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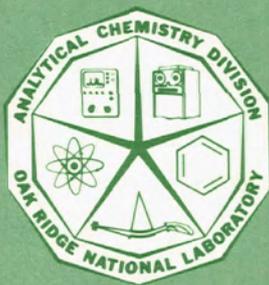


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ORNL-5518

# ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT  
Period Ending December 31, 1978



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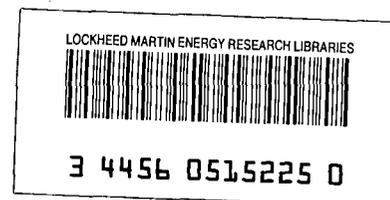
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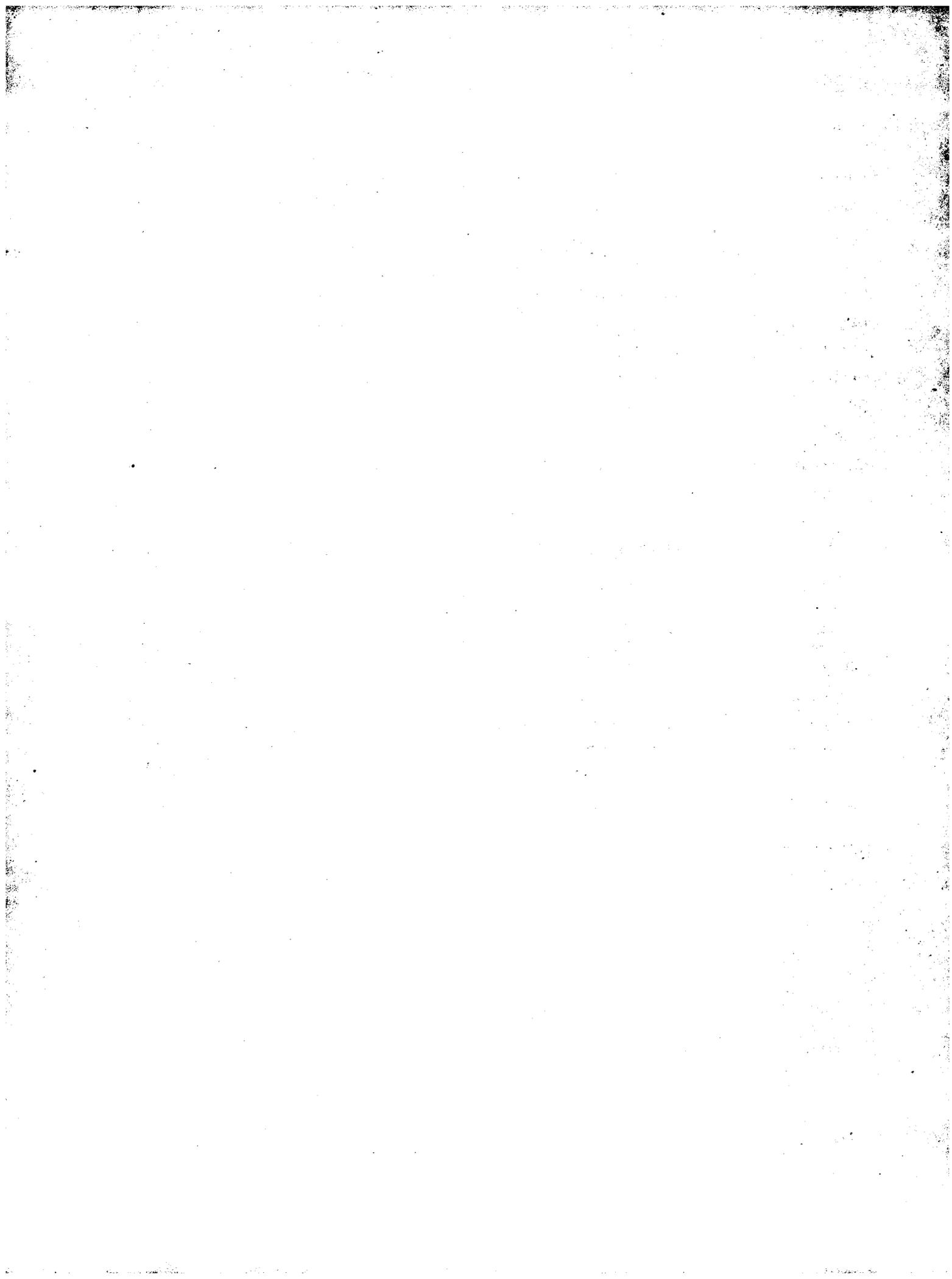
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## Introduction and Summary

W. D. Shults

The Analytical Chemistry Division of Oak Ridge National Laboratory is a large and diversified analytical chemical organization. As such, it serves a multitude of functions for a clientele that resides both within and outside ORNL. These functions fall into the following four general categories:

- 1. Basic Analytical Research, Development, and Implementation (RD&I).** The division maintains an RD&I 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 DOE programs, but attention is also given to needs in the analytical sciences themselves. This program comprises medium- to long-term projects and is supported primarily by DOE. The program constituted approximately 15% of the FY 1978 budget.
- 2. Programmatic Research, Development, and Utilization.** The division carries out a wide variety of analytical work that typically involves research and/or development plus the utilization of analytical research and development (R&D) results or special analytical capabilities to expedite programmatic interests. The effort in this category comes from division, ORNL, and DOE programs and from "Work-for-Others" agreements. Emphasis here is on short- to medium-term projects, depending on the programs themselves. This type of activity accounted for approximately 25% of the division's budget in FY 1978.
- 3. Analytical Service and Assistance.** The division performs chemical and physicochemical analyses and tests of virtually all types on both routine and nonroutine bases. 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 largely from other divisions and programs within ORNL; however, a significant fraction originates outside ORNL. Work that comes from outside ORNL of an analytical service-assistance nature often involves the use of talent and/or facilities in which the division is particularly strong or that are unusual or even unique. This effort accounted for approximately 45% of the budget during FY 1978.
- 4. Consultation, Collaboration, and Special Projects.** This work is distinguished from the analytical service-assistance function by the nature of interaction between the division and its clientele; that is, 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 comprised approximately 15% of the FY 1978 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 December 1, 1977, to December 31, 1978. The following paragraphs highlight progress in the various sections.

**Analytical Methodology Section (Chap. 1).** Spectroscopy continues to be prominent in the research effort of the Analytical Instrumentation Group. Work is under way in microspectrophotometry,

resonance ionization spectroscopy, optoacoustic spectroscopy, simultaneous multispectral detection, plasma emission (glow discharge) detection, and a totally new technique that we call time-of-flight optical spectroscopy. This group is also engaged in a major way in the development of in-line monitoring instrumentation for the Advanced Fuels Recycle Program, with personnel of the Instrumentation and Controls Division.

Study of microgram quantities of compounds of the actinides—their stability, reactivity, and thermal properties—has continued, with microscopic-level spectrophotometry and x-ray diffraction as the prime tools. During this period, our studies into the actinide halides have been extended. The chlorides and bromides of curium, americium, and plutonium, and the trifluorides of einsteinium, berkelium, and californium have been investigated. There is a natural bond between such studies and the resonance ionization spectroscopy (RIS) research program at ORNL directed by G. S. Hurst. J. P. Young serves as analytical liaison. The RIS team has completed and published RIS studies into the detection of single cesium fission fragments from californium-252 this year and has demonstrated that lithium atoms can be detected by the three-photon, two-saturated-energy states regime. New activities include studies into laser-induced nuclear polarization for investigating short-lived nuclei (led by C. E. Bemis) and development of ultralow-level counting techniques by combination of RIS and radioactivity detection (led by G. S. Hurst).

We have continued to study laser-based optoacoustic spectroscopy to assess its potential as an analytical technique. Modifications to the instrumentation included incorporation of a ratiometer, a gated integrator, and a photodiode detector in the reference channel; these changes have allowed the frequency response of the optoacoustic signals to be studied. We observe low- and high-frequency components that are dependent on both the cell cavity and the sample itself. Conclusions thus far are that this laser-based system offers more resolution and has comparable sensitivity to systems that use conventional light sources. An interesting spin-off from this research has been the design of a laser-power meter based on detection of optoacoustic response.

Research with rapid-scan spectrometry has continued, with emphasis on the detection of liquid chromatographic effluents. Improvements were made to afford three-dimensional presentation of

absorbance-wavelength-time data, plus a factor-of-two gain in sensitivity. The capability of this approach for quantitative work has been studied. We find this system to be equivalent in sensitivity to others used as liquid chromatographic (LC) detectors, but it possesses unique features that enhance its analytical utility. In the realm of gas chromatographic detection, we have continued to develop and apply plasma emission or "glow discharge" spectrometry because it offers excellent selectivity and sensitivity. Our procedures for determining trace and ultratrace quantities of arsenic (as arsine) and methylarsines are based on glow discharge detection; these have been refined and taught to personnel in other groups this year to meet the demand for this type of analysis. Work with plasma emission spectrometry is now focused on the detection and measurement of fluorine in organic and inorganic matrices.

The acquisition of multispectral data is of much interest in analytical chemistry at present, both from the instrumentation and the applications points of view. During this period, we began to investigate a new approach to multiwavelength spectroscopy in which optical signals are resolved in the time domain rather than the spatial domain. This project was initiated through ORNL's Exploratory Studies Program. Briefly, the idea is to exploit the wavelength dependency of the speed of light through a given dielectric; thus different wavelengths of light should be separable and detectable after passage through an appropriate medium. H. H. Ross and W. B. Whitten have confirmed the feasibility of this concept, using a 1.1-km fiber optic as resolving medium. They were able to obtain time resolution of about  $0.3 \text{ ns nm}^{-1} \text{ km}^{-1}$  (this is wavelength dependent) or a time differential of about 155 ns over the wavelength range 436–900 nm. The total system time resolution is of the order of 3 ns over this wavelength region, which is adequate for many analytical applications. This work is embryonic, but its potential is exciting; presentation and publication are scheduled for early 1979.

In the last annual report, a new project was reported: the development of in-line sensors for the Advanced Fuels Recycle Program (AFRP). Our role is to conceptualize and demonstrate feasibility of a wide variety of monitors for a nuclear fuel reprocessing facility; Instrumentation and Controls Division develops the needed software and hardware after a given concept is specified. We have made much progress during this period. Development of a

monitor for soluble neutron poisons is complete and has been reported. Basic work on a dual-wavelength monitor for uranium and nitric acid has been completed, and a prototype instrument is being designed for solutions of high acidity. The dual-wavelength approach is under study for monitoring organic as well as aqueous streams of low acidity. Feasibility of a "free acid" monitor, based on vapor phase condensation plus interrogation of the condensate, has been demonstrated, and engineering design has begun. We are studying the use of refractive index for monitoring pure  $\text{HNO}_3$  or  $\text{HNO}_3 + \text{UO}_2(\text{NO}_3)_2$  streams. Somewhat related to this program is a new Analytical Chemistry Division project directed at developing state-of-the-art analytical hot-cell instrumentation. This project was initiated in October 1978 to utilize and maintain modern electronics technology in our unique instrumentation systems.

A new activity in the Physicochemical Analysis Group last year, joint with the Environmental Sciences Division, was the study of chemical characteristics of ponded ash from a modern coal combustion power station. We have found that the ash comprises four phases—a glassy phase, a mullite (aluminosilicate) phase, a spinel (magnetite) phase, and a carbon-cinder phase. The composition and trace element distribution in these phases have been studied in some detail to determine if chemical species in fly ash are determined by or are dependent on the phase that attracts a given constituent. In general, the glass and mullite phases attract alkalis, alkaline earth elements, rare earth elements, scandium, and titanium. The magnetite phase attracts transition elements such as Mn, Co, Mo, V, Cr, and U. Sulfur is primarily associated with the carbon cinder. These findings can be of significance in understanding and dealing with both ecological impact and resource recovery. Emphasis in this Electric Power Research Institute program is moving toward surface characterization of fly ash and similar solid wastes.

Much progress has been made also in the instrumentation projects within the Physicochemical Analysis Group. Incorporation of a graphite monochromator into our x-ray diffraction unit, between the specimen and detector, has afforded marked improvement in signal-to-noise ratio, that is, sensitivity. The x-ray fluorescence (XRF) operation has been improved in two ways: additional memory and software was added to the analytical XRF system, and XRF capability has been added to our new scanning electron microscope. The magnetically focused photoelectron spectrometer has been revamped and is now in service. The ORNL-built

electrostatic electron spectrometer has been put into operation and is being used and evaluated concurrently.

A new research project was initiated with the electrostatic instrument, with special funding from ORNL's Exploratory Studies Program: positron scattering spectrometry. The basic hypothesis is that a positron beam scattered from a specimen should exhibit absorption peaks in its energy spectrum as a result of electron-positron annihilation, if energy-dependent resonant capture occurs for positrons. Additionally, annihilation of core electrons should produce Auger electrons that would be relatively free of secondary electron background (which accompanies electron excitation). Positive "particles" have been observed in initial experiments with the electrostatic spectrometer operated with reversed polarity and a positron source, but indications are that the "particles" may be ions rather than positrons. Accordingly, we are acquiring a  $^{58}\text{Co}$  source that should not produce ions. Further study of this concept is anticipated.

**Mass and Emission Spectrometry Section (Chap. 2).** Means for quantifying results obtained by ion microprobe mass analysis (IMMA) is an activity of major interest. We have studied various theoretical and empirical approaches to quantitation and have participated in collaborative studies with other laboratories during the past several years. During the current reporting period, we studied the use of matrix-corrected sensitivity factors in quantifying IMMA data and obtained excellent results. In this technique, sensitivity factors for elements of interest are normalized by reference to some matrix ion species, for example, the ratio  $\text{NiO}^+:\text{Ni}_2^+$ . Oxygen flooding was found to provide improved accuracy and precision. In essence, the matrix ion correction accounts for differences in matrix from one specimen to another. This technique made it possible for us to carry out a study of Chromel-Alumel thermocouples that lost calibration at about  $1100^\circ\text{C}$ . That study has been published.

Laser annealing of ion-implanted  $^{11}\text{B}$  in solar grade silicon is being studied in the Solid State Division and contrasted with thermal annealing. We have participated in this study by carrying out IMMA investigations. Our function is to determine boron profiles within the crystal with the IMMA. These profiles are then correlated with annealing conditions. We have found that virtually no boron is lost during laser annealing, that profiles become broader as the boron is implanted deeper into the crystal, and that little redistribution of boron occurs after a two-laser pulse

of about  $2 \text{ J/cm}^2$ . Because of the great demand for IMMA work, we are proceeding to computerize the system for both control and data processing.

Two spark-source mass spectrometry (SSMS) projects should be highlighted here. We have installed and tested a channel electron multiplier array as the detector for an MS-702A instrument. This approach to electro-optical detection of SSMS signals was found to provide a 100-fold gain in sensitivity over photoplates plus a dynamic range of about 100. Resolution is less than that of photoplates, but usable. A two-stage digitization system specifically for isotope dilution SSMS applications is being developed. Much progress has also been made toward establishing SSMS capabilities for highly radioactive materials. Feasibility studies were completed and reported this year, and a surplus instrument was acquired and made operative. The shielded cubicle and transfer system is being designed by the Engineering Division now. This system when completed will be unique; it should be capable of handling solid samples that read 40 R/h at 1 cm.

Research into and implementation of our "resin bead" technique for ultratrace mass spectroscopic analysis is accelerating. Research has emphasized means for measuring  $^{99}\text{Tc}$  and  $^{148}\text{Nd}$ . The former is of interest because of environmental significance; the latter is of interest for burnup measurements. Preliminary results with  $^{99}\text{Tc}$  indicate that use of the resin bead improves ionization efficiency by a factor of 50. If a suitable supply of  $^{97}\text{Tc}$  can be obtained for spiking, as little as 1 pg of technetium should be measurable with about 10% precision. It has been possible to determine 1 ng of neodymium on a single bead with about 3% precision, using thermal emission mass spectrometry (MS) and pulse counting. The important aspect of this procedure is that solutions of irradiated fuels may be analyzed without the usual time-consuming and error-producing chemical separations.

We have reported research into the use of the resin bead technique for uranium and plutonium analysis over the last several years. The results of this research are now being used broadly for nuclear safeguards purposes. We are continuing to develop and refine techniques while assisting and teaching others. A major accomplishment this year has been our demonstration that satisfactory results for uranium and plutonium can be obtained with a single-stage instrument. This demonstration means that many more laboratories should be able to adopt the technique than would be possible if sophisticated

MS systems were mandatory. We are exploring the possibility of developing a semiportable MS system for onsite monitoring of major isotope ratios. Meanwhile, real samples are being exchanged and analyzed for the International Atomic Energy Agency and the International Safeguards Project Office to implement the technique. Because of this work and other applications that utilize high abundance sensitivity MS, we initiated work last year to modernize and enhance the electronics in our spectrometers. The interface has been designed and installed, and both operating and data processing programs have been developed. A few bugs remain, but this highly flexible system is virtually complete.

A new gas inlet system was designed and put into use on our AEI MS-50/DS-50 organic MS system this year to improve analysis of mixtures that contain condensable organic vapors. Research with the MS-50 has emphasized studies of the chemistry of  $\text{C}_7\text{H}_7\text{O}^+$  as derived from various molecules. A large number of compounds and deuterated derivatives have been examined using the linked scanning modes of the MS-50 instrument. The objective is to gain fundamental information about the reactions and reaction mechanisms that involve the  $\text{C}_7\text{H}_7\text{O}^+$  moiety, ultimately yielding a better understanding of the effects of structural configuration on mass spectra.

Two ORNL-built MS systems are available for R&D work in organic MS. A single-stage machine was equipped with gas chromatographic (GC) capillary column capability this year and used extensively for support of EPA programs. The double-focusing instrument is currently undergoing extensive modifications to improve and expand its performance. Chemical ionization hardware is being designed for this machine. A second electrostatic analyzer stage is under design and will be added so that the system can be operated in a three-stage mode. This hardware development is being done in order to carry out research into collision- and photo-induced dissociation processes in organic MS.

**Analytical Services Section (Chap. 3).** This section has continued to provide a broad spectrum of chemical measurements in support of numerous ORNL and extra-ORNL programs. During this reporting period, work related to fossil energy programs has decreased, environmentally related work has remained virtually constant, and support for nuclear programs has increased.

The Reactor Programs Group has continued work for the various nuclear reactor/recycle programs at ORNL and serves as liaison between these programs

and other groups in the division. Study of fission product behavior in components of the Peach Bottom Reactor was completed, and the results were published. Subsequently, a study of tritium behavior was conducted, and we were able to account for about 90% of the tritium formed. The time-of-flight mass spectrometer, used for on-line studies in the HTGR program, was enhanced by addition of a data system and a hard-copy terminal. This system was used for several HTGR projects: a study of the efficiency of various traps for gaseous effluents, determination of reaction products of pyrolysis of "green stick," and comparison of several levitating gases used in the carbonization process. An extensive study of steam corrosion on graphite was also completed during this period.

Organophosphorus compounds are of special importance in nuclear fuel reprocessing. We examined the GC behavior of several relevant compounds (tributylphosphate and its degradation products) on Dexsil-300 and found satisfactory GC conditions for their analysis. The Fourier transform/infrared spectra of these organic compounds were also studied from 625 to 300/cm, and subtle differences were observable. Conditions were established for separating nitrate-nitrite and nitrate-azide by liquid chromatography. Considerable effort was put into assessing and refining procedures for Zr, U, Th, and "free acid" and into evaluating commercial instrumentation that might be usable remotely. Currently, we are emphasizing such physical measurement needs as surface area and density. A small satellite laboratory was established for onsite support of AFRP experimental programs.

Each of the other groups in this section must cope with a wide variety of analytical problems and special projects and characteristically must participate in collaborative studies with members of other divisions. An important function is that we maintain awareness of new developments in analytical technology and adopt them when appropriate. This year we acquired an ion chromatograph and began to apply this new technique to our problems. A new multichromatographic data system was acquired along with a thermometric titrator and several conventional titrators. Plans were developed for a divisional program aimed at upgrading our analytical instrumentation, particularly the hot-cell instrumentation.

Another activity that warrants mention is our testing program for coatings (paints) used in the nuclear industry. Capabilities are maintained

whereby the three major tests can be performed: decontamination factor, radiation resistance, and simulated loss-of-coolant accident. During this reporting period, 1800 steel-panel and concrete-block specimens were examined for 28 manufacturers and nuclear utility companies as part of this activity.

The division's computer-based Data Management System was placed into operation in the Intermediate-Level Radiochemical Laboratory and Transuranium Laboratory this year. Additional refinements were made on the system for divisional purposes, and a significant addition was made by providing customer access to some portions of the system. This means that customers within ORNL can enter the required information about samples as they are submitted and can access their analytical results at any time. This feature should prove especially valuable to major customers within ORNL. We are examining ways in which the Data Management System can be tailored and used to meet the specific needs of *programs* within the division.

**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. The section develops and provides methodology, materials, and hardware for biological and environmental studies and data to support these studies. There are four groups in the section: Energy Technology Programs, Environmental Programs, Tobacco Chemistry Programs, and Special Projects. Considerable overlap of technical interests exists between these groups and groups in other sections in the division. Because of the programmatic nature of the work in this section, much of the effort is directed at acquiring significant *information* as opposed to *data*.

The Energy Technology Programs Group participated in a collaborative study with the Pittsburgh Energy Technology Center (PETC) in which shale oils were combusted under controlled conditions for comparison with No. 6 fuel oil. During combustion, parameters such as O<sub>2</sub>, CO<sub>2</sub>, CO, NO, NO<sub>x</sub>, SO<sub>2</sub>, and total hydrocarbons were monitored, and particulates and volatile organics were sampled for analysis at ORNL. The results were surprising. The two shale oils—Parahoe and Laramie derived—had comparable elemental compositions and exhibited similar combustion behavior. No polycyclic aromatic hydrocarbons (PAHs) or heteroaromatics were observed in the combustion products. This latter finding is especially surprising because nitrogenous constituents comprise 1–2 wt % of the original oils.

Because of the relatively large amounts of nitrogen compounds in synfuel (1–2%) vs natural petroleum crudes (0.05–0.1%) and because of the large mutagenic activity of the nitrogen polycyclics, we have studied the nitrogen cyclic compounds in synfuels extensively. The approach is to fractionate and isolate classes of nitrogenous compounds and to characterize them chemically and biologically (Ames test). The important goal is to determine the exact structures of the compounds that are responsible for high mutagenic activity. This is an extremely difficult task because the compounds are present in tiny amounts, and few standards exist. We have found that the basic nitrogen cyclics (aromatic amines and aza-arenes) comprise only about 0.1% of the whole crude but exhibit great mutagenic activity. The neutral nitrogen cyclics (aza-arenes of the pyrrole type) exhibit less mutagenic activity than the basic compounds.

Considerable interest has also been evinced in the alkylated PAH compounds in synfuels because of their possible mutagenic activity. We are developing procedures to fractionate and isolate these compounds for biotesting and structural identification. Gel chromatography with Biobeads SX-12 and then LH-20 has yielded some success, but further work is needed. The LH-20 separation procedure discussed in the last report has been studied in great detail to compare its performance with that of solvent partitioning.

One major new activity warrants mention: the Gasifiers-for-Industry Program. This is an ORNL-led study of a modular gasifier soon to be operated at the University of Minnesota–Duluth. The program is intended to determine health and environmental impact. The Analytical Chemistry Division is responsible for preparation, distribution, and analysis of samples and dissemination of results. We are establishing protocols, quality assurance, and a sample management system now. This gasifier is scheduled to begin operation in the spring of 1979. Gasifiers of other types and at other sites are scheduled for study over the next several years.

