. R.; Stanton, J. S.* "A Data Management System for Analytical Chemistry Laboratories"	1980 Pittsburgh Conf. on Anal. Chem. and Appl. Spectros., Atlantic City, N.J., Mar. 10-14, 1980
	Laing, W. R.; Carter, J. A.; Emery, J. F.; Shults, W. D. "Analytical Chemistry Response and Three Mile Island"	26th Annu. Meet., Am. Nucl. Soc., Las Vegas, Nev., June 8-13, 1980
Layton, F. L.	Layton, F. L. "Leaching Studies of Synroc"	Met. and Ceram. Div. Alternate High-Level Waste Forms Program Sem., Mar. 20, 1980
	Layton, F. L. "Synroc Leaching Studies"	Anal. Chem. Div. Techn. Sup. Sec. Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Apr. 24, 1980
Lee, D. A.	Lee, D. A. "Pyrolysis Mass Spectrometry of SYNROC"	180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 24-29, 1980
	Lee, D. A. "Thermal Analysis"	Anal. Chem. Div. Techn. Sup. Sec. Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Mar. 26, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Lee, D. A.	Lee, D. A. "Thermal Analysis"	Met. and Ceram. Div. Alternate High-Level Waste Forms Program Sem., Apr. 17, 1980
Loundes, D. H.*	Loundes, D. H.;* Westbrook, R. D.;* Cleland, J. W.;* Christie, W. H. "Pulsed Ruby Laser Annealing of Zn, Mg and Se Ion Implants in Semiconducting Ga As"	3rd Laser Solid Interactions and Laser Process. Conf., Boston, Mass., Nov. 15, 1980
Lyon, W. S.	Lyon, W. S. "V. P. Guinn - 1979 Hevesy Award Winner"	4th Int. Conf. on Nucl. Methods in Environ. and Energy Res., Columbia, Mo., Apr. 14-17, 1980
	Lyon, W. S. "Nuclear Methods in Coal Research"	Invited, 4th Int. Conf. on Nucl. Methods in Environ. and Energy Res., Columbia, Mo., Apr. 14-17, 1980
	Lyon, W. S.; Bujdoso, E.;* Braun, T.* "The Flow of Journal Information in Analytical Chemistry"	Southeast-Southwest Reg. Am. Chem. Soc. Meet., New Orleans, La., Dec. 10-13, 1980
MacDougall, C. S.	MacDougall, C. S. "Study of the Nitric Acid Sugar Reaction"	Chem. Techn. Div. Fuel Reprocessing R&D Sem., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Jan. 14, 1980
	MacDougall, C. S. "CFRP Chemical Methods Development"	USDOE/UKAERE Breeder Info. Exchange Meet., May 1, 1980
	MacDougall, C. S.; Costanzo, D. A. "CFRP Chemical Methods Development"	CFRP Semiannual Techn. Program Rev. of Process R&D Tasks, Oak Ridge Nat. Lab., Oak Ridge, Tenn., Aug. 13-14, 1980
Mamantov, G.	Mamantov, G.; Norvell, V. E.; Klatt, L.; Tanemoto, K.;* Marassi, R.;* Ogata, Y.;* Matsunaga, M.;* Wiaux, J. P.;* Mamantov, C. B.* "Spectroelectrochemical and Other Studies of Sulfur and Its Halides in Chloroaluminate Melts Application to a New Rechargeable High Voltage Low Temperature Cell"	3rd Int. Symp. on Molten Salts, Hollywood, Fla., Oct. 5-10, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Marley, J. L.	Marley, J. L. "Analytical Requirements for the Hot Experimental Facility"	USDOE/UKAERE Breeder Infor. Exchange Meet., May 1, 1980
Maskarinec, M. P.	Maskarinec, M. P. "Evaluation of a Continuous Extraction Device for the Analysis of Solid Wastes"	Gordon Res. Conf., (Poster Session), New Hampton School, New Hampton, N.H., Aug. 11-15, 1980
	Maskarinec, M. P.; Manning, D. L. "Liquid Chromatography with Microbore Columns"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-23, 1980
	Maskarinec, M. P.; Manning, D. L. "Liquid Chromatography with Microbore Columns"	Union Carbide Corp. Specialists Meet., Tarrytown, N.Y., Sept. 23, 1980
Mueller, T. R.	Mueller, T. R.; McKown, H. S.; Warmack, R. J.; Smith, D. H. "An Interface and Data Acquisition Systems for Two Spectrometers"	28th Annu. Conf. on Mass Spectrom. and Allied Topics, New York, N.Y., May 25-30, 1980
Oakes, T. W.*	Oakes, T. W.;* Bird, J. C.;* Shank, K. E.;* Kelley, B. A.;* Harrison, L. L.;* Clark, B. R.; Rogers, F.* "Waste Oil Management at Oak Ridge National Laboratory"	1980 UCCND and GAT Waste Manage. Seminar, Friendship, Ohio, Apr. 22-23, 1980
Peterson, J. R.*	Peterson, J. R;* Young, J. P.; Haire, R. G.* "Bulk-Phase Studies of the Chemical and Physical Consequences of Radioactive Decay in the Solid State"	10th Journees des Actinides, Stockholm, Sweden, May 27-28, 1980
	Peterson, J. R.;* Young, J. P.; Haire, R. G.;* Ensor, D. D.* "Absorption Spectroscopy of of Transcurium Element Solids"	Invited, Southeast-Southwest Reg. Anal. Chem. Soc. Meet., New Orleans, La., Dec. 10-13, 1980
Ramsey, J. M.	Ramsey, J. M. "Spatial and Temporal Sample Wedging in Flame Atomic Absorption Spectrometry"	1980 Pittsburgh Conf. on Anal. Chem. and Appl. Spectros., Atlantic City, N.J., Mar. 10-14, 1980
	Ramsey, J. M. "Correlation Methods for the Measurement of Fluorescence Lifetimes"	Invited, 33rd Annu. Anal. Sum. Symp. sponsored by Anal. Chem. Soc. Div. and Anal. Chem., June 5-7, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Ramsey, J. M.	Ramsey, J. M. "Delayed Lasing: A New Approach to Absorption Spectroscopy"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-22, 1980
Rao, T. K.*	Rao, T. K.;* Epler, J. L.;* Guerin, M. R.; Clark, B. R.; Ho, C-h. "Mutagenicity of Nitrogen Compounds from Synthetic Crude Oils: Collection, Separation, and Biological Testing"	Appl. Short-Term Bioassays in the Fractionation and Analysis of Complex Environ. Mixtures, Williamsburg, Va., Mar. 4-7, 1980
Reynolds, S. A.	Reynolds, S. A. "Assay of Beta Emitters by Cerenkov Counting"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 22, 1980
Ricci, E.	Ricci, E. "XRF Multidetermination of Zr and Hf Tracer in Solutions Relevant to Energy Research"	1980 Annu. Meet., Am. Nucl. Soc., Las Vegas, Nev., June 8-13, 1980