The work of the Environmental Programs Group is focused on the hazardous organic components of environmental media. This group designed and proved a sampling system for the Environmental Protection Agency (EPA) this year and subsequently had several systems and many traps constructed at ORNL for a large study of a Yugoslavian gasifier. The system is Tenax based and is designed such that the sampled organic materials can be thermally desorbed and

collected on a cryogenically cooled capillary GC column and ultimately chromatographed by programming the temperature. A sampling system for PAHs in aqueous streams was also developed and put into use in a study of coking plant operations by the Environmental Sciences Division. This system is based on XAD-2 resin as adsorbent and was validated with  $^{14}\text{C}$ -labeled PAHs as well as GC performance.

We studied electrostatic precipitator (ESP) ash and fly ash in detail for the Electric Power Research Institute this year. The objective was to determine if ESP ash, which is available in large amounts, can be used as an R&D surrogate for fly ash. The ashes plus the respirable size fraction of ESP ash were examined for PAH content. The conclusion was that respirable size ESP ash can serve as a qualitative surrogate for fly ash. We also have begun to study solid waste leachates, in which case we are emphasizing EPA's "priority pollutants." We have validated analytical procedures and used EPA's Toxicant Extraction Procedure for organic components and have demonstrated that atomic absorption spectrometry is adequate for the specified 14 elements. This study is a collaborative effort with the Biology Division; it is likely to have much utility for surveillance of effluents from ORNL itself.

The Tobacco Smoke Chemistry Group has continued to provide routine and nonroutine analytical support plus R&D to the National Cancer Institute and several of its contractors. We analyzed some 160 different brands of foreign cigarettes this year for tar, nicotine, and CO. Our investigation of the chemiluminescence technique for determining NO and NO<sub>x</sub> led to the discovery that a reduced silver-laden cation resin is very effective for producing NO (which is the luminescent precursor) while precluding HCN interference. This approach is simple and rapid and potentially is the best method for measuring nitrogen oxides in smoke.

The determination of nicotine in physiological fluids—blood and urine—is attractive as a simple, nondestructive means for measuring dose to a given smoker. We have conducted a collaborative study with Borriston Research Laboratories in which dogs were exposed to cigarette smoke that contained  $^{14}\text{C}$ -nicotine. Levels of nicotine and its metabolites in the serum and urine were then monitored. The results of this study indicate that sampling blood is unsatisfactory for measuring dose and that 24-h urine samples would be required for accuracy. An improved method for determining nicotine in physiological

fluids was developed concurrently with this study and published.

The development of instrumentation for monitoring smoke exposure and dose is an important part of these programs. The optical particle detector (OPD) has been reported in previous reports. During this period the OPD has been evaluated as the central component of several smoke-monitoring systems that we are developing for several NCI contractor laboratories. As one example, a single-channel device was developed that combines an OPD with an infrared CO analyzer to document exposure of mice in the SEM II smoking machines used in the Microbiological Associates' Laboratories. (We were instrumental in making the SEM II machines operable.) This monitoring task is extremely important because of the great investment in exposure experiments that involve large numbers of mice over long periods of time. The device is designed to alarm when the animals are threatened by faulty exposures as well as to monitor and document exposure conditions.

**Nuclear and Radiochemical Analysis Section (Chap. 5).** The Nuclear and Radiochemical Analysis Section was formed in 1977 and was first reported in the last annual report. The section is now formally organized into three groups: Low-Level Radiochemical Analysis, Radiochemical and Activation Analysis, and Special Projects. The work load in this section has virtually doubled this year.

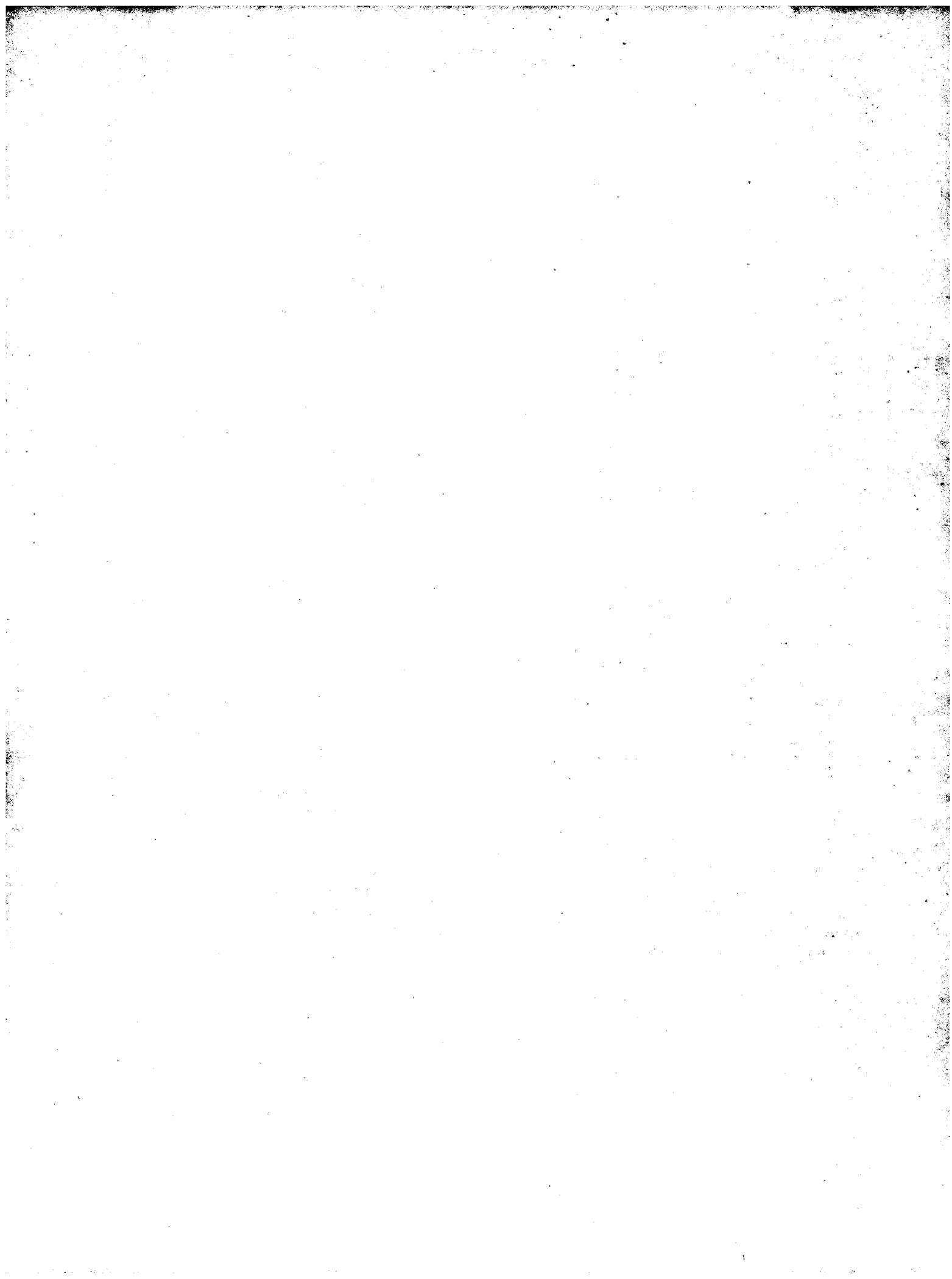
The Low-Level Radiochemical Group moved into laboratories in the Central Research Building (4500S) this year. These laboratories are centrally located, low-background facilities. Concurrently, we have acquired an ND-6603 analyzer system and a Ge(Li) detector and equipped an existing ND-3300 with NaI and surface barrier detectors in the new counting facilities. Accordingly, pico- to nanocurie levels of alpha and gamma activity are now handled by this group with much-improved efficiency. The work primarily comprises analytical support for such ORNL activities as the Clinch River Actinides Program, the Waste Management Program, studies

of the ORNL waste treatment plant operations, screening of oil well fluids, environmental surveillance, and fallout monitoring. An R&D project of special importance this year has been a study of radiochemical procedures for determining  $^{99}\text{Tc}$  in soils and vegetation. This nuclide is characterized by weak beta emission and long half-life and hence must be separated cleanly and efficiently from other nuclides before counting. A procedure has been devised that involves anion exchange, ferric hydroxide precipitation, methylethylketone extraction, and finally precipitation of tetraphenylarsonium perchlorate; recoveries are 50–70%. We plan to extend this study so that the procedure is applicable to water and tissue samples.

The Radiochemical and Activation Analysis Group also performs a variety of analyses for ORNL and Nuclear Division programs. Improvements in operating efficiency and quality assurance have been made this year, and we have implemented the division's Data Management System fully in this laboratory. Notable development activities here have been development of neutron activation analytical procedures for  $^{129}\text{I}$  and  $^{99}\text{Tc}$ . A procedure for collecting ultratrace amounts of uranium onto an anion exchange resin prior to (and amenable to) neutron activation analysis was also developed.

For several years we have been participating in a project with personnel of the Engineering Physics Division to measure decay heats of  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Pu}$ . That study was completed this year and published.

Chapters 6 and 7 contain information that reflects on the division as a unit. Information about the quality assurance and safety programs is presented in Chap. 6 along with a tabulation of analyses rendered. Publications, oral presentations, staff professional activities, educational programs, seminars, etc., are cited in Chaps. 7 and 8. Approximately 104 articles and reports have been published including entries in seven books, and 82 oral presentations were given during this reporting period.



# 1. Analytical Methodology

W. S. Lyon, Head

The Analytical Methodology Section is composed of two groups: Analytical Instrumentation and Physicochemical Analysis. Both perform research and development under DOE's Office of Basic Energy Sciences. In addition, the former does work for the Division of Biological and Environmental Research and the Advanced Fuels Recycle Program (AFRP). The Physicochemical Analysis Group has an Electric Power Research Institute (EPRI) funded project on chemical speciation of fly ash and also performs special analyses for other ORNL researchers, using primarily electron microscopy and x-ray techniques.

A new research project in the Analytical Instrumentation Group this year is time-of-flight optical spectroscopy, using a fiber optic waveguide; results are quite promising. Work on optoacoustic spectrometry and simultaneous multiwavelength spectrometry has continued. The helium glow discharge method for arsenic has been refined, written up, and turned over to service personnel, and a new method for determination of fluorine is under study. The "one-atom" method of resonance ionization spectroscopy has been applied to studies of the fission of  $^{252}\text{Cf}$ , whereas other work on the transuranics has mainly been concerned with spectrochemistry of unusual species. Under the AFRP program three new in-line methods have been reported.

For the Physicochemical Analysis Group this has been a year of consolidation and completion; both the electromagnetic and electrostatic spectrometers are now in operation and accumulating data. The electrostatic spectrometer is being used to evaluate positron scattering as a surface analysis technique. Our x-ray diffraction and x-ray fluorescence instruments have been modified and improved and are providing data for investigators in a number of ORNL programs. Several special problems have been studied, using combinations of scanning electron spectroscopy, transmission microscopy, and x-ray techniques. Work for EPRI involving study of fly ash has continued, with major emphasis on elucidation of fly ash matrices and how they affect trace element deposition.

## ANALYTICAL INSTRUMENTATION

H. H. Ross, Group Leader

### Analytical Research

**Time-of-flight optical spectroscopy.** A novel technique is being developed in which a fiber optic waveguide is used for time-of-flight optical spectroscopy. The variation in velocity with wavelength of a short pulse of light within the fiber produces spectral dispersion in the time domain. Thus the spectrum of a light pulse can be extracted from the time dependence

of the transmitted light if the dispersive properties of the fiber are known. Time domain spectroscopy represents an important alternative to conventional spectroscopy in which the wavelength dispersion is obtained as a function of some spatial coordinate such as the deviation of a ray by a prism or grating or the translation of an interferometer reflector. With dispersion in the time domain, only a single detector is required in a system that can be mechanically rigid. The technique also has an intrinsic capability of nanosecond time resolution, which could be important for analysis of fast processes.

The physical requirements for a time-of-flight spectroscopic apparatus are determined largely by the properties of the optical fiber. The change in velocity with wavelength is relatively small for most optical waveguide materials in the visible region of the spectrum— $0.3 \text{ ns nm}^{-1} \text{ km}^{-1}$  for silica at 600 nm, for example. Furthermore, the attenuation of light at short wavelengths in currently available fibers makes lengths of much more than 1 km impractical. Therefore, for spectral resolution of the order of nanometers, the time resolution of the system should be a nanosecond or better.

A time-correlated, single-photon counting technique was chosen for the initial investigations. In this method, a polychromatic light pulse from a nanosecond source is attenuated so that at most a single photon per pulse is detected after traversing the fiber, sample, etc. The time delay between the initial pulse and photon arrival is measured and stored. The time domain spectrum of a large number of pulses is obtained as a histogram of number of photons counted versus their transit time. Advantages of this technique are that the source may be of low intensity, a fairly high fiber attenuation can be tolerated, and conventional fast-timing nuclear electronics can be used.

The optical fiber for the preliminary study was a Corning type 5050 fiber, 1.1 km long, with a nominal attenuation of 5 dB/km at 820 nm and a bandwidth of 500 MHz at 900 nm. The fiber's propagation characteristics are substantially degraded if the fiber is under tension or if there are sharp bends such as would occur if the fiber crossed itself when wound on the storage spool. Accordingly, the fiber was wound in a single layer on a 30-cm-diam drum that had provision for the relief of winding tension.

The light source for most of the measurements was an Ortec model 9352 nanosecond spark source. The source was operated with a number of gases including nitrogen, hydrogen, oxygen, and dry air, with the latter two giving the shorter pulse lengths. Oxygen gives a more continuous spectral distribution than air over most of the visible and near-infrared region and also shows a shorter time decay at the longer wavelengths. The light from the pulser was focused onto the fiber by a 20 $\times$  microscope objective.

In a typical measurement, a timing signal from the light source is delayed by about 5.4  $\mu\text{s}$  (the approximate transit time of the fiber for the faster red light) and is then used to start a time-to-pulse-height converter. The photons emerging from the fiber are detected by a photomultiplier, whose output is converted by a discriminator to a timing pulse that

stops the time-to-pulse-height converter. Finally, the output of the time-to-pulse-height converter, a voltage proportional to the time increment for the detected photon, is sorted and stored by a pulse height analyzer to give the statistical time domain spectrum.

Measurements were made of the transit time and pulse broadening in the fiber as a function of wavelength. The spectral dispersion for this fiber (1119 m long) ranges from 0.98 ns/nm at 436 nm to 0.06 ns/nm at 900 nm with a time delay between 900- and 436-nm pulses of 155 ns. The time response of the measuring system, found by making similar measurements on a 1-m fiber, was found to vary from 2.2 ns at 436 nm to 3.0 ns at 900 nm with the oxygen lamp and from 1.8 ns at 436 nm to 3.7 ns at 900 nm with air in the source. Pulse broadening within the fiber also contributes about 1.4 ns to the total timing error. Because the squares of the various contributions are additive, the system time resolution is between 3 and 4 ns over the spectral range.

To test the practicality of time domain spectroscopy under more realistic experimental conditions, the absorption spectrum of  $\text{KMnO}_4$  in 1  $\text{NH}_2\text{SO}_4$  was measured. The spectrum obtained was in good agreement with that measured on a conventional spectrophotometer when oxygen was used in the spark source. With air, a weak but long-lived emission at long wavelengths where the fiber attenuation is low interfered somewhat with the strongly attenuated short wavelength light, causing a reduction in spectral accuracy.

These results, which are described in a recent manuscript,<sup>1</sup> clearly demonstrate the feasibility of fiber optic time-of-flight spectroscopy. This work has been supported by the ORNL Exploratory Studies Program. (*W. B. Whitten, H. H. Ross*)

**Development of the glow-discharge detector (GDD) as a fluorine-specific detector.** Work is in progress to improve the sensitivity of the GDD for detecting inorganic fluorine and for identifying and determining fluorine-bearing organics in gas chromatograph effluents. This work is in support of Ecological Sciences Division studies of fluorine contamination of waters, soils, and vegetation.

In detecting the light emitted by the GDD, we wanted to find the optimum external illumination system for the monochromator. The fact that the

1. W. B. Whitten and H. H. Ross, "Fiber Optic Waveguides for Time-of-Flight Optical Spectroscopy," submitted for publication in *Anal. Chem.*

GDD is necessarily fixed at the exit of the gas chromatograph would normally make it impossible to achieve the necessary flexibility because, in trying different arrangements, one needs to independently vary the focal length of lenses, the location of real images, and the source-to-slit distance. This problem was solved by mounting the monochromator and its optical bench on a platform, which was movable as a unit with respect to the GDD. We found that elongated electrode gaps (up to 15 mm) gave superior sensitivity in terms of mass per unit volume. However, use of these gaps requires enlargement of the GDD chamber, which considerably increases the dead volume of the GDD. Such an increase would be unacceptable in a detector to be used for transient signals. The illumination arrangement providing the highest and most stable light flux with the conventional GDD<sup>2</sup> was use of a 50-mm focal length lens at the slit, which focused an image of the discharge on the collimating mirror. An almost equally effective scheme was use of the exit pupil of the GDD as the light source in the same arrangement.

To find the optimum conditions for producing the atomic fluorine spectrum, we scanned the GDD spectrum of a mixture of 13 ppm CCl<sub>2</sub>F<sub>2</sub> (Freon 12) in commercial helium from 610 nm to 820 nm. The most intense of the 18 atomic fluorine lines detected was at 685.60 nm. The expected interference by the O<sub>2</sub><sup>+</sup> bandhead at 685.63 nm did not materialize, probably because the helium was at atmospheric pressure. The intensity of the signal was aided by (1) increasing the flow rate (up to 250 cm<sup>3</sup>/min), (2) increasing the current (up to 80 mA), (3) minimizing the concentration of H<sub>2</sub>O and air, and (4) using the cathode glow layer as the light source rather than the discharge in the electrode gap. With the flow rate at 65 cm<sup>3</sup>/min, the current at 40 mA, using 25- $\mu$ m slits in a Jaco 0.5-m monochromator and an RCA 4840 photomultiplier at 800 V, fluorine 685.60 gave a signal of about 350 nA. Signal drift was  $\leq 2\%$  over a period of 30 min.

Future work will be directed toward achieving higher sensitivity for fluorine with the GDD and/or other light sources using fluorine lines or selected fluoride bands. (C. Feldman)

**Laser spectroscopy studies.** The study of resonance ionization spectroscopy (RIS) has continued<sup>3</sup> in

collaboration with G. S. Hurst's group in the Health and Safety Research Division. A study of the ability to detect single atoms soon after they have been created, in this case by the fissioning of <sup>252</sup>Cf, has been completed and described.<sup>4</sup> This study was also done in cooperation with C. E. Bemis, Chemistry Division, and was used to gain experience in literally tossing out an atom and then detecting it. This ability provides the basis of many types of low-level counting applications of RIS at the few- or single-atom level. The results of our study show that most, if not all, of the cesium fission fragments come to rest as cesium neutrals and are detected individually as cesium atoms at the end of the fission fragment tract.

The problem of charge neutralization of energetic ions has never been properly addressed because of the difficulty of detecting low concentrations of neutral species at short periods of time after their formation. Resonance ionization spectroscopy has this single-atom detection capability and can examine an environment in a time-resolved manner. Our californium experiment gives the first experimental evidence that charge neutralization of a highly energetic ion can occur. The experiment was carried out in P-10 counting gas, 90% argon-10% methane. Many questions remain to be answered; for example, does the initial energy of the ion influence its final charge state? What is the influence of cover gas on the charge neutralization process? Can one influence the final charge state by altering the cover gas composition? Answers to these questions are important in assessing the usefulness of RIS to various low-level counting applications.

One low-level counting problem in which we are currently involved is the determination of solar neutrinos in cooperation with R. Davis and others at Brookhaven National Laboratory. Our part of the problem involves the detection of lithium formed from K-capture of boron in beryllium acetylacetonate. In this instance, lithium is created with a recoil energy of about 50 eV. Experiments are being set up to study the general detectability of lithium generated from this beryllium compound. The first step of the process has been completed in that we have

2. C. Feldman, "Element-specific Detector for Gas Chromatography," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 7.

3. J. P. Young, "Resonance Ionization Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 5.

4. S. D. Kramer, C. E. Bemis, Jr., J. P. Young, and G. S. Hurst, "One-Atom Detection in Individual Ionization Tracts," *Opt. Lett.* **3**, 103 (1978).

demonstrated the necessary 3-photon, 2-energy saturated RIS detection of lithium atoms this year. The RIS scheme for lithium is more complex than that for cesium, which involved a 2-photon, single energy process and thus represents a further basic advance in the practical application of RIS to many elements. For lithium detection, both space and time coincidences (within 100 ns) of the two laser beams are required and were achieved. A position-sensitive proportional counter has been designed and fabricated by R. E. Zedler (Instrumentation and Controls Division) so that both the Auger electron released in the formation of lithium and the photoelectron created by the RIS process must come from the same volume element to represent a lithium event. Such a requirement of space coincidence again will greatly minimize background for low-level counting applications.

Partial alignment of atomic nuclei has been shown to be possible by optical pumping, which will produce imbalance among sublevels of atomic ground states through degenerate hyperfine interactions, and the present state of the art has been reviewed.<sup>5</sup> Personnel of our division are involved with C. E. Bemis and J. R. Beene in the Chemistry Division and with personnel in the Health and Safety Research Division in developing a laser-based optical pumping technique called laser-induced nuclear polarization (LINUP) to be applied to amenable short-lived (<10-ms half-life) nuclei. By the resonant absorption of light, these short-lived nuclei can be oriented with respect to a cw laser; the short-lived species will fission while aligned, and the fission fragments will be anisotropically distributed. With the laser off or not tuned to a resonant absorption, fissioning will be isotropic. (*J. P. Young*)

**Optoacoustic spectrometry.** Optoacoustic spectrometry (OAS) provides a technique for recording the absorption spectra of opaque or highly scattering solids (and other sample types) that are inaccessible to conventional spectroscopy. One particular example of such an application of laboratory interest is the spectral characterization of new lanthanide and actinide compounds prepared at the Transuranium Research Laboratory (TRL). Several other DOE programs also have need of such a technique. In last year's report, the results of an examination of pulsed laser OAS with tuned amplifier detection were

reported. Some preliminary spectra of solids were given, and several experimental difficulties were noted. Our work this year was directed to the solution of several of these difficulties.

Several instrumentation modifications were made to improve the quality of the acquired spectra and the ease in obtaining them. Those developments center primarily around selection of a new signal treatment method that more closely matches the complex, pulsed nature of the observed acoustic signals. These signals not only are very complex but also demonstrate a waveform that varies substantially with sample. In general, two frequency domains are represented: a high-frequency component at approximately 15 kHz that decays with a half-life of 3 to 8 ms and a lower frequency signal with a rise time of a few milliseconds (depending on the sample). The former high-frequency component (actually not a pure tone) results from excitation of one or more cell cavity resonances by the laser-driven pressure pulse. The OAS cell used for these experiments has a complicated geometry, and thus the cavity resonant frequencies are difficult to calculate. The low-frequency signal component cannot be studied easily because the microphone in use pressure-equilibrates in a few milliseconds by means of the pinhole leak connecting the gas volumes in front of and behind the diaphragm.

For pulsed laser excitation, the relative proportions of the fast and slow signals vary dramatically. For example, finely divided decolorizing carbon exhibits a fast-to-slow signal ratio of 40, whereas for reticulated vitreous carbon, the same ratio is about 3. When the form of the observed signals varies so widely, the signal treatment scheme must be flexible enough to be adjusted to fit each case. To that end a gated integration method is now in use for detection of these acoustic signals. The gated integrator (or boxcar averager) enhances signal-to-noise ratio (S:N) for pulsed inputs by accepting signals only when the device is gated "on." Thus no noise is collected during the dead time between pulses. In addition, the position and duration of the on period can be adjusted to match as closely as possible the acoustic signal.

A comparison was made between this new signal-processing method and the tuned-amplifier method used previously. Conditions of very low absorbance were used. A methyl orange powder sample was examined at a wavelength (600 nm) very near its absorption spectrum onset. In addition, the laser beam was attenuated with neutral density filters with

5. W. Happer, "Optical Pumping," *Rev. Mod. Phys.* **44**, 169-249 (1972).

a net transmission of 1%. The OAS S:N resulting from analysis with a 5- $\mu$ s gate width was 7 as compared with 0.5 using the tuned amplifier. For both cases, the time constant was about 2 s. Given the prevailing laser repetition rate, the gated integrator averages 40 individual pulses. The S:N improvement ratio is expected to be proportional to  $\sqrt{n}$ . Large ( $\pm 10$ –20%) pulse-to-pulse amplitude variations are inherent in the dye laser output, and averaging several repetitions results in this S:N improvement. This observed S:N enhancement is especially impressive because a Helmholtz resonator cell was used for this experiment. That cell damps the acoustic signal and thus favors the tuned-amplification method.

Three additional changes have been made in our experimental technique to improve the overall system performance. The old divider, used to provide sample-to-reference signal ratios, has a somewhat limited dynamic range; thus normalization with respect to laser output intensity changes is inaccurate. A new ratiometer (a commercial unit) exhibits an input dynamic range of greater than  $10^3$  and has extended the wavelength coverage of any particular dye solution further into its tuning curve wings where the laser output diminishes.

With the advent of the dual-channel boxcar averager, an RC-filtered photodiode was substituted for the optoacoustic reference channel. With this scheme, a slightly wider tuning range per dye is observed because of reduced noise in the reference channel. However, baseline correction is not as

accurate and the “matched” nature of two acoustic cells is lost. Finally, the Helmholtz resonator OAS cell described last year has been modified with a threaded sample holder that allows introduction of samples without removing the light input prism.

As a result of these improvements, spectra acquired now are significantly better. An example of these higher quality spectra is shown in Fig. 1.1*a* where a forbidden  $f$ - $f$  holmium(III) transition is shown for a holmium oxide powder sample (10 mg). The crystal field splittings of this transition are clearly resolved for this weak absorption ( $\epsilon \sim 2$ ). The most closely spaced lines that are still resolved are separated by about 3 Å. Figure 1.1*b* shows a spectrum recorded for the same powder with a commercially available optoacoustic spectrometer (Princeton Applied Research Corporation, model 6001) based on a conventional cw light source. Although the overall envelope of this spectrum is similar, the resolution is obviously poorer (40 Å) because wide monochromator slits were required to reach this S:N level.

In addition to its use for acquisition of spectra of solids, the optoacoustic phenomenon can serve as the basis for other techniques. A simple laser power meter based on optoacoustic detection has been designed and will be constructed. The optoacoustic cell can withstand the full intensity of the laser beam and damps the 2- $\mu$ s laser pulse to a time regime that is suitable for a sample-and-hold amplifier (SHA). The SHA will increase the signal duty factor to almost 100%, in a fashion similar to pulse code modulation.

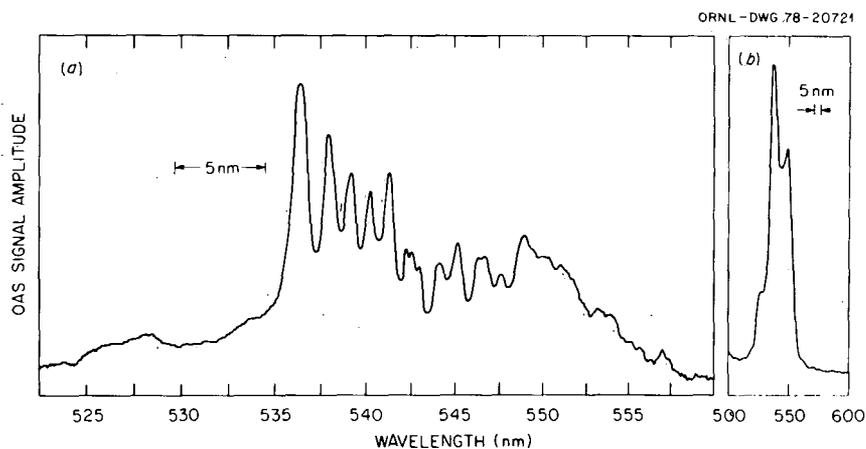


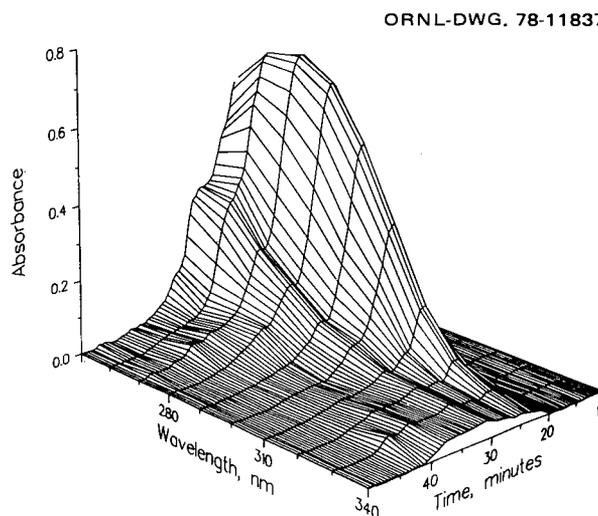
Fig. 1.1. Optoacoustic spectra of holmium oxide: (a) tunable laser spectrometer; (b) arc lamp spectrometer.

The spectra presented in Fig. 1.1 point to the overall conclusions regarding pulsed laser OAS reached thus far. The sensitivity of the laser method is comparable to that of conventional OAS, but much higher resolution can be attained. Offsetting that higher resolution is the greater difficulty in recording spectra that exhibit only broad features and that span wide wavelength ranges. Here, spectral segments obtained over several dye ranges must be joined to form a complete spectrum. Because this can be done only with difficulty, laser OAS should be reserved for samples that possess high inherent resolution. The new lanthanide and actinide compounds and alloys prepared at the TRL are such materials. They are available only in microquantities and usually have the form of optically dense powders. The line widths expected are comparable to those of holmium oxide. As an initial study, holmium metal was examined to determine whether or not an oxide coat on its surface could be detected. The metal turnings exhibited strong absorption, but the observed spectrum indicates that the absorbing species is not  $\text{Ho}_2\text{O}_3$ . Samples prepared under more carefully controlled conditions are currently under investigation. In addition, some  $\text{UO}_2$  microcrystals were obtained and their spectrum taken. (R. W. Shaw)

**Simultaneous multiwavelength spectroscopy.** The availability of relatively inexpensive semiconductor array detection systems makes it practical to extend simultaneous multiwavelength spectroscopy (SMS) to a variety of analytical problems. Last year's report<sup>6</sup> described a liquid chromatography detection system utilizing the SMS technique. Development of this system and assessment of its capabilities have continued.

Previous research had focused on the development of criteria and the corresponding algorithms that provided real-time guidance for the retention of only that information necessary to successfully interpret the particular chromatographic experiment. Although these algorithms substantially reduced the amount of data retained during each experiment, convenient methods of extracting the desired information as well as of summarizing the experimental data are required. Two-dimensional representations of the data (either absorbance versus time or absorbance versus wavelength) are readily prepared,

and successive overlays of these curves have been found useful in extracting the desired information, particularly if the chromatographic column resolves a significant number of the sample components. However, a convenient means of visualizing the interrelationships and summarizing the data from complex samples requires the absorbance-wavelength-time data to be represented as a three-dimensional surface. The chromatograms shown in Figs. 1.2 and 1.3 illustrate the value of these three-dimensional surfaces. These curves pertain to coal-derived liquid that was sampled at two successive stages within the Char-Oil-Energy Development (COED) process. Detailed interpretation of these data is presented elsewhere.<sup>7</sup> This detection system and mode of data presentation should find considerable use in evaluating the effect of process parameters on product composition, an important aspect of coal conversion technology.



**Fig. 1.2. Chromatogram of COED product oil.** Column: 70- $\mu\text{m}$  polyvinylpyrrolidone packing, 50 cm  $\times$  6 mm, 62°C. Eluant: isopropanol; flow rate, 0.60 ml/min; 100  $\mu\text{l}$  of 1/250 dilution of oil in isopropanol injected.

Acquisition of a spectrum at the peak of each elution profile without prior knowledge of the retention time or absorption spectrum was previously demonstrated for samples in a column that

6. L. N. Klatt, "Array Detector for Multiwavelength Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, pp. 2-3.

7. L. N. Klatt, "Simultaneous Multiwavelength Detection System for Liquid Chromatography," submitted for publication in *J. Chromatogr. Sci.*

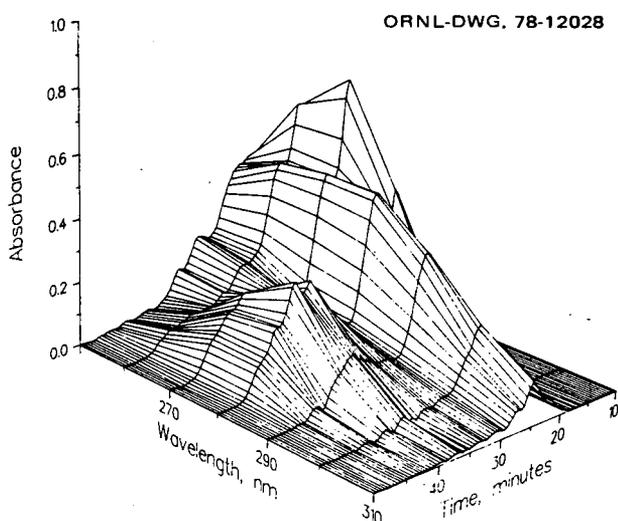


Fig. 1.3. Chromatogram of COED light hydrotreated oil. Column: 70- $\mu$ m polyvinylpyrrolidone packing, 50 cm  $\times$  6 mm, 62°C. Eluant: isopropanol; flow rate, 0.60 ml/min; 100  $\mu$ l of 1/50 dilution of oil in isopropanol injected.

resolved all components. This capability was successfully extended to situations in which the individual elution bands overlap significantly, that is, chromatographic resolution  $< 0.8$ . Deconvolution of the resulting spectra was accomplished via a subtraction technique. Propagation of noise limited this simple deconvolution method to mixtures of only two components. When three or more components elute with a profile width equal to that observed for a two-component mixture, the data acquisition algorithm behaves as though the profile contained a single component and retains a spectrum at the apparent peak of the profile only. In this situation one has no direct way of ascertaining whether this spectrum is that of a single species or a composite spectrum; consequently, a sophisticated spectrum deconvolution procedure has little value in this application.

The noise of the simultaneous multiwavelength detection systems was studied to ascertain what improvements could be made and to quantitatively compare this system with others. An initial study suggested that modifications to the rapid scan spectrometer would improve the S:N, and through implementation of these modifications a factor of 2 improvement in the S:N was actually achieved. The total noise of the current system can be allocated about equally between detector and amplifier noise, source instability, and noise resulting from the eluant

pump. The latter noise source could be eliminated through use of a commercially available pulseless eluant pump. Source instability can be eliminated through use of a double-beam optical system, which would, however, require a major development effort. The rms detector noise of 0.07 nA compares very favorably with other systems<sup>8</sup> and probably represents the state of the art of array detector technology.

Because the simultaneous multiwavelength detection system represents a significantly different detection concept for liquid chromatography, its quantitative capabilities were studied in detail. When the chromatographic column yields baseline resolution of all sample components, each one is monitored at its wavelength of maximum absorption. In situations in which the column does not resolve the individual sample components but spectral overlap is slight, each component is monitored at a wavelength free of interference, usually a secondary absorption band. If the spectral overlap is severe and the components are unresolved by the column, linear regression methods are used to deconvolute the elution profile and thereby quantitate the individual components. The accuracy and precision, as determined from recovery studies, were equivalent for all these cases. In each instance, peak-height data were more precise than peak-area information. This result is in agreement with results obtained with conventional liquid chromatography monitors.<sup>9</sup> Detection limits, expressed as an absorbance at the peak of the solute elution band twice the rms noise, are 0.006 to 0.008 absorbance units. After accounting for differences in the extent of ensemble averaging, these detection limits compare very favorably with results reported by other researchers.<sup>10,11</sup>

The results obtained from this project indicate that the simultaneous multiwavelength detection system possesses numerous unique capabilities and should be a useful characterization tool in many ORNL and

8. R. M. Hoffman and H. L. Pardue, "Performance Characteristics of a Vidicon Based Spectrometer with an Autoranging Amplifier," *Anal. Chem.* **50**, 1458 (1978).

9. R. P. W. Scott and C. E. Reese, "Precision of Contemporary Liquid Chromatography Measurements," *J. Chromatogr.* **138**, 283 (1977).

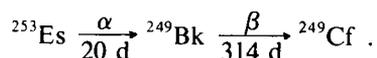
10. M. J. Milano, S. Lam, and E. Grushka, "Rapid Scanning Diode Array as a Multiwavelength Detector in Liquid Chromatography," *J. Chromatogr.* **125**, 315 (1976).

11. A. E. McDowell and H. L. Pardue, "Performance of a Silicon Target Vidicon Tube as a Multiwavelength Detector for Liquid Chromatography," *Anal. Chem.* **49**, 1171 (1977).

division programs. A manuscript summarizing this development effort has been submitted for publication.<sup>7</sup> (*L. N. Klatt*)

**Spectrophotometric studies at the Transuranium Research Laboratory.** In cooperation with J. R. Peterson and D. D. Ensor of the University of Tennessee and R. G. Haire of the Chemistry Division, spectrophotometric studies of transuranium compounds have continued.<sup>12</sup> This program is concerned with the preparation and characterization of various transuranium compounds of interest to the heavy element research program of the Office of Basic Energy Science. Once such characterization is made, the chemistry and physical nature of these compounds can be followed to gain knowledge about these man-made elements; such knowledge can then be applied to general consideration of the effects of radioactivity on the environment. Original characterization of a particular material is made by x-ray powder diffraction and spectrophotometric identification. A review article describing this operation was recently published.<sup>13</sup> Spectral identification is a much faster and more sensitive way to identify compounds or changes in compounds of interest; therefore, after verification of pure compounds by both techniques, we generally rely on spectral studies to follow the effects of changes in preparation, reaction, or storage.

Several general results can be summarized for compounds derived or made from the radioactive series:



Some preliminary results were discussed previously;<sup>12</sup> more have been collected this year. In the above series, the chemical consequences of essentially pure  $\alpha$ - or  $\beta$ -radioactive decay in solid-state compounds of these elements can be studied. The results of these studies, of interest in themselves, also provide information for a better understanding of transmutations that are a natural consequence of the storage of solid radioactive materials. Studies of this

decay series will continue, but among the findings to date is that the crystal structure and oxidation state of progeny compounds are dependent only on the state of the parent and are independent of the temperature and/or composition of the atmosphere under which the compound is stored. The growth of unnatural eight-coordinate  $\text{CfBr}_3$  has been followed for over three half-lives; the compound is now 90%  $\text{CfBr}_3$  and exhibits a heretofore unknown eight-coordinate  $\text{CfBr}_3$  x-ray pattern. Samples of eight- or nine-coordinate  $\text{BkCl}_3$  are seen to also generate eight- or nine-coordinate  $\text{CfCl}_3$ , respectively. A detailed study of the effect of cover gas (argon,  $\text{HBr}$ , or  $\text{H}_2$ ) on the storage of eight- or six-coordinate  $\text{BkBr}_3$  has shown that the growth of the daughter  $\text{CfBr}_3$  is not influenced by the cover gas. In the way of oxidation-state behavior, it was reported last year<sup>12</sup> that  $\text{EsX}_2$  with time generates a compound with a featureless spectrum. As time passed, whether  $\text{EsX}_2$  was stored in a vacuum or under  $\text{H}_2$ , the spectrum of  $\text{CfX}_2$ , the granddaughter, was identified. The oxidation state of the grandparent was unchanged even though  $\text{Bk(II)}$ , a possible daughter product, is unknown in the solid state. Other examples of oxidation-state maintenance is the trivalent daughter formations from various  $\text{Es(III)}$  and  $\text{Bk(III)}$  compounds. Also,  $\text{PuBr}_3$  has been identified in  ${}^{244}\text{CmBr}_3$  samples about 5 years old.

Synthesis and characterization of einsteinium, berkelium, and californium compounds have been extended to fluorides.  $\text{EsF}_3$ , trigonal and orthorhombic  $\text{BkF}_3$ , and  $\text{CfF}_3$  have been characterized; attempts to oxidize or reduce  $\text{EsF}_3$  have not been successful as yet. In cooperation with G. Eller, Los Alamos Scientific Laboratory, an interesting spectral study of  $\text{U}_2\text{F}_9$  was carried out to ascertain if an unusual oxidation state of uranium is present in the compound or if the compound consists of  $\text{U(IV)}$  and  $\text{U(V)}$  ions. Based on a reflectance spectral study of  $\text{U}_2\text{F}_9$ , a physical mixture of  $\text{UF}_4$  and  $\text{UF}_5$ , and on transmission spectra of small ( $<50\text{-}\mu\text{g}$ ) crystals of  $\text{U}_2\text{F}_9$ , it was concluded that the compound contains no unusual valence state of uranium. All absorption peaks can be accounted for from  $\text{U(IV)}$  and  $\text{U(V)}$ . The results of this work will be published in cooperation with G. Eller.

The spectral work at TRL is being extended to other actinides, that is, curium, americium, and plutonium. A discrepancy appears to exist in crystal structure assignments, particularly in  $\text{AmX}_3$ ; preliminary spectra of  $\text{AmCl}_3$ ,  $\text{AmI}_3$ , and  $\text{AmOI}$  have been obtained. Other spectral studies will follow. As part of this study and for general information, spectra of

12. J. P. Young, "Spectrophotometric Studies at the Transuranium Research Laboratory," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 6.

13. J. P. Young, R. G. Haire, R. L. Fellows, and J. R. Peterson, "Spectrophotometric Studies of Transurium Element Halides and Oxyhalides in the Solid State," *J. Radioanal. Chem.* **43**, 479 (1978).

$\text{CmCl}_3$ ,  $\text{CmBr}_3$ , and  $\text{CmI}_3$  have been obtained. In all cases where the trihalides are made, the compounds are thermally treated to obtain evidence for the possible existence of dimorphism. We have demonstrated that we can determine spectrally the difference between these two crystal structures. Dimorphism might be responsible for the structure discrepancies, as would the unsuspected presence of an oxyhalide. (*J. P. Young*)

#### Determination of arsenic and the methylarsines.

The arsine accumulation-helium glow detector procedure<sup>14</sup> is being used for determining and speciating arsenic in groundwaters, fly ash, scrubber ash, municipal refuse, and sewage sludge. These analyses are in support of Analytical Chemistry Division and Environmental Sciences Division investigations being carried out as part of the EPA Toxicity of Leachates Program.

To completely characterize the procedure, it was necessary to calibrate the commercial He-AsH<sub>3</sub> mixture used as a standard, to study the effect of buffer concentration on AsH<sub>3</sub> yield, to compare various procedures for liberating AsH<sub>3</sub> from the cold trap, and to minimize reagent blanks. It was found that (1) AsH<sub>3</sub> (~11 ppm) in helium can be determined by oxidation with Ce<sup>4+</sup> or liquid Br<sub>2</sub>, followed by determination of the resulting As<sup>5+</sup>; (2) to obtain complete reduction of As<sup>3+</sup> to AsH<sub>3</sub> by NaBH<sub>3</sub>, the reaction should be carried out in a buffer having a molarity  $\geq 0.25 M$ ; (3) using a room temperature air current to liberate the AsH<sub>3</sub> from the LN<sub>2</sub> trap produces a peak that is ten times as high as the peak obtained when the trap is warm in still air; (4) As<sup>3+</sup> contamination in the buffer can safely be eliminated with KMnO<sub>4</sub>, followed by H<sub>2</sub>SO<sub>3</sub>; and (5) when NaBH<sub>4</sub> is dissolved, any As<sup>3+</sup> or As<sup>5+</sup> impurities present in this reagent are slowly (~1 h) reduced to As<sup>0</sup>. Since As<sup>0</sup> is not reduced to AsH<sub>3</sub> in acid solution, the reagent exhibits a slowly decreasing blank level when used to determine arsenic in acid solutions. (*C. Feldman*)

**Spectroelectrochemistry in aqueous solutions and in chloroaluminate melts.** Spectroelectrochemistry involves the simultaneous acquisition of spectral and electrochemical data. This technique greatly simplifies the process of elucidating the overall mechanism of an electrochemical reaction. We have combined

this technique with our SMS system and are developing methodology applicable to the study of electrochemical reactions in aqueous and molten-salt media.

The manganese oxyanions in alkaline solutions were selected as a test system for the development of the combined SMS-spectroelectrochemical capability. These three ions, permanganate ( $\text{MnO}_4^-$ ), manganate ( $\text{MnO}_4^{2-}$ ), and hypomanganate ( $\text{MnO}_4^{3-}$ ), are ideally suited for this study because each species has an intense and distinct absorption spectrum. The chemical stability of these ions is highly dependent on the solution pH.<sup>15,16</sup> The electrochemistry of the manganese oxyanions in alkaline solution has been studied by Freeman and Mamantov.<sup>17</sup> In general, these species undergo reversible one-electron reductions; depending on the solution pH, disproportionation of the reduction products to MnO<sub>2</sub> and the reactant occurs.

The reduction of permanganate to manganate was studied in solutions ranging in pH from 9.4 to 14. At pH values below 14, disproportionation of manganate was confirmed. Evidence was obtained for the formation of an unknown species, which appears to be a product of the disproportionation reaction but is a precursor to the precipitation of insoluble MnO<sub>2</sub>. Similar experiments for the reduction of manganate to hypomanganate in solutions ranging from 4 M to 12 M KOH yield similar results, except that the rate of formation of the unknown species increases dramatically as the KOH concentration decreases from 12 M to 4 M. This species is characterized by a broad, rather featureless absorption spectrum extending from 600 nm into the ultraviolet region with a maximum centered at 475 nm. A hydrolyzed Mn(IV) species  $\text{HMnO}_4^{3-}$  and an Mn(V) species  $\text{HMnO}_4^{2-}$  were postulated by Schurig and Heusler<sup>18</sup> to explain kinetic data obtained from ring-disk electrode studies. One or both of these species could account for our results. The spectral characterization

14. C. Feldman, "Improvements in the Arsine Accumulation-Helium Glow Detector Procedure for Determining Traces of Arsenic," submitted for publication in *Anal. Chem.*

15. A. Carrington and M. C. R. Symons, "Structure and Reactivity of the Oxy-anions of Transition Metals. Part I. The Manganese Oxy-anions," *J. Chem. Soc.* **1956**, 3373.

16. B. Jezowska-Trzebiatowska and J. Kalcinski, "Kinetics and Mechanism of the Disproportionation of Manganate (VI)," *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **7**, 411 (1959).

17. D. B. Freeman and G. Mamantov, "Linear Sweep Voltammetry of Manganate (VII), Manganate (VI), and Manganate (V) in Alkaline Media," *Electrochim. Acta* **21**, 257 (1976).

18. H. Schurig and K. E. Heusler, "Application of the Rotating Disk-Ring Electrode to Investigate the Reduction of Permanganate in Alkaline Solution," *Z. Anal. Chem.* **224**, 45 (1967).

of this intermediate would have been exceedingly difficult, if not impossible, with a conventional spectroelectrochemical method.

Study of solution chemistry in molten-salt media is experimentally challenging and requires methodology different from that applicable to aqueous or organic media. To develop this methodology, the reduction of Nb(V) in chloroaluminate melts was selected as a model system. In basic melts Nb(V) undergoes a simple one-electron reduction,<sup>19</sup> and it possesses an intense absorption band at 297 nm.<sup>20</sup> The spectrum of the reduction product Nb(IV) has absorption maxima at 280 and 350 nm. In acidic melts the reduction of Nb(V) proceeds via an electron transfer-chemical reaction-electron transfer mechanism (coulometric  $n_{app} = 2.1$ ) to yield a product containing Nb(III), which precipitates from solution, presumably as Nb<sub>2</sub>Cl<sub>2</sub>. Because the precipitate remains within the optically transparent electrode (OTE), the Nb<sub>2</sub>Cl<sub>2</sub> can be quantitatively reoxidized to Nb(V).