Rogers, C. W.	Rogers, C. W. "Lectures - Efficient Numerical Calculations on Microcomputers and Fourth Generation Languages in the Laboratory"	Invited, Am. Chem. Soc. Short Course: Microprocessors and Minicomputers - Interfacing and Applications, Blacksburg, Va., Dec. 17-19, 1980
Ross, H. H.	Ross, H. H. "Optical Spectroscopy in the Time Domain Using a Radioisotope Light Source"	Invited, Shell Development Co., Dedication of New Radiochemical Facilities, Houston, Tex.
	Ross, H. H. "Analytical Methods for Safeguards at Nuclear Fuel Cycle Facilities"	Invited, Graduate/Faculty Seminar, Nucl. Eng., Dept., North Carolina State Univ., Oct. 30, 1980
	Ross, H. H. "Advanced Techniques in Liquid Scintillation Counting"	Invited, Oak Ridge Assoc. Univ., Apr. 16, 1980
Rubin, I. B.	Rubin, I. B.; Bayne, C. K. "A Bench Chemist's Viewpoint of Optimization Techniques"	Invited, Sum. Symp. on Anal. Chem., Duke Univ. Durham, N.C., June 4-6, 1980
	Rubin, I. B.; Bayne, C. K. "A Bench Chemist's Viewpoint of Optimization Techniques"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-22, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Russell, D. H.	Russell, D. H.; Mueller, T. R.; Rainey, W. T. "ORNL Multi-Sector Mass Spectrometer for High Resolution MS/MS"	1980 DOE Mass Spectrom. Work Shop, Seattle, Wash., Jan. 3-4, 1980
	Russell, D. H.; McBay, E. H.; Mueller, T. R. "High-Resolution MS/MS Via Multi-Sector Mass Spectrometers"	28th Annu. Conf. on Mass Spectrom. and Allied Topics, New York, N.Y., May 25-30, 1980
Samhoun, K.*	Hobart, D. E.;* Samhoun, K.;* Haire, R. G.;* Young, J. P.; Jaber, M.;* Peterson, J. R.* "Stabilization of Pr(IV), Tb(IV) and Am(IV) in Aqueous Solutions"	10th Journees des Actinides, Stockholm, Sweden, May 27-28, 1980
Scott, T. G.	Scott, T. G. "An Approach to Tailing Corrections in Alpha Spectrometry"	Info. Exchange in Alpha Spectrom., Idaho Falls, Idaho, May 20, 1980
Shults, W. D.	Shults, W. D.; Carter, J. A.; Emery, J. F.; Laing, W. R. "Analytical Chemistry Response and Three-Mile Island"	1980 Annu. Meet., Am. Nucl. Soc., Las Vegas, Nev., June 8-13, 1980
Smith, D. H.	Smith, D. H.; Christie, W. H.; Walker, R. L.; Carter, J. A. "Oak Ridge National Laboratory R&D Programs in Actinide and Other Inorganic Mass Spectrometry"	1980 DOE Mass Spectrom. Work Shop, Seattle, Wash., Jan. 3-4, 1580
Stewart, J. H.	Stewart, J. H. "Generic Specifications for Purchase of X-Ray Fluorescence Spectrometer"	ASTM C-26 Nucl. Fuel Cycle Meet., New Orleans, La., Jan. 14-17, 1980
	Stewart, J. H. "X-Ray Fluorescence in Support of CFRP Analytical Needs,"	CFRP Process R and D Program Rev., Oak Ridge Nat. Lab., Oak Ridge, Tenn., Mar. 9, 1980
	Stewart, J. H. "Technical Review of Process R and D Tasks of the Consolidated Fuel Reprocessing Program"	Oak Ridge Nat. Lab., Oak Ridge, Tenn., Aug. 14, 1980
Todd, P. J.	Todd, P. J.; McLafferty, F. W.;* McGilvery, D. C.;* Baldwin, M. A.* "The Performance of a Multiple-Sector Mass Spectrometer for Collisional Activation"	24th Conf. on Anal. Chem. in Energy Techn., Gatlinburg, Tenn., Oct. 7-9, 1980
	Todd, P. J.; McGilvery, D. C.;* Baldwin, M. A.;* McLafferty, F. W.* "A Tandem Double-Focusing Mass Spectrometer for Gas Phase Ion Studies"	28th Annu. Conf. on Mass Spectrom. and Allied Topics, New York, N.Y., May 25-30, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Tomkins, B. A.	Tomkins, B. A.; Kubota, H. "The Confident Determination of Benzo(a)pyrene in Natural, Synthetic, and Refined Crudes"	1980 Pittsburgh Conf. on Anal. Chem. and Appl. Spectrom., Atlantic City, N.J., Mar. 10-14, 1980
	Tomkins, B. A.; Feldman, C. "The Determination of Primary and Secondary Aromatic Amines by Gas Chromatography with a Glow Discharge Detector"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-22, 1980
Walker, R. L.	Walker, R. L. "Mass Spectrometry Used in Support of an Evaluation of a NDA Method for Determining Fissile Content of Spent Fuels"	Chem. Tech. Div. Seminar, Oak Ridge Nat. Lab., Oak Ridge, Tenn., Aug. 7, 1980
	Walker, R. L.; Scott, T. G. "Chemistry and Measurement of Tc in Environmental Samples"	Anal. Chem. Div. Annu. Info. Mtg., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-22, 1980
Walton, B. T.*	Walton, B. T.;* Buchanan, M. V. "Teratogenic Effects of Fossil Oils on Insects Developing in Contaminated Substrates"	180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 24-29, 1980
	Walton, B. T.;* Buchanan, M. V.; Jones, A. R.; Ho, C.-h. "Isolation, Identification and Physicochemical Properties of an Insect Teratogen"	Annu. Meet. of the Am. Soc. of Zoologists, Seattle, Wash., Dec. 27-30, 1980
Warmack, R. J.	Warmack, R. J. "Development in SSMS"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-23, 1980
Weinberger, A. J.	Weinberger, A. J.; Hulett, L. D. "Some Studies of the Structure and Chemical Composition of Fly Ash"	5th Annu. Spring Workshop, Assoc. of Off. Anal. Chem., St. Louis, Mo., Apr. 7-10, 1980
Whitten, W. B.	Whitten, W. B.; Ramsey, J. M. "Multiphoton Relaxation Rates from Delayed Laser Emission in Nd-YAG Crystals"	Am. Phys. Soc., New York, N.Y., Mar. 24, 1980
	Whitten, W. B. "Analytical Applications of Fiber Optic Waveguides"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-23, 1980
Wood, R. F.*	Wood, R. F.;* Young, R. T.;* Narayan, J.;* Westbrook, R. D.;* White, C. W.;* Christie, W. H. "Laser Processing for High Efficiency Solar Cells"	IEEE 14th Photovoltaic Specialist Conf., Jan. 7-11, 1980