The combined SMS-spectroelectrochemical methodology is being used to characterize the positive oxidation states of sulfur in acidic chloroaluminate melts. An understanding of the chemistry of these species is important for the development of a sodium-sulfur(IV) molten-salt battery.<sup>21</sup> Separate electrochemical<sup>22,23</sup> and spectroscopic<sup>24</sup> work has been reported for sulfur in these melts; however, correlation of the spectroscopic data with the electrochemical processes in chloroaluminate melts has not been reported. This correlation can be readily accomplished with our system.

At 225°C a cyclic voltammogram for a solution of elemental sulfur dissolved in AlCl<sub>3</sub>-NaCl (63/37 mol %) yields three oxidation waves. The second and third waves have been studied by coulometry and voltammetry and are attributed to the formation of S<sub>2</sub><sup>2+</sup> and S(IV), respectively.<sup>23</sup> The product of the first oxidation step is uncertain, and a considerable amount of effort was devoted to the study of this oxidation process. Thin-layer coulometric experiments on the first wave carried out at a platinum optically transparent electrode yielded  $n_{app}$  values between 0.12 and 0.25. An  $n_{app}$  of 0.125 would correspond to the formation of S<sub>8</sub><sup>+</sup> or S<sub>16</sub><sup>2+</sup>, whereas an  $n_{app}$  of 0.25 would correspond to the formation of S<sub>8</sub><sup>2+</sup>. The coulometric results suggest a mixed process, with all these species being formed, which is supported by spectroscopic data. Spectra acquired concurrent with the coulometric data exhibit absorption maxima at 600, 730, and 980 nm. Based on data reported by Fehrman et al.,<sup>24</sup> the 600-nm band is due to S<sub>8</sub><sup>2+</sup>, and the other bands can be attributed to either S<sub>8</sub><sup>+</sup> or S<sub>16</sub><sup>2+</sup>. All of these bands appear on initiation of the oxidation; however, the 730- and 980-nm-band intensities attain maximum values early in the electrolysis and then decrease, whereas the 600-nm band continues to increase until a constant intensity is observed. These results clearly indicate that the first wave is a mixed process and that an equilibrium between S<sub>8</sub><sup>+</sup> and S<sub>8</sub><sup>2+</sup> is present. The combined SMS-spectroelectrochemical methodology has provided the first direct evidence for the intermediates involved in this oxidation reaction. (*V. E. Norvell, G. Mamantov, L. N. Klatt*)

19. G. Ting, K. W. Fung, and G. Mamantov, "Voltammetric and Related Studies of NbCl<sub>5</sub> in Molten Chloroaluminates," *J. Electrochem. Soc.* **123**, 624 (1976).

20. L. E. Mc Curry, "Electrochemical Studies of Tantalum and Niobium in Molten Chloroaluminates" Ph.D. dissertation, University of Tennessee, Knoxville, 1978.

21. G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer, and E. J. Frazer, "Sulfur(IV) Cathode in Molten Chloroaluminates," Abstract 89, Meeting of Electrochemical Society, Atlanta, Ga., October 1977.

22. R. Marassi, G. Mamantov, and J. O. Chambers, "Electrochemical Behavior of Sulfur and Sulfide in Molten Sodium Tetrachloroaluminate Saturated with NaCl," *J. Electrochem. Soc.* **123**, 1128 (1976).

23. R. Marassi, G. Mamantov, M. Matsunaga, S. E. Springer, and J. P. Wiaux, "Electrooxidation of Sulfur in Molten AlCl<sub>3</sub>-NaCl (63-37 Mole %)" *J. Electrochem. Soc.*, in press.

24. R. Fehrman, N. J. Bjerrum, and F. W. Poulsen, "Lower Oxidation States of Sulfur. I. Spectrophotometric Study of the Sulfur-Chlorine System in Molten NaCl-AlCl<sub>3</sub> (37:63 mol %) at 150°C," *Inorg. Chem.* **17**, 1195 (1978).

### In-Line Sensor Development for the Advanced Fuel Recycle Program

**Introduction.** The Analytical Chemistry Division is continuing its joint effort with the Instrumentation and Controls Division to develop chemical measurement systems for fuel recycle process analysis. Our primary responsibility rests in the development of new, in-line chemical sensing systems for which no conventional device is known to exist. An important part of our effort this year has been our participation in an engineering review of the recycle process. We have identified specific analytical measurement problems and priorities as a result of this review. In the past year, we have completed several major projects, have made continuing progress in others, and have initiated R&D efforts in two new areas.

**The soluble neutron poison monitor.** The project has been completed, and a report has been issued detailing its design and performance.<sup>25</sup> The response of the monitor has been designed so that boron, cadmium, gadolinium, or a combination of these neutron poisons may be used with a single calibration function.

**Uranium analysis.** An improved method has been developed for the continuous in-line analysis of 20 to 200 g/liter uranium in 1–5 *M* nitric acid. Previous in-line uranium monitors have been based on the direct colorimetric measurement of the uranyl ion at 416 nm. This type of monitor is subject to errors as great as 20% as a result of variations in nitric acid concentration and temperature as well as sample turbidity. The uranyl absorption spectrum has been observed in the presence of various concentrations of nitric acid and was found to be linearly proportional to nitrate concentration at all uranyl absorbance maxima. A simultaneous, dual-wavelength procedure has subsequently been developed, which is used to calculate both uranium and nitrate concentrations based on uranyl absorbance at 416 and 426 nm. With this dual-wavelength technique, one can determine uranium and nitrate concentrations with an accuracy of 5% and 15%, respectively, in process streams. The dual-wavelength procedure can be corrected for temperature fluctuations because uranyl absorbance was also found to be linearly related to temperature. If the sample temperature varies by more than a few degrees Celsius, a correction function can be incorporated into the absorbance measurement. A prototype uranium monitor is currently being designed for the in-line analysis of uranium in high-acid process streams. Studies are currently under way to determine whether or not this dual-wavelength procedure can be applied to the analysis of uranium in low-acid aqueous and organic streams.

**Free acid monitor.** The development of a free acid monitor based on vapor phase condensation has been successfully concluded. The monitor is based on the ratio of partial pressure of water and HNO<sub>3</sub> in equilibrium above an acid solution at constant temperature. The prototype monitor can use condensate conductivity, refractive index, or direct titration to measure the acidity of the condensate. The condensate acidity can be related to the free acid of the feed solution. The effects of temperature and

solute concentration have also been assessed. The operating range of the monitor is dependent on the method used to measure the condensate acidity. Condensate conductivity is applicable over an acid feed range of 0.5 to 10.5 *M*. Refractive index can be used for acid in the range 4 to 13 *M*, and direct titration is used for a feed range of 4 to 15 *M*. The accuracy is dependent on an estimation of the solute concentration due to a common ion effect that increases the partial pressure of HNO<sub>3</sub> when neutral nitrate salts are present. For example, when 1 mol of a neutral nitrate salt is present, the apparent free acid is ≈10% greater than the true acid concentration. The engineering design is now under way to install the free acid monitor in the Advanced Fuel Reprocessing demonstration facility.

Measurement of the refractive index (R.I.) is also being evaluated as an analytical tool for monitoring free acid concentration in Purex process streams containing either pure nitric acid or acid in the presence of uranyl nitrate. The change in refractive index of nitric acid standards can be described with a second-order polynomial, dependent on acid concentration up through 14 *M* HNO<sub>3</sub>. This behavior indicates that an in-line refractometer may be more advantageous than other techniques for continuously monitoring free acid concentration in Purex streams containing concentrated nitric acid. If the refractive index can be measured to within 10<sup>-4</sup> R.I. units, nitric acid concentration can be determined directly with an uncertainty of 0.3 *M* HNO<sub>3</sub>.

The refractive index ( $n^{26}$ ) of acidic uranyl nitrate streams can be described in the following equation:

$$n^{26} = 1.3326 + k_1[\text{HNO}_3] + (k_2 - k_3[\text{HNO}_3])[\text{U}] ,$$

where the value 1.3326 represents the refractive index of water at 26°C, and  $k$  values represent constants obtained experimentally. The above equation suggests that the change in refractive index with free acid concentration is dependent on uranium concentration. Therefore, an in-line uranium monitor must be used in conjunction with a refractometer to determine free acid concentration in a uranyl nitrate stream. In other than pure reagent streams, the accuracy of the free acid determination will also depend on the presence of sample contaminants. Free nitrate is a major component in uranyl nitrate streams and will contribute to the total refractive index of the sample. However, if the uranium concentration can be analyzed independently with an accuracy of 5 g/liter and free nitrate concentration is controlled to within 0.1 *M*, a refractometer can be used to determine free acid concentration in uranyl

25. J. E. Strain, *An In-Line Neutron Poison Monitor*, ORNL/TM-6432 (September 1978).

nitrate streams with an uncertainty of 0.2 M HNO<sub>3</sub>. The availability and accuracy of other methods for determining free acid in uranyl nitrate streams will determine the practicality of such a dual monitor approach. (*D. A. Bostick, J. E. Strain, H. H. Ross*)

## PHYSICOCHEMICAL ANALYSIS

L. D. Hulett, Group Leader

### Electron Spectroscopy Instrumentation

The magnetic x-ray photoelectron spectrometer is being operated on a dependably functional basis without major technical difficulties. This state of operation was achieved during the past year as described below, and several studies are under way using the instrument's capabilities for determining both surface composition and oxidation states of surface constituents. Former problems with the x-ray anode and the spectrometer power supply were described in the 1977 progress report.<sup>26</sup> Several anode designs were tried but proved to be unsuccessful because of heat transfer problems. The design that was reported to be successful in the last report did not hold up under extended use. The aluminum-zinc braze between the aluminum anode material and the copper cooling base fractured after a few weeks' operation. The latest design uses an aluminum anode plug that fits into a slightly undersized hole in the copper base. The two pieces are assembled while the plug is cooled with liquid nitrogen and the copper base is heated to about 100°C. During operation, any heating of the anode material causes it to expand and tighten the interface with the water-cooled copper base for better heat transfer. This anode has been routinely operated at 600 W (12 keV/50 mA) for several months with no melting of the aluminum anode surface. Evaporation of tungsten anode from the filament still presents a problem. After about 3 months of normal operation, enough tungsten oxide coats the Macor insulator (which isolates the 12-keV anode from the ground) to cause arcing. This in itself presents only a minor inconvenience because the oxide coating can be readily removed from the insulator. It is suspected, however, that intermittent quantum jumps, which have been experienced in the photoelectron spectrum baseline, may be a result of

lighter oxide coatings. These coatings would be insufficient to permit arcing but could create alternate current paths and cause variations in the filament emission current. This problem may be eliminated by altering the shape of the insulator or by changing to a grounded anode system. The tungsten oxide also coats the anode and formerly caused a monotonic decrease in x-ray flux, with anodes that tolerated voltages up to about 8 keV. The new x-ray source can be used at the 12- to 14-keV range, which causes the electrons to penetrate the oxide coating and produces a high ratio of aluminum to tungsten x rays. Intermittent energy shifts in the photoelectron spectra, discussed in the last report, appear to have been eliminated following an overhaul of the relay-operated voltage divider that controls the spectrometer coil current. The coil current calibration is now recorded on a daily basis to reveal possible future malfunctions.

Our ORNL-constructed 20-cm mean radius spherical lens electrostatic spectrometer is now in operation. A resolution of 0.17% was achieved during initial testing, but this resolution should improve after proper beam baffling and alignments are made. Horizontal fringe field adjustments were made according to our calculations to put the ground potential at the mean radius. We plan to install vertical fringe field adjusters at the ends of the lenses for improved resolution. We are currently reading the output of a spiraltron detector on a multichannel analyzer, which is synchronized with a ramp generator that controls the potential of the lenses and allows a scan of about 70 eV in kinetic energy. Different energy ranges are scanned by changing the initial potentials of the lenses. We plan to interface the spectrometer to a PDP-11 computer for more versatility in experimental control and data output. We also plan to continue development of a position-sensitive detector.

In performing surface analyses by electron spectroscopy, contamination from outside sources must be avoided. To accomplish this, we are building an all-metal specimen transport system interfaced to an inert-atmosphere glove box. It will then be possible to prepare samples free from air and water-vapor contact and to transport them to and from the spectrometer with a minimum production of surface artifacts. This specimen-handling facility will be customer oriented. (*J. M. Dale, H. W. Dunn, L. D. Hulett, L. D. Hunt*<sup>27</sup>)

26. J. M. Dale and L. D. Hulett, "Photoelectron Spectroscopy Instrumentation," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, pp. 14-15.

27. Instrumentation and Controls Division.

### Electron Spectroscopy Studies

**Positron scattering for surface analysis.** This past year we initiated studies into positron scattering as a means of surface analysis, with support from ORNL's Exploratory Studies Program. It is proposed that, if energy-dependent resonance capture occurs for positrons incident on a surface, absorption peaks should be observed in the scattered positron beam as a result of annihilation of positron-electron pairs. Further, annihilation of core electrons will be a means of exciting Auger electrons, which should be detectable if a sufficient flux of low-energy positrons can be achieved. Auger electrons excited in this manner would not be accompanied by the high background of secondary electrons associated with electron-excited Auger spectra.

We are using our spherical lens electrostatic spectrometer (vide supra) for this investigation. The spectrometer can be converted from an electron analyzer to a positron analyzer by simply reversing the potentials applied to the spherical lenses. The only positron source that we have used to date is  $^{64}\text{Cu}$  ( $t_{1/2} = 12.8$  h), which decays by  $\beta^-$ ,  $\beta^+$ , and  $K$  electron capture and also by  $\gamma$  emission. This nuclide was chosen because it could be easily made at ORNL. A 0.95-cm-diam 0.05-mm-thick copper wafer was irradiated in the ORR or the HFIR and mounted in a depleted uranium shield that contained four electrostatic lenses for accelerating and focusing charged particles into the spectrometer. For our studies it is necessary to thermalize the positrons and then accelerate them to various known energies. Slow positron emission from metal surfaces has been reported in the literature.<sup>28</sup> We obtained positive particles (which were assumed to be positrons) using both clean  $^{64}\text{Cu}$  and oxidized  $^{64}\text{Cu}$  as sources. These particles could be accelerated to different energies, and their intensities decayed at the 12.8-h half-life rate. By reversing the polarity of the spectrometer lenses, we also observed slow negative particles (assumed to be electrons) that were more abundant by a factor of 50, compared to the positive particles. Because the electrostatic spectrometer is an energy analyzer and does not discriminate mass differences, it was necessary to determine whether the positive particles were positrons or ions. We were unsuccessful in attempts to detect the 511-keV gamma rays that

should have been created if positrons were being transmitted. Another test was made by superimposing a small magnetic field on the electrostatically focused particle beams. The focal point of the negative particles could be shifted by several volts, whereas negligible changes were observed for the positive particles. It is therefore concluded that the positive particles are ions created on the surfaces of the source chamber by radiation from the source. We are currently in the process of acquiring a  $^{58}\text{Co}$  source, which is the most widely used source for positron studies. The  $^{58}\text{Co}$  source does not emit  $\beta^-$  particles, which may be responsible for the positive ion formation. (*J. M. Dale, L. D. Hulet, H. W. Dunn, L. D. Hunt*<sup>27</sup>)

**Applied studies with photoelectron spectroscopy.** We have entered into a cooperative study with Professor T. Theis of the University of Notre Dame to investigate the possibility that concentrations of certain metal ions in natural waters may be controlled by sorption processes on manganese oxide surfaces. Many studies have been carried out on the properties of these oxides in aqueous systems, with emphasis on their high capacity for sorption of metal ions. Relatively little attention has been given to the role of redox effects in this process. It has been reported<sup>29</sup> that oxyhydroxides of manganese disproportionate and can catalyze the oxidation of certain metal ions by facilitating the electron-transfer process. This would tend to hold the metals and greatly decrease their concentrations in solution. This process and the wide distribution of hydrous oxides of manganese in soils and sediments may be the determining factors for the concentration of certain metal ions in natural waters. Our specific interest in this study is to determine if changes in chemical state of adsorbed metal ions on manganese dioxide can be detected by x-ray photoelectron spectroscopy. We have taken spectra for  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Pb}^{2+}$  adsorbed on manganese dioxide and are in the process of evaluating the data. The results appear promising because chemical shifts for nickel are evident.

In other applied studies, we are investigating the possibility that separation of light elements at grain boundaries is responsible for the fracture of a platinum-tungsten-rhodium alloy in cooperation

28. A. P. Mills, Jr., P. M. Platzman, and B. L. Brown, "Slow-Positron Emission from Metal Surfaces," *Phys. Rev. Lett.* **41**(15), 1076 (1978).

29. J. D. Hem, "Redox Processes at Surfaces of Manganese Oxide and Their Effects on Aqueous Metal Ions," *Chem. Geol.* **21** 199 (1978).

with J. Keiser of the Metals and Ceramics Division; we have started to determine the oxidation states of cerium in compounds prepared by C. Bamberger of the Chemistry Division for the chemical production of hydrogen. (*J. M. Dale, L. D. Hulet, H. W. Dunn, L. D. Hunt,*<sup>27</sup> *T. Theis*<sup>30</sup>)

### X-Ray Methods

**X-ray diffraction.** X-ray diffraction (XRD) is probably the most-used method available for inorganic compound identification. Commercial instruments for XRD work are supplied by many vendors. Detection sensitivities of commercial instruments are rather poor, however, 1–5% for most crystalline material. Background radiation from x-ray fluorescence and incoherent scattering is a main factor that limits detectability. Fluorescence background is especially severe for compounds containing iron and certain other elements. The  $\text{Cu K}\alpha$  radiation, which is commonly used for diffraction, has an extremely high cross section for inducing x-ray fluorescence from iron. We have been able to reduce background by at least an order of magnitude by adding a postmonochromator to one of our commercial diffractometers (GE-XRD-5).

To make x-ray diffraction measurements, the crystalline sample is irradiated with an intense beam of monochromatic radiation,  $\text{Cu K}\alpha$  in our case. The angles of coherent scattering of the beam, with respect to the incoming direction, are mapped by traversing a detector about the other side of the specimen. For our modified instrument, the background is removed by placing a graphite monochromator between the specimen and detector and adjusting it to pass only the coherently scattered  $\text{Cu K}\alpha$  radiation. Most of the fluorescence and incoherently scattered radiation is rejected. Signal-to-noise ratios of the diffracted beams have been dramatically increased. Our sensitivity is now such that for many cases we can detect as little as 0.1% of crystalline material in a matrix of similar atomic number. For high-Z materials in low-Z matrices (e.g.,  $\text{ThO}_2$  in LiF), as little as 0.01% can be detected. For the reverse case, small amounts of LiF in  $\text{ThO}_2$ , 0.5%, can be seen. Our modified XRD instrument has become extremely popular, being used in excess of 30 h per working week. (*H. W. Dunn, L. D. Hulet*)

**X-ray fluorescence analysis.** This method has been extensively used for quantitative analysis of great numbers of samples, both for routine determinations and for special problems. Important innovations were introduced into our XRF system.

1. The PDP-11 memory was increased to 24K, and the software handling system, originally based on cassette tapes, was expanded to include a dual floppy-disk drive. Operation of the floppy disks proved to be more reliable than that of the cassette tapes—as was expected—and substantially faster. Copying an entire disk, for example, takes about 30 s against the 2–3 h needed to copy a tape. The improved system can be switched from disks to tape and vice versa without difficulty by a simple console command.

2. Program ALKMO was written and used to determine elements from potassium through molybdenum in aluminum samples. An important feature of this program is that it may be adapted to the analysis of samples very different from aluminum, provided that the matrix composition is approximately known. This adaptation is accomplished by simply changing mass absorption coefficients in the program text—a simple operation in the NS-880 XRF system. Thus samples of kaolin and attapulgite were successfully analyzed. These minerals show absorption properties interesting for disposal of radioactive wastes.

3. New program ZIRCSO1 is designed to process XRF results for the determination of zirconium in aqueous and organic solutions pertinent to the Advanced Fuel Reprocessing program. By combining the fundamental parameter method with the comparator technique, it can analyze zirconium in samples whose compositions are different from those of the standards. This program is currently being tested and improved. (*E. Ricc*)

### Special Problems

**Effect of zone melting in the composition of stainless steel.** Some special projects were undertaken with our AMR 900 scanning electron microscope. A 15-cm stainless steel bar that had been subjected to zone refining was scanned lengthwise for composition; the spacious stage of the AMR made such an examination possible. The objective of this study was to determine if abrupt variations in the relative concentrations of iron, nickel, and chromium appeared at the beginning and end of the melt. Optical scanning electron microscopy (SEM) was combined with scanning electron microscopy–energy dispersive x-ray spectrometry (SEM–EDX) to

30. University of Notre Dame, South Bend, Ind.

determine the variation of the fluorescence count ratios  $FeK\alpha:CrK\alpha$  and  $FeK\alpha:NiK\alpha$  with respect to bar length. Our results show an undisturbed region in which the composition is iron, 65.3%; nickel, 21.1%; and chromium, 13.6%; the above ratios vary by only 1–5%. Much larger variations are observed, however, at the points where the melting started (13–16%) and ended (11–31%). Unexpectedly, a great jump (8–23%) was also observed about halfway between the start and the end of the melting. (*E. Ricci*)

**Assessment of zirconium fire hazard in reactor fuel disassembly.** A vital function of the Physicochemical Analysis Group is the solution of special problems originating in pure or applied science throughout ORNL. For this, our group's efforts are pulled together with those of the R&D group involved, and the problem is attacked via teamwork and collaboration. An example follows.

The Chemical Technology Division (CTD) is involved in a study of LWR fuel element disassembly techniques. One experiment involves cutting a porcelain-filled dummy fuel subassembly with an abrasive disk saw. Because of the Zircaloy cladding, there is a possibility of a zirconium fire or explosion, caused by pyrophoric zirconium particles during or after the cutting operation. Aside from our interaction with CTD personnel, we drew relevant information from experts (J. Googin and J. Cathcart) who had studied a zirconium fire that had occurred at ORGDP. Zirconium poses a fire hazard only if it is metallic, finely divided ( $\sim 1 \mu m$ ), and highly concentrated ( $\sim 90\%$ ). The danger is enhanced if the zirconium powder is damp, but it practically disappears for particle sizes  $> 5 \mu m$  or for concentrations  $< 75\%$ .

We attacked the problem with two techniques: SEM-EDX and x-ray fluorescence (XRF). The CTD had obtained sawdust samples from two cutting experiments; some samples were from air filters, and some consisted of powder that was screened for various particle sizes. We analyzed semiquantitatively by SEM-EDX samples from different sieves as well as individual particles of the deposit on the first filter (directly exposed to the dust). Results for particle sizes  $> 1190 \mu m$ ,  $> 297 \mu m$ , and  $< 45 \mu m$  showed substantial amounts of Zr, Al, Fe, and Pb, with the Zr concentration generally increasing as particle size decreased. The zirconium concentration in the  $< 45\text{-}\mu m$  samples (finest powder) was found to be  $29.5 \pm 0.5\%$  by quantitative XRF. But detailed examination by SEM and SEM-EDX of individual particles from the first filter indicated no general

trends for sizes 640, 19, 4, 1.4, and  $0.8 \mu m$ ; zirconium was present in varying amounts in each of these particles, as were also Ca, Fe, Cr, and Ni. The proportion of small particles ( $0.8\text{--}4 \mu m$ ) was not large in the mixture. Further, qualitative EDX on a fresh saw blade identified Ca, Ti, Fe, Cr, Ni, Pb, and Zr. Based on these data, our conclusion was that zirconium concentration in the fine powder is too low to pose a fire hazard, even if the zirconium were metallic. Examination of individual particles confirms further that zirconium always appears with other elements in various concentrations, even in the smallest particles, which, in turn, do not appear in large proportion. The presence of zirconium in the saw blade can only give a positive error in the zirconium analyses, and it does not affect this conclusion. (*E. Ricci*)

**Studies of the retention of asbestos fibers in rat lung.** We participated in a joint study with the Environmental Protection Agency to determine quantitatively the retention of asbestos fibers in individual lobes of rat lungs. Rats were sacrificed after being subjected to doses of asbestos. Thin paraffin sections of the left lobe, right lobe (superior, middle, inferior), and median lobe as well as the trachea of one rat lung were examined by light and scanning microscopy for the presence of asbestos fibers and associated changes in cellular structure.