SPEAKER	AUTHOR(S) AND TITLE	PRESENTED AT
Wood, R. F.*	Wood, R. F.;* Loundes, D. H.;* Christie, W. H. "Pulsed Laser Annealing of Ion-Implanted Ga As: Theory and Experiment"	3rd Laser Solid Interactions and Laser Processing Conf., Boston, Mass., Nov. 15, 1980
Yeatts, L. B.	Yeatts, L. B.; Griest, W. H.; Guerin, M. R. "Comparative Research Material for Generic Health Effects Investigations of Synfuels"	Southeast-Southwest Reg. Am. Chem. Soc. Meet., New Orleans, La., Dec. 10-13, 1980
Young, J. P.	Bemis, C. E.;* Beene, J. R.;* Young, J. P.; Kramer, S. D.* "Study of the Fission Isomer Am (S.F.) Using Laser Induced Nuclear Polarization"	Invited, 180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 25-29, 1980
	Young, J. P.; Haire, R. G.;* Peterson, J. R.;* Ensor, D. D.* "Chemical Consequences of Radioactive Decay in the Solid State: Extent of Progeny Compound Growth in the Decay of $^{253}EsCl_3$ and $^{253}EsBr_3$"	180th Nat. Am. Chem. Soc. Meet., Las Vegas, Nev., Aug. 25-29, 1980
	Young, J. P. "Resonance Ionization Spectroscopy"	Anal. Chem. Div. Annu. Info. Meet., Oak Ridge Nat. Lab., Oak Ridge, Tenn., July 21-23, 1980
	Young, J. P. "Chemical Consequences of Radioactive Decay"	Chem. Div. Seminar, Oak Ridge Nat. Lab., Oak Ridge, Tenn., Jan. 23, 1980
Young, R. T.*	Young, R. T.;* Wood, R. F.;* Narayan, J.;* Westbrook, R. D.;* Christie, W. H. "Laser Techniques for the Fabrication and Study of Polycrystalline Solar Cells"	IEEE 14th Photovoltaic Specialists Conf., Jan. 7-11, 1980