*Left lobe.* A region of the lung in which a number of macrophages had moved in to partially surround the "foreign" asbestos fibers (shown in Fig. 1.4)



Fig. 1.4. Scanning electron micrograph of a section of the left lobe of rat lung showing asbestos fibers engulfed by macrophages, 2850 $\times$  (reduced 29%).

contained fibers that ranged in size from 0.3 to 2.0  $\mu\text{m}$  in width by 1.25 to 6.0  $\mu\text{m}$  in length. Fibers ranging in size from 1.4 to 6.0  $\mu\text{m}$  in width by 4.2 to 6.6  $\mu\text{m}$  in length were seen in another area of the lobe. An optical micrograph showed a number of fibers engulfed by a macrophage as well as a few lying on cell walls.

*Superior lobe.* The largest concentration of fibers was observed in this lobe. A cluster of macrophages and fibers at 2000 $\times$  is shown in Fig. 1.5. The fibers vary in size from 0.5 to 4.0  $\mu\text{m}$  in width by 1.0 to 4.0  $\mu\text{m}$  in length. In other parts of the tissue, some fibers were observed lying at random within the lung area and were not associated with macrophages. A light micrograph showed a number of fibers associated with macrophages along with other fibers located at random within the open regions of the lung sections.

*Median lobe.* Fibers were numerous in sections from this lobe. Figure 1.6 shows representative regions. Most of the fibers in this lobe appeared to be protruding from the surfaces or lying across them.



Fig. 1.5. Scanning electron micrograph of a section of the superior lobe of rat lung showing many asbestos fibers of varying sizes engulfed by macrophages, 2000 $\times$  (reduced 29%).

The size range of the fibers was 0.7 to 2.1  $\mu\text{m}$  in width, 2.8 to 14  $\mu\text{m}$  in length. Many fibers were seen by optical microscopy, most of which were phagocytized. Fibers of varying size were also observed in the middle and inferior lobes as well as in the trachea.

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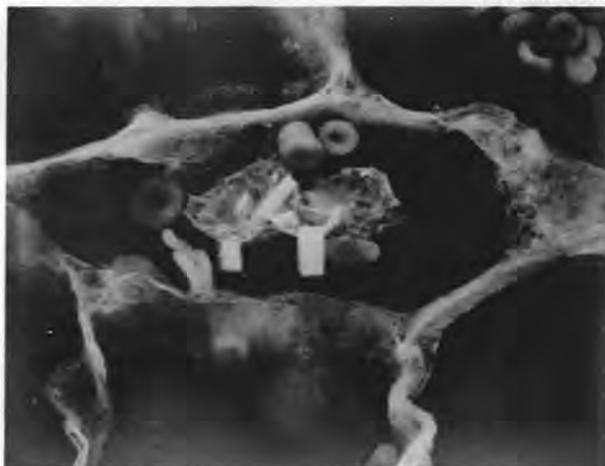


Fig. 1.6. Scanning electron micrograph of a section of the median lobe of rat lung showing asbestos-containing macrophages along with some red bloods near the asbestos, 2000 $\times$  (reduced 29%).

The combined optical-SEM approach for observing the interactions of asbestos with lung tissue was found to be qualitatively useful; optical microscopy quickly revealed the large detail; SEM revealed the submicron particulates as well as changes in the surrounding tissue. For quantitative measurements of the amount of asbestos in the lungs, however, other methods such as ashing the whole lung or individual lobes and examining by combined scanning electron microscopy-transmission electron microscopy (SEM-TEM) would be faster and more reliable. For a discussion of determination of asbestos in lung tissue by mass spectrometry, see Sect. 2.0 of this report. (F. L. Ball, A. J. Weinberger, W. D. Gude<sup>31</sup>)

### Chemical Speciation of Fly Ash

A large portion of the electrical power produced in the United States comes from the burning of coal in steam plants. Fly ash is the mineral residue that results. In the United States the annual production of fly ash is estimated to be about  $4 \times 10^7$  tons per year, a quantity that one can visualize as a pile, 1 m high by

31. Biology Division.

4.5 km square. Thus it is easy to understand the concern about how fly ash affects our environment and the interests in determining its composition. Elemental composition of fly ash has been surveyed, but this is not enough. To predict whether or not elements will escape from the fly ash into the environment and to know their effects, one must determine chemical species—compound forms and oxidation states. This type of work has occupied a major part of the effort in our group this past year. It was funded by the Electric Power Research Institute (EPRI).

Fly ash is a complicated mixture of aluminum-silicon-iron compounds, with smaller amounts of alkali and alkaline-earth elements plus many heavy elements present in trace quantities. Using optical and scanning electron microscopy, x-ray diffraction, and Mossbauer spectroscopy, we have determined that the bulk of the fly ash consists of at least four matrices: (1) a glass containing silicon, aluminum, and iron; (2) a crystalline mullite phase (aluminosilicate); (3) a magnetic spinel (substituted magnetite); and (4) a carbon-cinder material. Trace elements such as Cr, Ni, Co, Cu, As, Mo, Pb, Ba, rare earths, and many others are dispersed in these matrices. Some of them such as arsenic, molybdenum, and sulfur appear to be concentrated on surfaces and can be eluted rather easily. The glow discharge spectroscopy method, described earlier, can be used for distinguishing between 3+ and 5+ oxidation states of arsenic. We have found that the inorganic forms of sulfur are mostly sulfate<sup>32</sup> and that they can be easily leached from the surfaces of fly ash as CaSO<sub>4</sub>. The remainder of the trace elements are considerably more difficult to speciate than these, however.

We have spent considerable time determining the distributions of trace elements in the different matrix types of fly ash. We are hypothesizing that chemical states of trace elements are determined to a large extent by the matrices in which they are dissolved. Ashes from two local Tennessee Valley Authority plants (Bull Run and Kingston) were separated into magnetic and nonmagnetic components. The magnetic component was mostly Fe<sub>3</sub>O<sub>4</sub> and its variations.

The nonmagnetic component consisted of glass-mullite and carbon-cinder materials. The carbon-cinder phase was further isolated by individual particle picking under a low-power microscope. Neutron activation analysis was then applied to the three isolated matrix types. We found that alkali, alkaline earths, rare earths, scandium, and titanium are preferentially concentrated in the nonmagnetic glass-mullite phase. Elements such as Mn, Co, Mo, V, Cr, and U are concentrated in the magnetic spinel matrix. None of the elements are exclusively segregated in one matrix over others. The preference factors range from 2 to 4. Sulfur was the only element exclusively concentrated in the carbon-cinder matrix.

Thus we have a measure of support for our thesis that chemical species of some of the trace elements are defined by the matrix in which they are dissolved. Perhaps many of them are contained as isomorphic substitutions. For example, Ti<sup>4+</sup> may replace Si<sup>4+</sup>, and the trivalent rare earths may replace aluminum in the glass-mullite matrices. In the case of the magnetic matrix, it is well known that transition elements such as manganese can be isomorphically substituted for Fe in Fe<sub>3</sub>O<sub>4</sub>. Specific information about how trace elements are incorporated into their respective matrices is highly desirable. In the glass-mullite phase, for example, it is important to determine which elements are incorporated into the amorphous glass and which are contained in the crystalline mullite. We have found that, if this phase is etched in 1% HF solution, the amorphous glass is removed, leaving a highly purified form of crystalline mullite. We plan to refine this separation procedure to measure trace element distributions in the two matrices. (L. D. Hulett, A. J. Weinberger, J. M. Dale)

**Automated x-ray fluorescence analyzer.** A joint project of the Physicochemical Analysis Group and the Reactor Programs Group of the services section is to specify, purchase, set up, and use an automated XRF system. This XRF equipment will be capable of handling both radioactive and cold samples. J. H. Stewart, on loan from K-25, has primary responsibility for this project. In addition to visiting other laboratories to observe existing equipment, some experiments were performed to simulate future work. For example, the existing Y-12 Plant laboratory energy-dispersive and wavelength-dispersive analyzers were used to confirm that both were suitable for determination of elemental distribution coefficients between tributyl phosphate (TBP) and aqueous

32. L. D. Hulett, H. W. Dunn, J. M. Dale, J. F. Emery, W. S. Lyon, and P. S. Murty, "The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron, X-Ray and Nuclear Physics Methods," p. 27 in *Measurement, Detection, and Control of Environmental Pollutants*, IAEA SM 206/1, International Atomic Energy Agency, Vienna, Austria, 1977.

extraction phases. This determination was important in choosing a candidate instrument because wavelength-dispersive instruments are more expensive than energy-dispersive instruments. A detailed series of qualitative and quantitative tests was then performed using commercial vendor energy-dispersive equipment. The tests included detection of 10-ppm concentration levels of multiple elements, quantitative analysis of simulated fission product solutions, and demonstration of the detection of 50-ppm levels of uranium and thorium using the 100-keV energy lines excited by a  $^{57}\text{Co}$  source.

Initial reports from the Karlsruhe analytical laboratories, which recommended a filter-paper

technique for analysis of fission product solutions, were evaluated and found to be less precise and accurate than our direct solution analysis technique. Later Karlsruhe reports confirm these ORNL data, and the solution analysis technique will be used in the Karlsruhe laboratories unless the radiation level is very high.

Purchase specification for the high-volume XRF system has been completed, and bid responses are expected in late January 1979. (*J. H. Stewart, L. D. Hulet, D. A. Costanzo*)

## 2. Mass and Emission Spectrometry

J. A. Carter, Section Head

R. L. Walker, Associate

The Mass and Emission Spectrometry Section is currently involved with a variety of multifaceted projects of concern to ORNL, the UCC Nuclear Division, and the Department of Energy. These projects all involve some form of spectrometry, and our developmental activities range in scope from ion optical design of special instruments to elucidation of physical and chemical processes through analysis of mass and emission spectrometric data.

The ultrahigh sensitivity of secondary ion mass spectrometry (SIMS) has continued to generate worldwide interest in techniques for quantifying surface and depth profile data. For example, in the continued study of thermocouple failure, we have found that sensitivity indexes, if indexed by matrix ion species ratio, can be employed with significant improvement in accuracy and reproducibility, even in the absence of a standard reference matrix. This technique has recently been used to measure quantitatively the chemical changes that have taken place in failed Chromel-Alumel thermocouples. Because of SIMS depth-profiling capabilities, we have continued our collaborative effort with the Solid State Division by establishing ion implantation and annealing redistribution profiles in solar-grade silicon. The recently acquired PDP-11/34 computer system is being interfaced to our ion microprobe mass analyzer (IMMA) for instrument control and data acquisition and processing.

In organic mass spectrometry, we are continuing our investigation of the structure and chemistry of the  $C_7H_7O^+$  ion (tropylium or benzylic structure) derived from a variety of compounds, using metastable scanning techniques and labeling experiments ( $k_H/k_D$  studies). The ORNL double-focusing spectrometer is being redesigned and converted to a three-sector instrument by addition of a second electrostatic analyzer. The value of this spectrometer as a research instrument has been increased by drastic reduction of noise level and by installation of a high-gain multiplier. Additional modifications that have been made to the instrument are a chemical ionization source, high-speed vacuum pumping, a gas-inlet system, and changes in source mounting. Experiments leading to the use of capillary gas chromatographic mass spectrometry (GCMS) on both high- and low-resolution spectrometers have been carried out. Design and installation of a capillary injector suitable for splitless injection and septum purge were completed, and a Nutech desorber was installed for use with Tenax tubes. A new gas-inlet system has been designed and installed on the MS-50 for use in quantitative gas analyses. The DuPont 490B spectrometer has been used in support of projects for the division as well as for others at ORNL, ORGDP, and the Y-12 Plant.

The interface between the high abundance sensitivity thermionic mass spectrometer and a PDP-11/34 computer is complete and operative; data-reduction software packages have been demonstrated to work correctly. A mass spectrometric and isotope dilution technique employing resin bead technology has the capability of detecting  $^{99}Tc$  down to 10 pg;  $^{96}Ru$  in a new separation was acquired for making  $^{97}Tc$  spike materials. The channel electron multiplier array (CEMA) detector system has

been developed further for spark-source mass spectrometry (SSMS) and has a demonstrated sensitivity improvement of 100. The possible use of CEMA detectors sparked interest in the writing of a computer program to design mass spectrometers with second-order double focusing.

New R&D funding was received from the Office of Safeguards and Security for further refinement of the resin bead-mass spectrometric (MS) technique for safeguarding the nuclear fuel cycle. A single-stage mass spectrometer and PDP-11 data system were used to demonstrate that the resin bead technique was feasible with commercial mass spectrometers equipped with pulse counting. Supportive safeguards development work continued through the International Safeguards Project Office (ISPO) for the IAEA; the microsample resin bead-MS methodology will be fully tested by analyzing reprocessing facility samples from Germany and Japan.

The Advanced Fuels Recycle Program (AFRP) is continuing to support design and construction of an SSMS instrument capable of analyzing highly irradiated samples. Engineering design of the source containment, track, and sample insertion system will be completed by the middle of FY 1979; the instrument has been acquired and is operational.

For support work, a new V.G.-1201 gas mass spectrometer was acquired, which has improved sensitivity, resolution, and capability, compared with our old instrument. In collaboration with the Metals and Ceramics Division, a new time-of-flight mass spectrometer system was installed for the analysis of gases in HTGR irradiated fuel microspheres. Some 66,000 results in support of ORNL, UCC-ND plants, DOE facilities, and EPA projects were reported during this period.

## INORGANIC MASS SPECTROMETRY RESEARCH AND DEVELOPMENT

**Ion microprobe mass analyzer.** Secondary ion mass spectrometry is recognized as the most sensitive surface analytical technique in use. This ultrahigh sensitivity has made SIMS the chosen technique for studying a variety of unique chemical and physical surface problems. Currently the single largest area of research in SIMS has been the development of both empirical and theoretical methods for data quantification. To date no single all-encompassing quantification technique has evolved, but several methods have appeared that show great promise in capitalizing on the sensitivity of SIMS. The results of some of our studies in this area and the problems to which they were applied are described in the following paragraphs.

In the investigation of nickel- and iron-based alloys, we have observed that significant changes in sensitivity factors (SFs) occur for relatively small changes in alloy composition.<sup>1</sup> Other workers have

observed this effect, and it has been suggested that one might be able to adjust SFs by applying some matrix-sensitive correlation factor that would account for changes in the matrix composition. Japanese workers have shown that in some cases relative SFs can be indexed by a matrix species (e.g.,  $M^{++}/M^+$ ) and that a working curve can be generated from a single standard.

We have expanded our investigation of thermocouple failure analysis to include nickel-based materials. In the analysis of sheathed Chromel-Alumel thermocouples, we observed large changes in concentration for several elements in the thermoelements. This fact made the residual pressure single SF method for reducing observed ion counting rates to concentrations inadequate because suitable standards that bracket the altered wire and sheath compositions were not available. This problem was solved by using SFs indexed by a matrix ion species. In the nickel-based alloys studied in this work, we found that the ratio  $\text{NiO}^+:\text{Ni}_3^+$  was very sensitive to oxygen surface coverage. Increasing oxygen pressure in the sputtering region at a given primary beam current density formed more  $\text{NiO}^+$  at the expense of the trimer  $\text{Ni}_3^+$ . The use of this observation as an SF calibration technique is predicated on the fact that conditions that induce changes in elemental ion

1. D. H. Smith and W. H. Christie, "A Comparison of a Theoretical Model and Sensitivity Factor Calculations for Quantification of SIMS Data," *Int. J. Mass Spectrom. Ion Phys.* **26**, 61 (1978).

yields also affect matrix ion species yields. As a test of this method, we determined SFs for chromium from a Chromel standard wire and both the NBS NX 980 and NX 1285 nickel-based standards. Sensitivity factors were determined by recording elemental count data for a number of different oxygen pressures in the sputtering chamber. As oxygen pressure was increased for a given standard, the  $\text{NiO}^+:\text{Ni}_3^+$  ratio also increased. Sensitivity factors determined from these standards were plotted as a function of the  $\text{NiO}^+:\text{Ni}_3^+$  indexing ratio and are shown in Fig. 2.1. In this technique, it is not necessary to know the oxygen surface coverage or the oxygen pressure in the sputtering region because they are implicitly included in the measured indexing ratio.

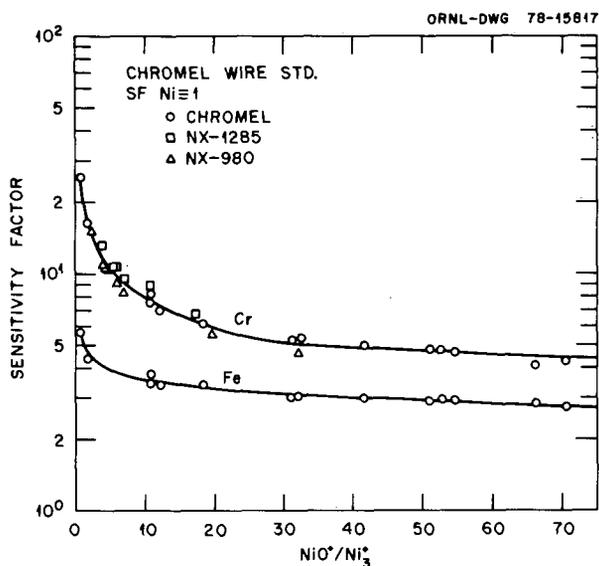


Fig. 2.1. Indexed sensitivity factor response curves.

Although the three standards were different in composition (see Table 2.1), the SFs for chromium indexed by the  $\text{NiO}^+:\text{Ni}_3^+$  ratio fell on the same curve. If this method is to have general applicability, then SFs indexed in this fashion should fall on the same curve for reasonable changes of composition in the various standards used. Uncertainties in the assay values for minor elements, in the standards used in this study, precluded making a critical assessment of this feature of the method. We were able to test the model in the case of chromium in the Alumel wire standard. Using the SFs shown in Fig. 2.1, we calculated via SIMS analysis that the Alumel standard contained 0.0008 at. % chromium. This value was independently verified by SSMS analysis. We found this result somewhat striking considering that the chromium levels in the standards used to determine the SFs were over four orders of magnitude higher than in the Alumel specimen. Indexed SF plots for Al, Si, Mn, Fe, and Co were prepared in a similar manner, and each exhibited a response similar to that observed in Fig. 2.1 for chromium. The shape of these SF curves supports the observation that higher accuracy and more reproducible results would be expected with oxygen flooding in the sample region when oxidizable metallic samples are being analyzed. In this system of nickel-based alloys, we found that oxygen pressures of  $5.3 \times 10^{-4}$  to  $10.7 \times 10^{-4}$  Pa and current densities of 0.2 mA/cm<sup>2</sup> tended to keep the  $\text{NiO}^+:\text{Ni}_3^+$  ratio above 20 and thereby allowed use of SFs from the flat portion of the response curve. It is interesting to note that the SF indexing technique approached a single SF method if sufficient sample oxygen surface coverage was maintained.

In our study of decalibrated Chromel-Alumel thermocouples, two sheath materials were examined

Table 2.1. Nominal compositions (at. %) of materials investigated

	Chromel	Alumel	304 <sup>a</sup> S.S.	Inconel 600	NBS NX- 980 <sup>b</sup>	NBS NX- 1285 <sup>b</sup>
Al	0.02	4.19	0.0014	0.40	0.55	0.38
Si	0.92	3.53	1.95	0.41	0.22	0.49
Cr	10.37	0.0008	19.96	17.42	16.73	17.85
Mn	0.01	3.01	1.99	0.21	0.40	0.32
Fe	0.35	0.031	66.42	7.39	8.93	6.92
Ni	88.33	88.76	9.32	74.28	72.31	73.16
Co	0.04	0.48	0.014			

<sup>a</sup>Minor elements carbon, phosphorus, and sulfur omitted.

<sup>b</sup>C, S, Ti, and Cu omitted.

(Inconel-600 and type 304 stainless steel). The stainless steel sheath, being an iron alloy, was analyzed by using a different set of indexed SFs based on iron as the reference element. The indexing ratio used was  $\text{FeO}^+:\text{Fe}^+$ . A different response was observed in this system. As oxygen surface coverage increased, the observed SF range decreased, and at high coverage the SF values tended to converge on the reference element value  $\text{FE} \equiv 1$ . The slopes of the SF lines would preclude using single SFs in the analysis of chromium and nickel in the altered type 304 stainless steel samples encountered in this work.

Table 2.2 summarizes the major analytical results obtained using indexed SFs to study two sheathed Chromel-Alumel thermocouples that were significantly decalibrated.

Conclusions in this study were that Chromel-Alumel thermocouples, sheathed in reactive metals

(Inconel-600 and type 304 stainless steel), decalibrate significantly when exposed to temperatures above  $1100^\circ\text{C}$ . The decalibration was caused by alteration of the composition of the Chromel and Alumel thermoelements. The nature of the compositional alteration was influenced by the chemical environment present, specifically the sheath composition. Examination of Table 2.2 shows that manganese had intruded into the Chromel and Alumel wires of thermocouple I. The source of this manganese was the stainless steel sheath, which had become depleted in manganese. As indicated in Table 2.2, different trends were observed for thermocouple II, which was sheathed in a nickel-based alloy, Inconel-600. The use of single, unindexed SFs for calculating these data was found unacceptable. An oxygen pressure  $\geq 2.7 \times 10^{-4}$  Pa in the sputtering region was shown to give a more reproducible set of SFs. Indexing with a

Table 2.2. Analysis of decalibrated thermocouples using indexed sensitivity factors

Section	Al	Si	Cr	Mn	Fe	Ni	Co
<b>Thermocouple I (stainless steel sheath)</b>							
Alumel wire, at. %							
Near hot junction	0.047	4.03	0.80	5.62	0.29	88.65	0.56
As received reference	4.38	3.99	0.0008	2.80	0.07	88.26	0.50
Nominal composition	4.19	3.53	0.0008	3.01	0.03	88.76	0.48
Chromel wire, at. %							
Near hot junction	0.015	0.96	10.27	3.30	0.47	84.94	0.036
As received reference	0.023	1.06	10.80	0.01	0.29	87.78	0.035
Nominal composition	0.021	0.92	10.37	0.01	0.35	88.33	0.040
Type 304 stainless steel							
Near hot junction	0.0036	0.55	16.34	0.24	73.23	9.61	0.016
As received reference	0.0024	1.38	17.52	0.64	71.19	9.25	0.016
Nominal composition		1.95	19.96	1.99	66.42	9.32	
<b>Thermocouple II (Inconel-600 sheath)</b>							
Alumel wire, at. %							
Near hot junction	2.01	5.85	0.176	0.82	0.122	90.43	0.59
As received reference	4.09	3.39	0.0010	2.68	0.075	89.04	0.73
Nominal composition	4.19	3.53	0.0008	3.01	0.031	88.76	0.48
Chromel wire, at. %							
Near hot junction	0.202	1.03	11.87	0.410	0.38	86.03	0.07
As received reference	0.013	1.01	11.15	0.014	0.36	87.38	0.08
Nominal composition	0.021	0.92	10.90	0.008	0.36	87.69	0.05
Inconel-600, at. %							
Near hot junction	0.18	0.29	8.81	0.027	7.70	83.00	
As received reference	0.40	0.40	16.48	0.211	7.72	74.79	
Nominal composition		0.41	17.42	0.210	7.39	74.28	

matrix ion species ratio allowed the correct set of SFs to be chosen for any combination of analytical conditions (oxygen pressure, current density, sample composition, etc.). Using indexed SFs and oxygen flooding achieved a substantial improvement in analytical accuracy over the residual pressure single SF method. A detailed account of this work has been submitted for publication.<sup>2</sup>

We have continued our collaborative effort with workers in the Solid State Division in determining the effect of laser and thermal annealing techniques on the distribution of ion-implanted <sup>11</sup>B in (100) single crystal silicon.<sup>3,4</sup> Our results show that substantial redistribution of the as-implanted boron profile occurs for laser energy densities greater than 1.1 J/cm<sup>2</sup>. Redistribution of the implanted boron by pulsed laser annealing is significantly greater than that observed for thermal annealing (900°C, 30 min). Broadening of the as-implanted profile was found to be laser pulse energy and pulse number dependent.