ANALYTICAL CHEMISTRY DIVISION SEMINARS AT ORNL

Speaker	Title	Date
Ogan, K. Perkin-Elmer Corp. Norwalk, CT	"Environmental Application of High-Pressure Liquid Chromatography"	Dec. 13, 1979
Harper, A. Dept. of Chem. Univ. of Georgia Atlanta, GA	"Pattern Recognition in Chemistry"	Jan. 18, 1980
Nibbering, N.M.M. Lab. for Organic Chem., Univ. of Amsterdam, The Netherlands	"Some Recent Studies on (an)ionic Cycloaddition and Anionic Addition-Elimination Reactions in the Gas-Phase"	Mar. 17, 1980
Lockmuller, C. H. Dept. of Chem., Duke Univ., Durham, NC	"Novel Concepts in Bonded Phase Structure for Liquid Chromatography"	Apr. 30, 1980
Kissinger, P.T. Purdue Univ., W. Lafayette, IN	"Environmental and Toxicological Applications of Liquid Chromatography with Electrochemical Detection"	May 20, 1980
Wright, J. Univ. of Wisconsin, Madison, WI	"Application of Probe Ion Techniques to Solid State Chemistry and Trace Analysis"	June 9, 1980
Watson, R. L. Texas A&M Univ., College Station, TX	"X-Ray Excitation by Heavy-Ion Bombardment"	July 7, 1980
Schaap, H. Electricity Comm. of Victoria, Australia	"Some Studies of Australian Brown Coal: Its Ash and Environmental Aspects"	Aug. 6, 1980
Hercules, D. M. Univ. of Pittsburgh Pittsburgh, PA	"Analytical Chemistry of Surfaces Using Modern Spectroscopy"	Aug. 7, 1980
Guinn, V. P. Univ. of California Irvine, CA	"Some Interesting Criminal Cases Involving Neutron Activation Analysis"	Aug. 11, 1980
Ratynski, W. Inst. of Nuclear Research, Swierk, Poland	"Applicability of Uranium Lα X-Ray Lines for Determination of Low Uranium Concentrations"	Aug. 14, 1980

ANALYTICAL CHEMISTRY DIVISION SEMINARS AT ORNL

Speaker	Title	Date
Burtis, C. Chem. Tech. Div., ORNL, Oak Ridge, TN	"The Development of a National Reference System in Clinical Chemistry"	Aug. 28, 1980
Fenselau, C. The Johns Hopkins Univ. School of Medicine, Baltimore MD	"Synthesis and Mass Spectrometric Analysis of Glucuronides"	Oct. 30, 1980
Taylor, J. W. Dept. of Chem. Univ. of Wisconsin, Madison, WI	"Problems of Structure and Analysis Using Electrons, Ions, and Synchrotron Radiation"	Nov. 19, 1980

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

	Anal. Chem.	*Anal. Chim. Acta*	*Anal. Lett.*	ANSI Methods	ASTM Methods	*Clin. Chem.*	*Environ. Sci. Technol.*	EPA Reports	*J. Chem. Ed.*	*J. Environ. Qual.*	*J. Polym. & Colloid Sci.*	*Mol. Crys. Liq. Cryst.*	*Opt. Lett.*	ORNL Reports	Proceedings	Proposals	*Science*	*Sep. Sci. & Tech.*	Surgeon General Report	*Radiochem. Radioanal. Lett.*	Total
Carter, J. A.	1																				1
Caton, J. E.						2															2
Clark, B. R.	1															1					2
Costanzo, D. A.														1							1
Dyer, F. F.	1	3																			4
Eldridge, J. S.	2													2	2						6
Emergy, J. F.	2																				2
Feldman, C.	4									1											5
Griest, W. H.	1							1								1					3
Guerin, M. R.								1						1		1			1		4
Holmberg, R. W.	1						1														2
Hulett, L. D.	2										1			3							5
Keller, J. M.														1							1
Klatt, L. N.									1												1
Laing, W. R.														2		1					3
Lee, D. A.														1							1
Lyon, W. S.	2		1				1									2	1			4	11
MacDougall, C. S.	3																				3
Maskarinec, M. P.																1					1
Mueller, T. R.	1																				1
Ramsey, J. M.	4																				4
Reynolds, S A.	3			1	5									1	1						11
Shaw, R. W.																5					5
Shults, W. D.	2	3														3					8
Tomkins, B. A.						1												1			2
Walker, R. L.			1																		1
Whitten, W. B.												1									1
Young, J. P.	3												2			1					6
Total	33	6	2	1	5	3	2	2	1	1	1	1	2	12	3	16	1	1	1	4	97

DIVISIONAL MAN-POWER AND FINANCIAL SUMMARY
FY 1980

Source	Funding (in thousands)	Man-years
DOE programs		
Basic Energy Sciences	1,047	12.5
Environment Research and Development	1,194	16.5
Nuclear Materials Security and Safeguards	100	1.0
Consolidated Fuel Reprocessing Program	460	6.0
Reactor Research and Development	80	1.0
Defense Nuclear Waste	49	0.5
Fossil Energy	53	1.0
Total DOE programs	2,983	38.5
Work for others - federal agencies		
National Cancer Institute	365	5.5
Department of Defense (U.S. Army)	470	7.0
Environmental Protection Agency	546	4.5
State Department (I.S.P.O.)	118	1.5
Miscellaneous	12	0.0
Total work for others - federal agencies	1,511	18.5
Work for others - nonfederal agencies		
Council for Tobacco Research	109	1.0
Electric Power Research Institute	193	2.5
Protective coating companies	57	1.0
IBM	15	0.5
Miscellaneous	50	1.0
Total work for others - nonfederal agencies	424	6.0
ORNL divisions - support	5,607[a]	89.0
Others	627[a]	10.0
Total financial plans	11,152	162.0