For these measurements, the primary ion beam (O<sub>2</sub><sup>+</sup>, 16.0 keV, 15 × 10<sup>-9</sup> A, 5-μm diam) was raster scanned over a 2000-μm<sup>2</sup> region, whereas <sup>11</sup>B<sup>+</sup> sputtered ions were detected from about 15% of the rastered area using an electronic aperture. Sputtered ion intensities of <sup>11</sup>B<sup>+</sup> were normalized to the <sup>30</sup>Si<sup>+</sup> ion intensity from the matrix to compensate for any change in the secondary ion extraction efficiency. The depth scale was calibrated from the expected peak position of <sup>11</sup>B ions implanted at different energies in the range 35 to 80 keV. Concentration scales were estimated from the expected peak concentrations of samples implanted in the dose ranges 1 × 10<sup>14</sup>/cm<sup>2</sup> to 1 × 10<sup>16</sup>/cm<sup>2</sup>.

Plotted data show a striking change in the <sup>11</sup>B concentration profile at laser energies above 1.1 J/cm<sup>2</sup>. The profile becomes almost flat topped, and boron spreads deeper into the sample as the laser energy is increased. Modification of the profile is observed as a function of the number of laser pulses

delivered to the surface. At pulse energies of about 2.0 J/cm<sup>2</sup>, flattening and spreading of the boron distributions are observed for the first two pulses. After two pulses at this energy, there is little further boron redistribution.

J. C. Wang and others in the Solid State Division have shown that ion-microprobe-determined redistribution profiles of laser-annealed <sup>11</sup>B in (100) silicon can be explained by invoking standard concepts. In this study, boron ions were implanted at 35 keV in (100) silicon to a dose level of 1.04 × 10<sup>16</sup>/cm<sup>2</sup> and were subjected to laser annealing with a ruby laser at 1.7-J/cm<sup>2</sup> energy and 60-ns pulse duration. Comparison of profile areas of the redistributed boron versus the as-implanted standard demonstrates that no measurable amount of boron is lost from the silicon during laser annealing.

The model of Wang et al. shows that, under the conditions described above, the near-surface region of the silicon melts and remains molten long enough for mass diffusion in the molten state to explain the ion-probe-measured boron redistribution. Frequently invoked concepts such as "radiation-enhanced" diffusion need not be considered. Wang et al. feel that the small discrepancies around 3000 Å in depth are due to neglect of melt-front motion. Because the IMMA data have uncertainties of ±15%, this trivial point was not pursued.

In the course of our investigation of Pt-Pt-Rh thermocouple decalibration, we observed a strong Pt<sup>+</sup> ion enhancement in platinum and Pt-Rh alloys diffused with aluminum when bombarding with O<sub>2</sub><sup>+</sup> primary ions.<sup>5-7</sup> Platinum and Pt-Rh alloys diffused with magnesium at similar concentration levels did not show this effect under O<sub>2</sub><sup>+</sup> bombardment. In an attempt to shed more light on the subject, we have prepared platinum and Pt-Rh wires containing a variety of group IIa, IIIb, and IVb elements. Each element (Mg, Al, Si, B, or Ca) was separately introduced in the wires by reaction with the corresponding metal oxide at low oxygen partial

2. W. H. Christie, R. E. Eby, R. L. Anderson, and T. G. Kollie, "Ion Microprobe Investigation of Decalibrated Chromel versus Alumel Thermocouples: A Quantitative SIMS Analysis Using Indexed Sensitivity Factors and Oxygen Flooding," submitted for publication in *Appl. Surf. Sci.*

3. R. T. Young, C. W. White, G. J. Clark, J. Narayan, W. H. Christie, M. Murakami, P. W. King, and S. D. Kramer, "Laser Annealing of Boron Implanted Silicon," *Appl. Phys. Lett.* **32**, 139 (1978).

4. C. W. White, W. H. Christie, B. R. Appleton, S. R. Wilson, P. P. Pronko, and C. W. Magee, "Redistribution of Dopants in Ion Implanted Silicon by Pulsed Laser Annealing," *Appl. Phys. Lett.* **33**, 662 (1978).

5. W. H. Christie, D. H. Smith, R. E. Eby, and J. A. Carter, "Quantification of SIMS Data; Results, Problems and Promises," *Am. Lab.* **10**(3), 19 (1978).

6. T. G. Kollie, W. H. Christie, and R. L. Anderson, "Large Decalibrations in Ta-Sheathed Al<sub>2</sub>O<sub>3</sub>-Insulated Pt/Rh Thermocouple Assemblies During Heating to 1330°C," *J. Less-Common Met.* **57**, 9 (1978).

7. W. H. Christie, T. G. Kollie, R. E. Eby, and R. L. Anderson, "Ion Microprobe Investigation of Large Decalibrations in Inconel-Sheathed Magnesia-Insulated Platinum-Rhodium/Platinum Thermocouple Assemblies During Use at 1200°C," *J. Less-Common Met.* **59**, 17 (1978).

pressure and high temperature. Strong  $Pt^+$  enhancement was observed from wires diffused with aluminum or boron, but not from wires diffused with magnesium or calcium when sputtering with  $O_2^+$ .

Attempts to prepare wires diffused with carbon failed, due possibly to the limited solubility/temperature range for this system as evidenced by published phase diagrams. However, platinum samples overcoated with carbon via vacuum evaporation show  $Pt^+$  enhancement at the Pt/C interface, suggesting that carbon also produces  $Pt^+$  ion enhancement under  $O_2^+$  bombardment.

The Pt-Al intermetallic phase relationships are well known, and we ascribed the enhanced  $Pt^+$  ion yield to the fact that under  $O_2^+$  bombardment in situ Pt-Al oxides are formed. As the aluminum content increased, the products formed in the sputtering region would increase in insulator-like character. This would result in an insulator band gap or increased surface work function and would account for the increased  $Pt^+$  ion yields. This idea was supported by the observation that under  $N_2^+$  bombardment, no  $Pt^+$  ion yield enhancement was observed in the wire diffused with aluminum.

Enhancement or lack of enhancement of  $Pt^+$  ion yield in these systems appears to be dependent on the thermodynamic stability of the complex ions formed in the sputtering region. Table 2.3 summarizes the results found for Mg and Ca (group IIa) and for B and Al (group IIIb). In this table, the observed intensities for the complex ions shown are summed, and the observed  $Pt^+$  ion signal is ratioed to this sum. This ratio gives a measure of the stability of the complex ions in the sputtering region. The stability of the group IIa complex ions is clearly exhibited. These ions are formed at the expense of the  $Pt^+$  ion yield and explain the lack of enhancement observed for  $Pt^+$  in the presence of magnesium or calcium. Preliminary results indicate that silicon also produces a strong enhancement of  $Pt^+$  ion yields.

Two theories concerning the formation of sputtered complex secondary ions are: (1) they are formed by a concerted reaction of excited atomic species in vacuo in near surface space due to the thermal spike produced by the bombarding ion and (2) they are formed on the surface and are thermally desorbed by the thermal spike. The results of our investigation tend to support a model somewhere in between the two theories. We believe that the excited atomic species are all present in the highly agitated region ( $\sim 3000$  atoms) where the energetic bombarding ion has impacted.<sup>8</sup> Complex ions that have sufficient

Table 2.3. Ratios of platinum ion yields to summed complex ion yields from platinum intermetallic compounds of Mg, B, Ca, and Al

Compound	Ratio
<b>Magnesium (<math>Pt^+/\Sigma CPX^+ \approx 0.038</math>)</b>	
Pt	8.0
PtMg	100.0
PtMgO	90.0
PtMgO <sub>2</sub>	6.5
PtMg <sub>2</sub> O	5.0
PtMgO <sub>3</sub>	5.0
PtMg <sub>2</sub> O <sub>2</sub>	11.0
PtMg <sub>2</sub> O <sub>3</sub>	3.5
<b>Boron (<math>Pt^+/\Sigma CPX^+ \approx 26</math>)</b>	
Pt	100.00
PtO	0.90
PtB	0.70
PtBO	1.30
PtBO <sub>2</sub>	0.12
PtB <sub>2</sub> O	0.03
PtB <sub>2</sub> O <sub>2</sub>	0.65
PtB <sub>2</sub> O <sub>3</sub>	0.10
PtB <sub>3</sub> O <sub>3</sub>	0.04
<b>Calcium (<math>Pt^+/\Sigma CPX^+ \approx 0.0004</math>)</b>	
Pt	0.06
PtCa	22.00
PtCaO	100.00
PtCaO <sub>2</sub>	6.00
PtCa <sub>2</sub> O	2.80
PtCaO <sub>3</sub>	0.10
PtCa <sub>2</sub> O <sub>2</sub>	5.40
PtCa <sub>2</sub> O <sub>3</sub>	2.50
<b>Aluminum (<math>Pt^+/\Sigma CPX^+ \approx 6.6</math>)</b>	
Pt	100.00
PtO+H	1.20
PtAl	7.00
PtAlO+H	4.50
PtAlO <sub>2</sub> H	1.30
PtAl <sub>2</sub> O+H	0.48
PtAl <sub>2</sub> O <sub>2</sub>	0.48
PtAl <sub>2</sub> O <sub>3</sub> +H	0.10

thermodynamic stability are formed in this region, and those that have excess energy above that required to leave this region escape from the surface and are available for detection.

8. W. H. Christie, T. J. Kollie, and R. E. Eby, "Investigation of  $Pt^+$  Secondary Ion Yield Enhancement Observed in Platinum and Platinum-Rhodium Alloys," presented at 26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978.

During this period we have received and made operational a PDP-11/34A minicomputer that will be dedicated to the computerization of IMMA. Communication between IMMA and the computer will be via a custom-designed interface unit based on KT11-H printed circuit modules. Communication between the peripheral devices and the computer will be achieved through FORTRAN-callable subroutines. We have installed an updated RT-11 operating system on the PDP-11 with single-job and foreground/background monitors. High-level languages available on this system are FORTRAN-IV, BASIC, and FOCAL. A major application of this system will be in-depth profiling studies in which the concentration of a number of elements is monitored as a function of depth in the surface region. (*W. H. Christie, R. E. Eby, R. W. Stelzner*)

**Computer control for high abundance sensitivity mass spectrometers.** The objective of this program is to develop and maintain state-of-the-art capability and performance in mass spectrometric analysis. Chiefly because of expected high sample loads, we have chosen to concentrate our efforts on high abundance sensitivity machines. A computerized version of such a machine was developed for IAEA,<sup>9</sup> and we have a similar machine in operation here. Although this machine represents a major step in the direction of computerization of mass spectrometry, new electronic developments have opened additional avenues for analytical improvements.

Proposals for an improved machine were presented in the previous annual report.<sup>10</sup> The interface between the spectrometer and a PDP-11/34 computer is complete and operative except for the processing of actual mass spectrometric data. An operating program was developed, which is considered to be an improvement over that used with the IAEA machine. The data reduction (post acquisition) programs have been demonstrated to work correctly. Test programs were written and tried, and useful ones were included in a disk diagnostic library for use in troubleshooting. We are also developing a program that can emulate the IAEA scheme, which

will be useful in comparing analytical performance with the IAEA approach as well as for use as an operating diagnostic.

Because of the great flexibility in operating parameters available to the operator, the complete configuration may prove too cumbersome for routine analyses. We are exploring several approaches to the use of microcomputer-based controllers that would be managed by a host minicomputer and will incorporate experience gained with the new system into our thinking. Several such systems could operate a number of spectrometers simultaneously and thereby increase sample throughput. (*T. R. Mueller, D. H. Smith, D. L. Donohue, R. L. Walker*)

**<sup>99</sup>Tc by isotope dilution mass spectrometry.** Development of the mass spectrometric method, which was started late last year, has continued during this period, using the single resin bead for loading the <sup>99</sup>Tc. A graded set of <sup>99</sup>Tc standards (30, 3, 0.3, and 0.03 ng) were adsorbed on anion resin beads for analysis and evaluation of ionization efficiency on rhenium filaments. Ionization efficiency was measured on one bead from each concentration by integrating the thermally produced ions. Table 2.4 summarizes these measurements. These data compare with the efficiency for solution loading previously measured at about one ion per 10<sup>6</sup> atoms loaded. The 0.03-ng sample did not run well, but if one uses the 0.3- and 3-ng beads, the average is about 1/15,000 for bead loading or an improvement in efficiency of about 50 over solution loading.

Table 2.4. Ionization efficiency of <sup>99</sup>Tc on resin bead

Loading (ng)	Efficiency (ions per atoms loaded)
30	Too much to integrate
3	1/18,000
0.3	1/13,000
0.03	1/70,000

We have not as yet obtained <sup>97</sup>Tc needed for the tracer. We have obtained <sup>96</sup>Ru, and the irradiation and production of <sup>97</sup>Tc from this material is expected in the first quarter of the next calendar year. Meanwhile, some cooperative work with T. J. Anderson of the Savannah River Laboratory has been carried out with <sup>97</sup>Tc as tracer. A graded set of standards containing descending amounts of <sup>99</sup>Tc

9. D. H. Smith, H. S. McKown, W. H. Christie, R. L. Walker, and J. A. Carter, *Instruction Manual for ORNL Tandem High Abundance Sensitivity Mass Spectrometer*, ORNL/TM-5485 (June 1976).

10. T. R. Mueller, D. H. Smith, R. L. Walker, and L. K. Bertram, "Computer Interface and Sweep Controller for Multi-stage Mass Spectrometer," *Anal. Chem. Div. Annu. Prog. Rep.* Nov. 30, 1977, ORNL-5360, p. 22.

were spiked with 0.90 ng of  $^{97}\text{Tc}$  and adsorbed on two anion resin beads. Results are given in Table 2.5. The data above were obtained from a single resin bead. Two beads were used for adsorption, resulting in a maximum of 0.45 ng of  $^{97}\text{Tc}$  per bead. Adsorption on beads has been measured using  $^{99}\text{Tc}$  and is about 85% efficient; therefore, it is estimated that each bead contained about 0.3–0.4 ng of  $^{99}\text{Tc}$  tracer. The integrated ion signals from this amount averaged  $3.4 \times 10^6$  counts of  $^{97}\text{Tc}$ , and samples were not run to exhaustion because of the increase in molybdenum background at higher filament temperatures. We stopped taking data when the  $^{97}\text{Mo}$  signal equaled the  $^{97}\text{Tc}$  signal as determined from  $^{98}\text{Mo}$  or  $^{100}\text{Mo}$  signals. Based on work done to the present time (10 pg has been measured), we estimate the lowest limit of measurement is 1 pg of  $^{99}\text{Tc}$  with a precision of about 10%, limit now mainly controlled by background. Further work is planned, which we hope will reduce the hydrocarbon background in the 99 mass position or establish correction procedures applicable to mass 99, which would lower the ultimate sensitivity. An encouraging aspect regarding hydrocarbon background is that the background does not come from the resin bead loading. We looked at clean, baked-out filaments with and without resin beads and could see no difference in the hydrocarbon background level. (*R. L. Walker, E. G. Miller, H. C. Smith*)

**$^{148}\text{Nd}$  measurement for burnup analysis.** We have measured  $^{148}\text{Nd}$  by thermal emission–pulse counting mass spectrometry without chemical separation, using a highly enriched tracer of  $^{150}\text{Nd}$ . The determination of neodymium was made on dilute solution from a dissolved single irradiated fuel microsphere. The small amount of fission products from the irradiation of a single microsphere results in a difficult analysis problem, using conventional separation and measurement technology. This led us to attempt the measurement directly because of the high sensitivity of our pulse counting, two-stage instruments. Ion signals obtained from direct filament loading of 1-ng samples are quite satisfac-

tory, using pulse counting techniques. The largest error associated with the direct measurement is caused by interferences in neodymium masses 148 and 150 from  $\text{BaO}^+$ , normal samarium, and fission samarium. Normal neodymium contamination could also cause a bias, if present, because  $^{142}\text{Ce}$  from the sample interferes in the only nonfission isotope of neodymium and makes correction for the bias impossible.

The approach that we used is the two-isotope method of isotope dilution. Barium must be “burned” away before taking data on the  $\text{Nd}^+$  ion and scanning masses 148, 150, 151, and 152. Masses 151 and 152 are used for correcting samarium based on fission yield and normal abundance data tables.

Examples of an unspiked analysis of an irradiated plutonium microsphere are shown below for duplicate loadings with three measurements on each filament.

	Observed 148/150 neodymium	S.D.	Corrected 148/150 neodymium	S.D.
Filament No. 1	1.573	0.010	1.622	0.006
Filament No. 2	1.549	0.051	1.601	0.024

The magnitude of the samarium correction is usually relatively small, 3–5% of the neodymium. Using this method, the overall precision of the measurement is estimated to be about 3%. (*R. L. Walker, E. G. Miller, H. C. Smith*)

**Electro-optical ion detector for SSMS.** The CEMA detector has been installed in our AEI-MS702R mass spectrometer. Originally, the detector was mounted on a ceramic substrate resembling a photoplate cassette that could be inserted into and withdrawn from the magnetic analyzer region. This mode allowed the detector to be initially evaluated, but it proved too difficult to make design changes under those conditions. Therefore, the CEMA was mounted directly on a flange located over the magnet

Table 2.5. Measurement of  $^{99}\text{Tc}$  by isotope dilution

	$^{99}\text{Tc}$ added (ng)	$^{97}\text{Tc}$ added (ng)	99:97 ratio observed (S.D.)	Measured $^{99}\text{Tc}$ (ng, S.D.)
Std-1	11.6	0.90	$13.14 \pm 0.08$	$11.8 \pm 0.1$
Std-2	1.16	0.90	$1.311 \pm 0.007$	$1.18 \pm 0.01$
Std-3	0.116	0.90	$0.1251 \pm 0.0004$	$0.113 \pm 0.003$
Std-4	0.0106	0.90	$0.0115 \pm 0.0003$	$0.0104 \pm 0.0003$

gap. Focusing of the image was achieved by racking the detector into the spectrometer's focal plane via a bellows. After use, the CEMA could be retracted, allowing the normal photographic plate detector to be used. Magnetic shielding was used to eliminate interference caused by the fringe magnetic field. This allowed the detector to be used at the maximum accelerating voltage and at the magnetic field conditions for maximum resolution and throughput.

Results obtained thus far indicate that the CEMA is about 100 times more sensitive than the photographic plate. The resolution is less than that of a photoplate but, at 400, is more than sufficient to separate the isotopes of any element. The detector has a basic dynamic range of about 100, which will be improved to  $10^3$  to  $10^4$  with a signal averaging data system. In addition, the simultaneous detection of all mass spectral lines within a given range will increase the precision of the technique, compared with more standard detection systems.

The available optical readout systems include a TV camera using a silicon vidicon tube and a linear photo diode array, with charge coupled output registers for maximum signal-to-noise characteristics. The vidicon system is the most sensitive system but is difficult to digitize with high resolution. The diode array detector provides precisely timed video information, which is easily digitized. The resolution of the diode array is higher than that of the CEMA and is not a problem.

A two-channel digitization system has been constructed and is under evaluation. This allows two mass spectral lines to be digitally integrated for a set period of time or charge accumulation at the monitor. This system is designed for isotope dilution measurements and should provide higher precision and accuracy over a wider range of spike and sample concentrations. (*D. L. Donohue, J. A. Carter*)

**Computer program to design mass spectrometers.** A computer program has been written to calculate the aberration coefficients for any double-focusing mass spectrometer consisting of an electric sector followed by a magnetic sector. The calculation uses second-order transfer matrix representation and includes effects of fringing fields corrected to third order. Similar calculations have been performed previously but did not include effects of fringing fields or the full three-dimensional representation. These effects were seen to have considerable influence on second-order aberration coefficients, which affect mass resolution and sensitivity.

The calculation for determining parameters for a new mass spectrometer proceeds as follows. A set of

acceptable design parameters (lengths and angles) is chosen for the desired mass spectrometer. This selection is based on experience or earlier calculations, using the previously written program. The program first checks that first-order focusing conditions are satisfied, then calculates the ten  $17 \times 17$  matrices necessary for second order. The matrices are multiplied to give a full set of transfer coefficients, which completely describe the focusing properties of the mass spectrometer. The calculation is iterated over the desired range of parameters until satisfactory focusing conditions are produced.

An advantage of the transfer matrix method is that any number of sector fields and lenses may be coupled together by introducing their respective matrices into the matrix multiplication. Thus we hope to apply these calculations to present and future mass spectrometers within the division. (*R. J. Warmack, D. H. Smith*)

**Analysis of water by mass spectrometry.** One of the more difficult problems in analytical mass spectrometry is the accurate determination of moisture in fixed and condensed gas samples. This is due in part to incomplete and nonreproducible transport of the water molecules through the sample system. Also, fractionation of the water molecules may take place on the surface of the ionizing filament.

A technique is being developed to concentrate the moisture and to convert quantitatively the moisture to another gas, which can be determined by standard gas mass spectrometric techniques. The moisture in the sample is condensed onto  $\text{CaC}_2$  by the use of a refrigerated trap at liquid nitrogen temperature. The remaining noncondensables are slowly pumped away, and the trap is isolated and heated to  $90^\circ\text{C}$  for 0.5 h to promote the carbide reaction. The contents are then analyzed for the acetylene  $\text{C}_2\text{H}_2$  produced by the following reaction:



The  $\text{C}_2\text{H}_2$  is equivalent to one-half the water content of the sample.

An ambient air sample containing 1% moisture was analyzed by this method, which showed that essentially all the moisture had been converted to  $\text{C}_2\text{H}_2$ .

The method can be used to determine the amount of moisture desorbed from solids.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  was placed in a small furnace attached to the  $\text{CaC}_2$  trap. The residual atmosphere was pumped from the furnace and sample. The furnace was heated to  $140^\circ\text{C}$ , and the released moisture was transferred to

the  $\text{CaC}_2$  trap; the conversion to  $\text{C}_2\text{H}_2$  was completed and measured with the mass spectrometer. Care must be used in evacuating the sample furnace. The theoretical  $\text{H}_2\text{O}$  content of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  is 14.7 wt %. After pumping for 2 min, a 0.26 wt % loss of  $\text{H}_2\text{O}$  occurred. This method should be very useful for a total gas analysis for which the moisture content is of particular interest. Quantitative determinations may be made when a micromanometer is placed into the system. (*J. R. Walton*)

## ORGANIC MASS SPECTROMETRY

**High-resolution (MS-50) organic mass spectrometry studies.** We are investigating the chemistry of the  $\text{C}_7\text{H}_7\text{O}^+$  ion by a variety of methods. One technique that has proved useful is the metastable linked scan, which scans  $E/V^{1/2}$  while maintaining  $\mathbf{B}$  constant, where  $E$  is the electrostatic potential,  $V$  is the accelerating potential, and  $\mathbf{B}$  is the magnetic flux. This scan mode is useful for examining unimolecular reactions with rate constants of about  $10^6/\text{s}$ . The  $E/V^{1/2}$  scans of  $\text{C}_7\text{H}_7\text{O}^+$  ion derived from a large number of chemical sources (alkylated phenols, protonated tropone, benzyl ethers, etc.) have yielded kinetic data on the chemistry of this ion. The data have been used to obtain daughter ion profiles and also to determine  $k_{\text{H}}:k_{\text{D}}$  ratios (using protonated and deuterated species) as mechanistic probes. Although such data are often difficult to interpret, certain facts are readily apparent. For example, the linked scans of the  $\text{C}_7\text{H}_7\text{O}^+$  ions derived from *ortho*-, *meta*-, and *para*-cresols are different, suggesting that the decomposing ions have not sampled a common potential energy surface. The  $k_{\text{H}}:k_{\text{D}}$  studies on these same ions (labeled by replacement of the phenolic hydrogen) yielded different ratios (that from *meta*-cresol being greater than those from the *ortho*- and *para*-cresols). Ring and alkyl side chain labeled compounds are being prepared to complete these  $k_{\text{H}}:k_{\text{D}}$  studies. We hope that a consistent picture can be developed concerning the ion chemistry of the  $\text{C}_7\text{H}_7\text{O}^+$  ion when derived from many chemical sources.

We are assembling control circuitry for another linked-scan mode, maintaining  $\mathbf{B}/E$  constant at constant  $V$ , which is a more sensitive mode yielding more complete kinetic data because no defocusing of the ion source occurs. Additional thermodynamic data must be obtained to make definitive statements as to mechanisms involved in the ion chemistry of the  $\text{C}_7\text{H}_7\text{O}^+$  ion. We expect to obtain these data with the ORNL double-focusing instrument, which is being

rebuilt as described below. Accelerating potential scans (HV scans) with this instrument can be used to obtain the translational energy distribution of the reaction products and to estimate unimolecular reaction energy profiles. (*D. C. Canada, D. H. Russell, W. T. Rainey*)

**Double-focusing mass spectrometer.** To improve the research capabilities of the organic mass spectrometry group, we have recently begun a program to update the ORNL double-focusing mass spectrometer. This instrument was designed and constructed at ORNL, and a principal limitation of it has been an unusually high signal-to-noise level. The origin of this noise was recently traced to the filament power supply and was corrected by replacing the defective unit with a Lambda model LCS-CC-01 power supply. This modification reduced the noise level about 100-fold.

To improve the sensitivity of this instrument, we recently installed a new Hamamatsu electron multiplier assembly. The rated gain of this multiplier is about 15 times greater than the original RCA unit. Because of the difficulties in accurately measuring the multiplier gain, we have not verified this increased sensitivity. However, our studies indicate that the instrument has sufficient sensitivity and dynamic range to function well as a research instrument.

The design of this instrument is such that one would expect high energy resolution for the electric sector. A high energy resolution is required to perform high-quality ion-kinetic energy spectroscopy. We have recently verified that this instrument is indeed capable of high-energy resolution, that is, about 5000. This resolution was measured prior to correcting the noise problem; thus we may now expect even higher energy resolution.

As a first step in obtaining a high-quality research instrument, we purchased a programmable high-voltage power supply (Spellman model RHSR-15PN60) to perform high-voltage defocused metastable scans. We are also constructing an all-glass heated inlet system, which is almost complete. Ground glass valves, operated by magnetic actuators, and an expansion volume have been assembled and are being installed in the heated box with a short heated glass tube connecting the spectrometer source.

We are currently in the design stage of obtaining chemical ionization (CI) on this instrument. Chemical ionization will greatly improve the analytical capabilities of this group as well as permit the research and development applications we have planned. A number of source design changes and

more efficient vacuum pumping are required to achieve CI. Specifications for these design modifications have been delivered to the Y-12 machine shops.

Modifications to the vacuum system include installation of a 6-in. diffusion pump (replacement for the existing 4-in. pumping system) and purchase of a 1400-liter/s mechanical pump (Leybold-Hereaus). These changes to the vacuum system will provide more than adequate pumping speed to achieve high-quality CI conditions (3–5-torr source pressure).

To further enhance the analytical capabilities of the ORNL double-focusing instrument, we are designing a second electric sector (ESA), which will be installed after the magnetic sector (MA). This three-sector geometry (ESA, MA-ESA<sub>2</sub>) has numerous applications in the study of low-energy unimolecular decomposition processes, that is, rate constants of 10<sup>6</sup>–10<sup>5</sup>/s, and also makes possible the use of third-body-induced dissociation reactions. By installing high-pressure gas collision chambers in the field-free regions between ESA and the magnet and/or the magnet and ESA<sub>2</sub>, it is possible to cause a normally stable ion to decompose after collision with a thermal neutral. The mass and intensity of each decomposition product from the collisional activation process may be determined by scanning the potential of ESA<sub>2</sub>. Previous studies have shown that substantial structural information may be obtained in these experiments.<sup>11</sup>

An alternate approach to these studies may be obtained by using a reversed-geometry instrument, that is, source-magnet-electrostatic sector detector. In the normal geometry, energy analysis precedes mass analysis. However, the three-sector design has several advantages. For example, in a revised-geometry configuration, it is not easy to examine first field-free region decomposition processes, whereas, in a three-sector configuration, this can be done by performing accelerating voltage scans. The first field-free region metastables are important if one is interested in investigating the kinetics of unimolecular reactions, for example, field ionization kinetics.

In addition to collision-induced dissociation, the three-sector instrument will be used to investigate the potential for photoinduced dissociation (photodissociation) of high translational energy ions. Several

studies<sup>12</sup> that suggest the potential of this technique for ion structure determinations have been reported by physicists. As yet, this methodology has not been employed by chemists. The advantage of this method of inducing decomposition is the role of selection rules for optical transitions, a restriction not imposed on high-energy collision processes. (*D. H. Russell, W. T. Rainey*)

**ORNL single-stage organic mass spectrometry.** Preliminary experiments leading to capillary GCMS with both high- and low-resolution mass spectrometers have been carried out with the ORNL single-stage organic mass spectrometer. A modified injector port was installed on the PE-3920 chromatograph to permit splitless injection of samples; the port uses injector/septum purge to eliminate interference from solvent peaks, tailing of gas chromatographic (GC) peaks, and septum bleed. Mass-flow controllers are used to maintain constant flow of both the helium carrier and purge streams. Solenoid valves are used to switch gas flows as required for injection and column programming. In the injection mode, only the carrier flow passes through the injector port, carrying the solvent and sample to the column head, which is maintained at a low temperature. During this time, the purge stream is vented to the atmosphere. The time assigned to the injection mode is controlled by an electrical timer and varies from 0 to 5 min. At the end of the set time, the timer switches the solenoid valves to the purge mode, introduces the purge stream into the injector port at the column head, and opens an exit to air, allowing the total volume of the injector to be swept in a reverse direction by the purge stream. A charcoal trap (located before the solenoid valve) controls the purge outlet and prevents condensation of organics and consequent fouling of the valve. Control of the exit purge stream is maintained by an adjustable outlet restriction, which was constructed from capillary tubing and has a sliding wire insert. Column oven temperature programming or elevation to the isothermal temperature is started at the time the purge mode is initiated.

We are installing and testing a Nutech desorber and controller for use with Tenax adsorption tubes for environmental (air) analyses. This work is being undertaken as part of our interagency agreement with EPA for qualitative analysis of organic

<sup>11</sup> For specific examples see: R. G. Cooks's "Collision-Induced Dissociation of Polyatomic Ions," p. 402 in *Collision Spectroscopy*, R. G. Cooks, ed., Plenum, New York, 1978.

<sup>12</sup> F. von Busch and G. H. Dunn, "Photodissociation of H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>," *Phys. Rev. A* **5**, 1726 (1972).

pollutants in air. The desorber unit replaces the injector port of the gas chromatograph and connects directly to the chromatographic column. An internal aluminum block containing the switching valve and the desorption chamber is maintained at the desorption temperature. During desorption, the Tenax tube is introduced into the chamber, and a purging helium stream carries the effluent to a capillary tubing trap, which is maintained at liquid nitrogen temperature. This trap is cooled by a stream of liquid nitrogen generated in an external Dewar flask. After 5–10 min desorption, the valve is switched for injection, and the trap heater is turned on. After another 5–10 min, all sample components have been transferred to the head of the column (at 40–50°C), and column programming can be started. Temperatures of the block, trap, and capillary tube leading to the column head are adjustable and have proportional control and digital readout. We are using a glass SCOT column with an SP2100 stationary phase yielding  $N_{\text{eff}} = \sim 45,000$  as measured for this system. This equipment will be transferred to X-10 for attachment to the PE-3920 chromatograph interfaced to the DuPont 490 spectrometer. Makeup helium is added at the column exit to prevent peak broadening caused by detector and tube volumes and to allow use of the jet separator inlet of the spectrometer. The Tenax adsorption tubes can be used many times without composition or background problems. Therefore, the apparatus will be of value in environmental studies in the Oak Ridge area after completion of the EPA program. (*W. T. Rainey, C. A. Pritchard*)

**MS-50 high-resolution gas mass spectrometry.** Because of the need for high-resolution, quantitative gas analyses, considerable time was spent during this year in evaluation of the gas inlet system used with the AEI MS-50. Difficulties with both leaks to atmosphere and internal leakage through valves led to redesign and reconstruction of a new gas inlet system. Special care was used to maintain minimum volume in the system consistent with reasonable pumping speed and to eliminate sources of memory when handling condensable gases. The new system has been constructed and installed and is being evaluated.

The system consists of two sample inlets into 1-ml or 2-liter expansion volumes, which can be connected through a fixed gold leak (0.02 mm) into the spectrometer source. Pressures in the expansion volumes are measured by an MKS Baratron transducer covering the range 1.2 to  $10^{-2}$  torr. The system is contained in a thermostatically controlled

oven, with both the tube to the spectrometer and the sample bulb heated by separate heaters. Initial experiments with pure gases ( $\text{H}_2$ , He, Ar,  $\text{N}_2$ , and  $\text{C}_3\text{H}_8$ ) showed the expected linear relationship between  $\ln P$  and time, characteristic of a molecular leak and desirable for a gas inlet. The mass spectrometer source pressure remained at  $<4 \times 10^{-7}$  torr with these gases at inlet pressures of  $<1$  torr.

Evaluation of the system will be continued over a long period of time to determine the stability of the total system and the consistency of calibration factors under normal operating conditions. Because the spectrometer is being used in several modes of operation, it is necessary to ensure repeatability of conditions necessary for quantitative analyses. For instance, daily checks of the  $\text{CH}_4:\text{C}_2\text{H}_6$  ratio in a standard gas mixture have shown a reproducibility of  $\pm 6\%$  when refocusing from other operational conditions. (*D. C. Canada, E. H. McBay, W. T. Rainey*)

**Organic mass spectrometry support.** As in the past, the Organic Mass Spectrometry Group has given support to a wide variety of programs throughout the three-plant area when organic qualitative or quantitative analyses were required. The major effort has been applied to collaborative work with other investigators in the Analytical Chemistry Division. In addition, considerable effort has been devoted to programs of the Metals and Ceramics, Health and Safety Research, and Chemistry divisions as well as the Y-12 and ORGDP analytical laboratories.

The DuPont 490B spectrometer has been used primarily for GCMS analyses in programs of the Bio-Organic Analysis Section for qualitative analyses of complex fractions of tobacco smoke condensate and fossil fuels. The versatile software available in the DuPont 494 data system has been used to advantage in gleaning useful information from the tremendous amount of data collected during long GCMS runs. The internal library search system has been used to speed identification of components, although in many cases the library was insufficient and the samples too complex to permit easy, unambiguous identification. The mass chromatogram technique, using selected ions characteristic of compound types, has been used to assist in determining the presence of some types. For instance, GCMS and mass chromatograms were valuable in studying the separation efficiency of a scheme using Sephadex LH-20 for fractionating shale oil. Subfractionation of effluents by N. Goeckner followed by GCMS yielded much useful data; however, the use of mass chromatograms greatly simplified the interpretation of the data,

confirming or negating the presence of specific compound types or functional groups and permitting an evaluation of the separation scheme.

The ORNL single-stage spectrometer was also used in support of research personnel, especially as a backup for the DuPont 490 and for classified samples, even though the manual data handling was more laborious. Both instruments were involved in assisting personnel of the Health and Safety Research Division in their study of mixtures of dielectric gases useful as insulating media in high-voltage transmission. Mixtures of various gases, such as sulfur hexafluoride, perfluorocyclobutane, perfluorocyclobutene, and perfluoro-2-butyne were exposed to high-voltage arcs, and the resultant gases were analyzed by GCMS. For instance, mixtures of various compositions of sulfur hexafluoride and perfluorocyclobutane were analyzed after exposure to sparking under various total energy inputs. Perfluoroethylene was identified in the product gases, and its yield was estimated to be roughly proportional to the energy input.

We have continued our contract for use of the mass spectral search system (MSSS), which is available to us on a time-sharing basis via telephone. A complete version of the NIH-EPA chemical information system (CIS) was released for general use on July 1, 1978, through computers of the Interactive Sciences Corporation (ISC) via Telenet. The responsibility for operation and dissemination of the entire CIS now lies with the Brookhaven National Laboratory. The MSSS data base has been updated to include about 32,000 spectra. Options also include the Probability Based Matching Program, which is especially valuable in handling spectra of impure materials and was formerly available only through the Cornell University Computer Service. (*W. T. Rainey, D. C. Canada, C. A. Priichard, E. H. McBay*)

### MASS SPECTROMETRY PROJECTS FOR SAFEGUARDS

**Introduction.** One of the principal concerns of nuclear safeguards is to assay uranium and plutonium at various stages of the nuclear fuel cycle. Both concentrations and isotopic composition of these two elements are required to monitor the flow of fissionable material and to provide early detection of clandestine activity. Recent restrictions imposed on the shipment of fissile material have caused the Division of Safeguards and Security (DSS) of DOE to reassess many of their analytical techniques with a view to minimizing the quantity of sample required.

Mass spectrometry plays an important role in both quantitative and isotopic analyses of uranium and plutonium. The recently developed resin bead sample loading technique coupled with pulse counting mass spectrometers provides safeguards with an unprecedented combination of sample size sensitivity, ease of shipping, and minimum expense.

Both international and domestic safeguards personnel are currently in the process of assessing this resin bead technique. Ultimate tests of the procedure will come with analysis of field samples being collected from reprocessing facilities in Germany and Japan.

Because the sophisticated mass spectrometers required to analyze samples loaded on resin beads ( $\leq 1$  ng U and Pu) are available in only a few laboratories throughout the world, DSS is keenly interested in expanding this capability. To this end, we built an ORNL-type two-stage mass spectrometer for the IAEA in Vienna, and this past year we successfully demonstrated the compatibility of the technique with the more common single-stage instrument.

**Mass spectrometry development projects for the Division of Safeguards and Security:** A number of projects have been initiated at the request of the DSS. Among these projects are a demonstration of the compatibility of the resin bead sample loading technique with a conventional mass spectrometer, construction of a new sweep control panel, and a literature survey to determine the feasibility of tracing yellow cake to its origin.

To demonstrate the compatibility of resin bead sample loading with conventional mass spectrometers, we reactivated our thermionic single-stage mass spectrometer, which had been idle for several years. The vacuum system was cleaned and revamped; installation of a new sublimation/ion pump and source can was required. A multiplier, used in pulse counting mode, was installed. Because of the heavy sample load expected from DSS and because our 15-year-old analyzers are terminally ill, we built a new sweep control/computer interface panel. It is a slightly modified version of the unit installed in the new mass spectrometer that we built for the IAEA in Vienna. The principal revision allows us to scan 16 masses rather than 8. A number of resin bead samples, both standards and "real life," were analyzed with the spectrometer. Precisions and accuracies were comparable to those obtainable on conventional mass spectrometers using large sample loadings, thus completing the demonstration of compatibility of resin bead sample loading with a

single-stage mass spectrometer. A report describing the results has been written and published as ORNL/TM-6563.

A continuing problem of concern in thermal ionization mass spectrometry is the fractionation of isotopes as the sample is evaporated from the filament. An investigation into this problem is under way, with the hope of being able to quantify it in some degree. Another project undertaken at the behest of DSS is the development of a portable mass spectrometer for onsite monitoring of major isotope ratios. This project will be carried out jointly with the National Engineering Laboratory at Idaho Falls, which will have primary responsibility for development of the mass spectrometer; we will investigate sample preparation and loading. Consultation with Idaho personnel by J. A. Carter and D. H. Smith during a visit to Idaho led to overall ground rules for the project as well as discussion of technical design criteria for the instrument. Acquisition of a quadrupole mass spectrometer for assessment is planned for the forthcoming year.

A literature search was performed to see if the problem of tracing uranium ores through yellow cake to its origin has been previously addressed. It apparently has not. Therefore, further work has been suggested, such as the isotopic measurement of uranium and plutonium and trace analysis of key minor constituents, in the hope that the combination of a number of monitoring parameters can provide unambiguous assignment of origin. (*D. H. Smith, L. K. Bertram, R. L. Walker, H. Simmons, J. A. Carter*)

**Technical support to the IAEA.** Technical assistance was requested by the IAEA in solving problems associated with the ORNL-built tandem instrument and its application to the resin bead sample-loading technique.

The first interchange of uranium- and plutonium-loaded resin beads with the IAEA Safeguards Laboratory led to several conclusions.

1. Analysis of beads shipped from one laboratory to the other required no special precautions beyond those ordinarily taken. Both uranium and plutonium ran very well.
2. The IAEA instrument had a consistent negative bias of 1.0–1.5% on the  $^{235}\text{U}/^{238}\text{U}$  measurement from a mixed resin bead sample. Numerous resin bead samples, of both IAEA and ORNL origin, were analyzed at each site to confirm the reality of the bias. No bias was observed in the ORNL measurements from beads prepared at either site.

Telephone conversations failed to locate the source of this bias, and, because there were several other problems at IAEA, we were urgently requested to send an ORNL representative to Vienna. Once there, the bias was traced to a subtle programming flaw. After correction, the resin bead uranium analyses were indistinguishable from those of other loading techniques. Recommendations were made concerning sluggish pumping on the source region. Several computer program modifications were also made.

Transfer of the resin bead sample loading technique to the IAEA was tested by analyzing several samples a week for 6 weeks at each laboratory. Comparison of results showed good agreement, indicating that the IAEA had largely mastered the intricacies involved. Also demonstrated by this experiment was the viability of the resin bead as a vehicle upon which samples can be shipped (the beads were loaded in Vienna) and confirmation that fairly long term storage of samples on the beads causes no degradation of analytical results. We have analyzed samples 6 months after loading on beads and obtained excellent results.

The IAEA has taken samples at the WAK reprocessing facility in Karlsruhe, Germany. These samples were shipped on beads, both to us and to the IAEA laboratory near Vienna. Each laboratory will analyze the samples, and results will be compared. The object is to demonstrate the viability of resin bead sampling in such applications. We have received the beads and found them to be intact, again demonstrating their utility as a shipping medium. We are currently in the process of analyzing the samples; early results indicate the material sampled was of low burnup ( $\sim 7000 \text{ MWd}/10^3 \text{ kg}$ ), thus presenting us with a most difficult case with regard to Pu:U ratio. We feel that, if we obtain satisfactory analyses from these samples, we will have a convincing proof of the value of the resin bead technique in safeguards applications. (*R. L. Walker, D. H. Smith*)

**Consultation for International Safeguards Project Office (ISPO) on Tokai Advanced Safeguards Technology Exercise (TASTEX).** At the request of ISPO and in support of TASTEX Task J, J. A. Carter and D. H. Smith consulted with Japanese staff members at Tokai. After a thorough briefing on their reprocessing procedures, a sampling protocol to be used by IAEA inspectors was agreed on. Fortunately, it will cause very little inconvenience to the Japanese because of the simplicity of obtaining samples on resin beads. Lengthy and fruitful discussions on both resin bead sampling and mass spectrometry took place.

A tentative schedule for implementing the technique was also agreed on, which included training of two Japanese staff members at ORNL October 30–December 1, 1978. The next step requires the Japanese to take samples at their facility and ship them to ORNL for analysis. Results obtained here will be compared to those obtained in Japan by more conventional techniques. K. Kagami and S. Irinouchi of Tokai completed the training period program on schedule.

The Japanese agreed to investigate the possibility of carrying out resin bead sampling with remote manipulators, and we agreed to determine the amount of radioactivity that can be expected on a single resin bead loaded with a dissolver solution sample. Measurements and calculations show a  $\beta$ - $\gamma$  activity of  $3.5 \times 10^{-6}$  millirem per hour and an  $\alpha$  activity of 1.45% of permissible levels per bead. From this we conclude that including 10–20 beads in one shipment should be both convenient and well below current international maxima for transportation of unshielded radioactive materials. Fortunately, the Japanese procedure does not require that the samples be taken in a hot cell, where the difficulty in coordinating remote manipulators introduces severe problems. An alternative sampling point occurs, at which time the samples would be in a glove box after separation of uranium and plutonium from each other and from fission contaminants. This would require separate loads for uranium and plutonium, thus simplifying subsequent mass spectrometric analysis.

A summary report of our progress has been published as ORNL/TM-6612. (*J. A. Carter, D. H. Smith, R. L. Walker*)

## ISOTOPIC AND ELEMENTAL SPECTROMETRY

**Spark-source mass spectroscopy for irradiated materials.** A facility is being designed for the analysis of high-level  $\gamma$ -emitting samples by SSMS. The first planned use of this facility will be the analysis of processing solutions from LWR and HTGR spent fuels. Dilution of aliquots to lower their activity will be unnecessary in most cases; thus improved sensitivity and accuracy of analyses can be expected.

A feasibility study<sup>13</sup> has been completed that effectively demonstrates the remote operation of an

AEI MS-702 spark-source mass spectrometer. In that study, all front panel controls were moved to a separate console, which included a television monitor and controls for manipulating the spark-source electrodes. The source shielding was represented by a Plexiglas mockup. Source parts were handled by a master-slave manipulator. The study provided insights into the design and operation of the actual facility and showed that the quality of analytical data did not deteriorate because of remote operation.

Following many of the results obtained from the feasibility study, the Engineering Division has begun the design of the shielding cubicle and its sample transfer system. The ion source will be enclosed by the cubicle, which consists of an inner liner of stainless steel about 122 cm long  $\times$  76 cm deep  $\times$  135 cm high  $\times$  0.5 cm thick. The liner will provide containment of alpha contaminants. At least 10.16 cm of lead will surround the liner to provide  $\gamma$  and  $\beta$  shielding. For <sup>137</sup>Cs, which has the most energetic  $\gamma$  (0.66 MeV) of any of the expected radioactive elements in the spent fuel samples, the maximum levels of  $\gamma$  activity allowed will be 10 mCi or 40 R/h at 1 cm. The samples will be loaded by two CRL model G manipulators. A view port of 30.48-cm-thick leaded glass will be provided.

The facility will be located in Building 2026 adjacent to a high-level handling cell, where the sample electrodes will be prepared. An existing conveyor belt access port will be used for sample transfer between the preparation cell and the mass spectrometer. This connection will be made through a lead-shielded, stainless-steel conduit. The entire cubicle and mass spectrometer will be made movable so that access to the conveyor belt can be retained. A shielded glove port will be added to the cubicle to facilitate cold or low-level entry.

A surplus AEI MS-702 mass spectrometer was obtained from General Electric Nuclear Devices and will be used in the facility. Completion of the design and fabrication of the facility is expected in FY 1979 and routine operation in FY 1980.

The facility will be the only one of its kind to provide elemental trace analyses of highly radioactive  $\gamma$ -emitting solids. (*R. J. Warmack, J. C. Franklin, D. L. Donohue, L. Landau, J. A. Carter*)

**Analysis of gas contained in irradiated HTGR fuel particles.** A Bendix MA-3 time-of-flight (TOF) mass spectrometer and a 16K PDP-8/A minicomputer (12-bit word) have been purchased and installed for analysis of gases liberated by crushing irradiated HTGR fuel particles. Initial testing of the instrumentation was carried out in the mass spectrometry laboratory, but it has now been moved to ORNL and

13. J. A. Carter, J. C. Franklin, D. L. Donohue, L. Landau, and W. R. Musick, *High Radiation Level Spark Source Mass Spectrometry: Instrumental and Laboratory Feasibility Study*, ORNL/TM-6203 (1978).

attached to the particle crushing facility. Individual irradiated fuel particles will be crushed in the crusher enclosed in a glove box, and the liberated gases will be transported through a vacuum line to the TOF-MS outside the glove box. The pulse of gas will be analyzed in a dynamic mode with the spectrometer under computer control. The data will be processed to yield the absolute quantity of each component.