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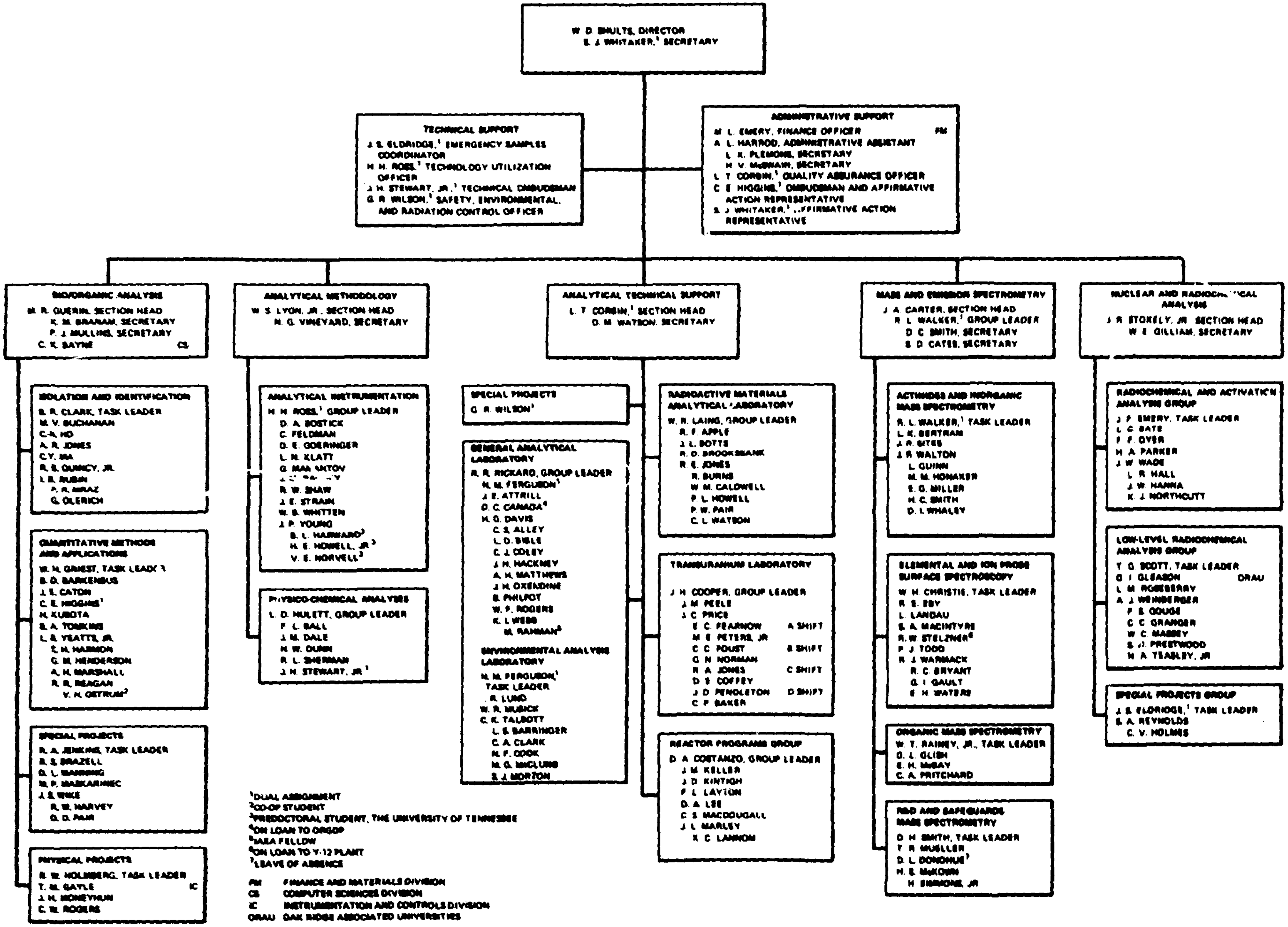
[a] Reflects Laboratory general and administrative expenses and general plant services.

ANALYTICAL CHEMISTRY DIVISION

DECEMBER 31, 1980



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S. A. REYNOLDS
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[2] CO-OP STUDENT
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[4] ON LOAN TO ORGDP
[5] IAEA FELLOW
[6] ON LOAN TO Y-12 PLANT
[7] LEAVE OF ABSENCE

FM FINANCE AND MATERIALS DIVISION
CS COMPUTER SCIENCES DIVISION
IC INSTRUMENTATION AND CONTROLS DIVISION
ORAU OAK RIDGE ASSOCIATED UNIVERSITIES