A calibration system has been installed as a permanent part of the apparatus and will allow introduction of known volumes of standard gas mixtures at measured pressures into the analysis system to simulate the gas pulses generated when crushing particles. Estimates of the expected gas pulses suggested that a volume of about 2 ml at 0.020 torr would approximate a pulse volume. Therefore, standard volumes of 1.76 ml have been installed. In the initial testing with a low-volume inlet system, pulses of a standard gas mixture contain about 1% of CO, CO<sub>2</sub>, O<sub>2</sub>, and Ar; sometimes xenon gave pulses that persisted for 2–5 s and gave >5-V output at sensitivities of 10–100× below practical maximum. However, when installed in the crushing facility, the increased volume of the system and the low conductance of the interconnecting tube resulted in pulse times of 10–20 s with corresponding reduced outputs.

The minicomputer will be used to control the masses selected for acquisition, to store the data, and to process and output the results. Control of the mass selection will be via predetermined voltages to the gating circuitry. Preliminary experiments have shown the voltage stability of the TOF-MS to be adequate for operation for a reasonable time without requiring recalibration. When operating in the static mode, the peak top widths (for 10% decrease in intensity) were 1–2 mV wide. The peak widths at 10% above baseline level were 5–15 mV wide. Therefore, the mass selection voltages generated by the computer must be accurate and stable to at least ±0.5 mV over the time of the experiment to ensure satisfactory quantitative data. Data must be acquired rapidly to allow integration of the gas pulses. Therefore, minimum damping and electrometer sensitivity must be used to allow rapid system response. Work is under way to optimize these parameters for best quantification. This work is part of the same program but not immediately connected with TOF spectrometry studies reported in Sect. 3 of this report. (*W. T. Rainey*)

**Asbestos in lungs by isotope dilution mass spectrometry.** The EPA is interested in determining the amount of asbestos and asbestos-related metals

that are retained in the lung after exposure to asbestos fibers. Two types of asbestos fibers were chosen for the study—amosite and a mineral identified as PMP-8. The fibers were high-iron-content asbestos with Si ≈ 25%, Fe ~ 25%, Mg ~ 3.5%, and Mn ~ 1.5%. We analyzed samples of the mineral to determine starting amounts of metals available to animals from various doses.

The animals, injected over several weeks to levels of up to about 5 mg of asbestos fibers, were sacrificed periodically covering a span of 1 year. The complete lungs along with a series of lungs not exposed to asbestos were analyzed for the major constituents present in asbestos by isotope dilution techniques. The analytical protocol includes the ashing of the lungs at about 600°C. After about 16 h, the lung ashes are weighed and separated into two equal portions—one for the silicon determination and the other for the remaining metals of interest.

The portion of sample chosen for silicon measurements is dissolved and spiked with enriched <sup>29</sup>Si (0.002 g of <sup>29</sup>Si per pair of lungs). Sample and spike are dissolved in diluted HF. The desired compound for filament loading, BaSiF<sub>6</sub>, is precipitated by the addition of BaCl<sub>2</sub>. The BaSiF<sub>6</sub> is decomposed in the mass spectrometer by increasing the temperature to 200°C or less. The abundance of silicon isotopes is determined from the SiF<sub>3</sub><sup>+</sup> ions, and the concentration of silicon is calculated from the <sup>28</sup>SiF<sub>3</sub><sup>+</sup>:<sup>29</sup>SiF<sub>3</sub><sup>+</sup> ratio in the spiked sample. Recovery of the method has been demonstrated by the analysis of small samples of pure amosite and PMP-8. The other half of the ashed lungs is used for the measurement of Fe, Mg, Mn, Br, and Ni, employing SSMS.

A 0.010-g portion of the unspiked sample is dissolved in HNO<sub>3</sub>/HCl and spiked with enriched <sup>57</sup>Fe and <sup>25</sup>Mg. Portions of this solution are dried on a pair of graphite electrodes and on a pair of silver electrodes. The electrodes are loaded into an SSMS and analyzed. The 57/56 and 26/25 are used to determine iron and magnesium concentrations in the solution. Manganese, chromium, and nickel concentrations are determined using <sup>54</sup>Fe as an internal standard. These data for Si, Fe, Mg, Mn, and Ni are used to establish the total asbestos concentration in the lungs. Concentration ranges for the three major elements were typically present at 50 to 1500 μg per pair of lungs. Blank lungs (those not deliberately exposed to asbestos) had average metal levels of 90 μg iron, 19 μg silicon, and 20 μg magnesium.

Cursory examination of the data immediately showed reductions of iron, silicon, and magnesium levels retained by the animals to about 50% of the

amount administered. After the initial exposure, the amount of asbestos (as measured by elemental constituents) found in the lung decreased with time to an essentially stable level. Within a given period, there was a variability of about 30% of the value between animals. Future work on this program is planned, although the magnitude of the effort has not been established. For a discussion of transmission and optical microscopy studies of asbestos in lung tissue, see Sect. 1 of this report. (*J. C. Franklin, J. R. Sites, L. Landau, M. Honaker, R. C. Bryant, H. Caudill*<sup>14</sup>)

**Trace metals in solid municipal wastes and leachates.** Municipal refuse, sewage sludges, and sludge leachates contain many toxic elements. The Toxicity of Solid Wastes Project is concerned with the concentrations of 13 elements in this category, namely, Cd, Ni, Cu, Zn, As, Pb, Se, Hg, Be, Ag, Th, Cr, and Sb.

The samples are of necessity very nonhomogeneous; therefore, large sample sizes are needed. The samples also contained high percentages of organic material and silica. The organic material was digested with HNO<sub>3</sub> in a high-pressure Parr bomb at 200°C, but the bombs would only accommodate 0.1-g samples so that larger samples were digested by refluxing in HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> for several days. In both cases the silica was left behind.

The digested samples and the leachates were examined by inductively coupled plasma (ICP) optical emission and by SSMS. The samples were also spiked with isotopically enriched Cu, Cd, Zn, Se, Pb, and Cr and analyzed by isotope dilution SSMS. Some of the spikes were also used as internal standards for analyzing other elements; for example, <sup>77</sup>Se spike was not only used to determine the selenium content by isotope dilution but was used as an internal standard to determine arsenic. (*J. C. Franklin, D. L. Donohue, L. Landau, S. A. MacIntyre*)

**Determination of alloy components in irradiated weld metals.** To verify the chemistry of reactor containment vessel alloys, series of irradiated and nonirradiated weld metal samples were analyzed for Mn, Si, Cr, Ni, Mo, and Cu, both by Paschen emission spectrometry and by SSMS. Two standard steel samples, very similar to the weld metals and certified by the Bureau of Analyzed Samples, Ltd., London, were analyzed five times on the Paschen spectrometer to establish error limits for the minor

constituents. Our values agree with the Bureau values to within 5% of the reported value for Mn, 7% for Si, 2% for Cr, 1% for Ni, 1% for Mo, and 7% for Cu.

The irradiated samples were handled in the hood; they were cut to the proper size and shape for use as SSMS electrodes using bolt cutters to prevent the formation of radioactive chips from sawing. The samples for the Paschen were similarly cut, then cleaned and weighed. They were subsequently dissolved in HNO<sub>3</sub> and HCl, spiked with a strontium standard solution for use as an internal standard, and sparked using the rotating graphite electrode technique. The unirradiated samples were sawed with an abrasive wheel but were otherwise treated similarly to the irradiated ones.

The unirradiated samples were also part of a round robin and were analyzed by Babcock and Wilcox, Jones and Laughlin, and Y-12 as well by as ourselves. Table 2.6 shows comparison values from all of the laboratories. (*J. C. Franklin, L. Landau, G. I. Gault, E. H. Waters*)

Table 2.6. Laboratory comparison values (wt %) of nonirradiated weld metal

	ORNL	Y-12	B&W <sup>a</sup>	B&W <sup>a</sup>	J&L <sup>b</sup>
Mn	1.45	1.64	1.56	1.57	
Si	0.49	0.43	0.51	0.50	
Cr	0.17	0.17	0.17	0.17	
Ni	0.61	0.63	0.62	0.61	0.66
Mo	0.40	0.31	0.38	0.37	
Cu	0.18	0.13	0.18	0.19	0.18

<sup>a</sup>B&W, Babcock & Wilcox (two laboratories).

<sup>b</sup>J&L, Jones & Laughlin.

**Inductively coupled plasma emission spectrometry (ICP/ES).** The ICP emission spectrometer is used routinely to measure major and minor constituents in fly ash by the KOH fusion technique. This work has been done for several ORNL projects and reflects the increased interest in coal technology in recent years. Other geological samples have been analyzed in this way, notably shale and shale ash.

An evaluation of the ICP/ES for the determination of various elements in municipal refuse leachates was performed. This program was undertaken in cooperation with the Environmental Sciences Division and involved the drafting of a protocol for the analysis of hazardous trace metals leached from municipal refuse under laboratory conditions.

Several of the elements studied (As, Pb, and Cd) were not as sensitive by ICP/ES as hoped because of the lack of sensitive emission lines in the presence of high-alkali background emission. It was concluded that other techniques such as SSMS should be used along with the ICP spectrometry to obtain the highest quality results. (*D. L. Donohue*)

**New gas mass spectrometer.** A new V. G. Micromass MS 1201 gas mass spectrometer has recently been installed and is in the final checkout stage. It replaces a 25-year-old machine. The spectrometer has high sensitivity options with a base pressure of  $10^{-9}$  torr. The magnet is 12 cm,  $60^\circ$ , and the receiver has quickly interchangeable Faraday cup and electron multiplier detectors. Source and receiver slits are continuously variable, which permits a resolution of 2500 to split CO and N<sub>2</sub> at mass 28. The equipment is sufficiently sensitive to "see" the small amount of xenon in air (80 ppb) split away from the small residual background. The fast amplifier for the multiplier permits oscilloscope presentation using a 0.1-s sweep. The magnetic field is controlled with a very stable Hall probe. One distinguishing feature is the digital integrator along with its related digital programmer. One can peak jump, including H<sub>2</sub>, Xe, and above, using any of 16 chosen masses. The output signal is presented in a seven-figure neon display; the output signal can also be recorded on a strip chart recorder, on a ten-column paper-tape printer, or on the oscilloscope. All these features have compatible connections for computer control and data accumulation. The pressure in the expansion volume (50 cm<sup>3</sup> or 2000 cm<sup>3</sup>) is continuously monitored with a Baratron, which makes linearity studies and relative gas sensitivities quite easy. All of these features have been demonstrated on this mass spectrometer in this laboratory and will soon be applied to our regular samples. (*J. R. Sites, L. Guinn, M. M. Honaker*)

**Mass spectrometry services.** The Mass Spectrometry Service Laboratory continues to serve a wide variety of divisions and programs throughout ORNL, with major support to Chemical Technology and Operations divisions. Examples of the more

challenging activities follow. Several sets of pure SF<sub>6</sub> were analyzed to help certify the very large tanks of fill gas for the new Holifield Heavy-Ion Facility. The major gases from thermally decomposed insulation were identified. Many samples of mixtures of americium and curium were analyzed for a special transuranium production run. We analyzed a special <sup>244</sup>Pu product that had been isotopically purified by irradiation to burn out the lighter isotopes. A <sup>240</sup>Pu source of high isotopic purity was also analyzed. A large number of U-Pu samples submitted on resin beads were run in support of the LWR irradiated fuels program. Finally, as part of a reactor control rod study for Babcock and Wilcox, isotopic analyses were made of cold and irradiated samples of dissolved, unseparated Ag-Cd-In alloy. (*J. R. Sites, M. M. Honaker, L. Guinn, D. I. Whaley, R. L. Walker*)

**Special isotopic analysis.** During the past year we have had many requests for special isotopic analyses because of our capability to measure nanogram-size samples with high abundance sensitivity. Some examples of these interactions are as follows: Minor isotopes in the parts-per-million range were accurately measured in special uranium metal and uranium alloys for Y-12 programs. Many uranium and lithium isotopic analyses were carried out for researchers at ORGDP and the Mound Laboratory who are working on isotope separation methodology. These analyses can be very crucial because measurement of small differences in isotopic ratios are necessary to evaluate separation efficiency. Involvement in the National Uranium Resources Evaluation (NURE) program continues as does preparation and certification of standard solutions for the Y-12 Plant internal quality control program. Certification of the uranium concentration in water-control samples used in the national quality control program administered by the Ames Laboratory is also performed. Measurements were also made of Th 230:232 ratios in ThO<sub>2</sub>, U, and Th in shale, U and Pu for flux monitors, and Eu and Gd for neutron cross section measurements. (*R. L. Walker, E. G. Miller, H. C. Smith, H. Simmons*)

### 3. Analytical Services

L. T. Corbin, Head

The volume and spectrum of work in the Analytical Services Section have increased during the past year. Accordingly, several personnel changes were made to add more technical expertise in certain groups and to strengthen the entire section.

The analytical support and services provided by this section reflected a recurring but short-lived interest in thorium as an integral part of a future nuclear fuel cycle, the viability of alternate fuel cycles in general, gel sphere-pac fuel preparation, and reevaluations of old fuel recycle technologies. Also, resource evaluation, alteration, and recovery as evidenced by the work with fossil-derived fly ash, refuse-derived fuels, and solvent-refined coals dictated the course taken in performing analytical work. Analytical hot-cell capabilities—facilities and instrumentation—are being improved.

The Reactor Programs Group has continued to direct its major efforts to establishing analytical capabilities and providing technical assistance to meet the immediate needs of a number of reactor technology development programs including the High-Temperature Gas-Cooled Reactor, Advanced Fuel Recycle, and Thermal Reactor Fuel Refabrication programs. Ongoing activities include the monitoring of gaseous effluents from fuel microsphere preparation processes, studies on the distribution and transport of tritium in the Peach Bottom Reactor, and gas and liquid chromatographic studies of organophosphorus compounds used as extractants in fuel reprocessing. Work has been initiated to study the effects of steam corrosion on structural reactor graphite. Techniques being established to characterize the graphite include gas and mercury porosimetry and BET surface area. Development of accountability assay methods for uranium and thorium has continued.

The Analytical Chemistry Division Sample Transaction System was expanded by the addition of four computer programs. The system provides for the entry of timekeeping information, calculation of the monthly time distribution report, curve fitting and plots, and customer access to Analytical Chemistry Division analysis files.

Our program for testing protective coatings (paints) used in the nuclear industry continues to grow. We are the only installation qualified to perform the complete battery of tests.

#### **SAMPLE TRANSACTION SYSTEM**

Four laboratories and one customer area now use the Sample Transaction System (STS). Over 100,000 analytical results were reported through it this year. The STS has been quite successful here and has attracted considerable interest from colleagues at other DOE installations.

As part of our ongoing effort to expand and improve the STS, we have written a number of new programs this year. These include:

1. **CARDS**—allows terminal entry of timekeeping data. The program is self-prompting, and programmed defaults eliminate repeat entries. Corrections to stored data can be made. Charge numbers are checked against a master list of valid numbers.
2. **BILLIN**—calculates complete monthly time distribution report. Options to add charges, delete charges, and to exclude charges from standby distribution are available.

3. DISTIL—processes data from the ASTM simulated distillation curve method. This program allows the choice of a least-squares fit or a three-point smoothing function for the data plot. The quality of the plot is such that it may be used in customer reports.
4. ENQUIR—allows interactive communication between the customer's terminal, Analytical Chemistry Division terminals, and the Data Management System. Request sheet information can be entered by the customer, and completed results may be assessed.

J. S. Stanton of the Computer Sciences Division has written a report summarizing our STS [*Analytical Chemistry Division Sample Transaction System, ORNL/CSD/TM-52 (April 1978)*].

A program for quality control is scheduled to be on-line in January 1979. It will allow input from local terminals and will provide the Quality Assurance Officer with statistical data and plots.

## ENVIRONMENTAL ANALYSIS LABORATORY

W. R. Laing, Group Leader

Analytical Chemistry and the Environmental Sciences Division (ESD) are jointly investigating effluents from fly ash piles. Here are some representative accomplishments in the Environmental Analysis Laboratory (EAL) this past year. A new technique was tested for leaching ash samples for the analysis of trace elements. In this test NBS fly ash 1633 was leached overnight with HNO<sub>3</sub> and HF in Teflon beakers. The solution was evaporated to dryness, 5 ml HClO<sub>4</sub> added, and evaporated again. A dilution was prepared in deionized, distilled water and analyzed by atomic absorption. Results of fly ash leach tests are shown in Table 3.1. This procedure will save considerable time and have lower reagent blanks than the old complete dissolution technique.

Industrial Safety and Applied Health Physics Division began a program to follow the mercury content of locally available fresh and canned foods. Peaches, watermelons, apricots, apples, canned tuna, shortening, corn, beans, and tomatoes were among samples submitted. Less than 5 ng of mercury per gram was found in all of the foods except tuna; it contained 280 ng of mercury per gram—well below the permissible concentration of 500 ng/g.

Table 3.1. Leaching test results from NBS fly ash

Element	Certified value ( $\mu\text{g/g}$ )	Found ( $\mu\text{g/g}$ )
As	61 $\pm$ 6	61
Cd	1.45 $\pm$ 0.06	1.9
Cr	1.31 $\pm$ 2	132
Cu	128 $\pm$ 5	118
Fe	<i>a</i>	62
Hg	0.14 $\pm$ 0.01	0.10
Mn	493 $\pm$ 7	515
Mo	<i>a</i>	35
Ni	98 $\pm$ 3	118
Pb	70 $\pm$ 4	70
Se	9.4 $\pm$ 0.5	9.5
Zn	210 $\pm$ 20	218

<sup>a</sup>No certified value.

A series of sediment samples collected from the area of the Almaden, Spain, mercury mines was analyzed for methyl mercury and total mercury. Methyl mercury contents ranged from <1 to 430 ng/g and increased as the total mercury content increased. Total mercury ranged from 60 to 2600 ng/g.

Vegetation samples are ashed at 480°C, and the ash is dissolved in Ultrex HNO<sub>3</sub> to prepare solutions for analysis. Certain elements such as Cd, Mn, Pb, and Zn have been reported to be volatilized under some ashing conditions. Analysis of NBS orchard leaf standards showed recovery of all four elements to be satisfactory and indicated no expected problems with a 480°C ash.

Over 200 samples were analyzed for selenium, using the extraction method of Talmi,<sup>1</sup> followed by graphite furnace atomic absorption. To determine whether or not the preparation and analysis techniques were adequate, a variety of standard materials were analyzed for selenium. The results are shown in Table 3.2. The conclusion was that the extraction and analysis procedures are satisfactory for a variety of sample materials.

Over 500 samples of vegetation and bonemeal were analyzed for fluoride by leaching with KOH, adding H<sub>3</sub>PO<sub>4</sub> to complex metals, adjusting the pH, and then

1. Y. Talmi and A. W. Andren, "Determination of Selenium in Environmental Samples, Using Gas Chromatography with Microwave Emission Spectrometric Detection System," *Anal. Chem.* **46**, 2122 (1977).

Table 3.2. Determination of selenium by atomic absorption

Standard material	Certified value ( $\mu\text{g/g}$ )	Found ( $\mu\text{g/g}$ )
NBS coal 1632	$2.9 \pm 0.3$	3.1
NBS fly ash 1633	$9.4 \pm 0.5$	9.1
NBS liver 1577	$0.1 \pm 0.1$	1.2
NBS leaves 1571	$0.08 \pm 0.01$	<1
Eastman gelatin	$39 \pm 6$	34
IAEA fish A-6	$3.1 \pm 0.6$	3.0
IAEA oyster MA-M-1	$2.3 \pm 0.1$	3.4

following with an ion-selective electrode. Over a period of 2 months, a sample of bonemeal was analyzed 15 times with a relative standard deviation of 4.17%. A switch was constructed for alternately connecting one of two ion-selective electrodes to a single mV meter to increase the speed of the analysis.

In studies designed to provide input for the Resource Conservation and Recovery Act (RCRA), municipal sludge and extract were analyzed for 13 elements by atomic absorption and spark-source mass spectrometry. The results, from microgram per milliliter to picogram per milliliter, were in good agreement and will be evaluated by the Environmental Protection Agency.

A Dionex model 10 ion chromatograph has been assembled and tested. The instrument operated in a stable and reproducible manner and exhibited excellent sensitivity. Using a 10-ml aliquot of deionized distilled water and a concentrator column, results of 3 ng F/ml, 23 ng Cl/ml, <1 ng NO<sub>2</sub>/ml, 9 ng PO<sub>4</sub>/ml, 3 ng Br/ml, 6 ng NO<sub>3</sub>/ml, and 9 ng SO<sub>4</sub>/ml were obtained. Applications to environmental samples are planned for the next year.

This laboratory participated in an intercomparison study of bulk rainwater samples distributed by the Environmental Measurements Laboratory (DOE). Twenty-three laboratories participated in this study, and the Environmental Analysis Laboratory determined 19 components on each of the eight samples. In an analysis of the data, it was found that 72.3% of our results were within one standard deviation of the mean, 98.7% were within two standard deviations, and 100.0% were within three standard deviations.

A four-plant (ORNL, Y-12, K-25, and Paducah) environmental quality assurance program was begun. Quality control samples, prepared by Environmental Resources Associates, were shipped quarterly to each plant and analyses performed monthly. Results will be evaluated by the Y-12

Statistical Analysis Section and an annual report issued.

## RADIOACTIVE MATERIALS ANALYTICAL LABORATORIES

J. H. Cooper, Group Leader

### Reactor Fuel Reprocessing Analyses

The study of reactor fuel reprocessing is continuing. In addition to the analyses reported last year,<sup>2</sup> <sup>237</sup>Np was measured in fuel dissolver solutions. Neptunium, plutonium, and uranium, all in the hexavalent state, were extracted into methyl isobutyl ketone from aluminum nitrate solution. A reducing solution stripped all three from the organic. The tetravalent neptunium was separated from plutonium (3+) and uranium (6+) by extraction into thenoyltrifluoroacetone. Recoveries of neptunium were determined by spiking the samples with <sup>239</sup>Np. Levels of <sup>237</sup>Np alpha activity of 10<sup>4</sup> to 10<sup>5</sup> counts min<sup>-1</sup> ml<sup>-1</sup> were measured in samples containing plutonium alpha activity levels of 10<sup>8</sup> to 10<sup>9</sup> counts min<sup>-1</sup> ml<sup>-1</sup> and uranium of 300 g/liter.

The Zircaloy cladding is partially dissolved when LWR and FBR fuels are dissolved. To measure the amount of cladding that was dissolved, we analyzed samples of the dissolver solution for zirconium by the Arsenazo-III colorimetric method. Thorium and uranium, which interfere in this method, were removed by adsorbing the uranium and zirconium on anion exchange resin and eluting the thorium with 12 M HCl. Zirconium was eluted with 6 M HCl. A solution containing 111 ppm zirconium and 40 g/liter of thorium was analyzed by this method. Zirconium recoveries were 109 and 110 ppm.

Free acid in solutions containing hydrolyzable cations was determined by several methods. Solutions containing plutonium were analyzed by titrating the acid after the plutonium was precipitated with potassium iodate and filtered out. The acid in thorium-containing solution was measured by titrating it in a concentrated LiCl solution. Titration in acetone medium was used to measure free acid in uranium-containing solutions.

Inadequate supplies of reagents for the dithiol colorimetric measurement of molybdenum necessitated a change in this determination. The thiocyanate

2. J. H. Cooper, "Radioactive Materials Analysis Laboratories," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 41.

colorimetric method was adopted using ethyl-, butyl-, or amylacetate as the extractant.

The Chemical Technology Pilot Plant is producing  $^{233}\text{U}_3\text{O}_8$  for a special reactor experiment. The oxide powder, which must be kept as dry as possible, is sealed in small cans for the experiment. The material was originally sent to the laboratory for moisture analysis after it had cooled to room temperature and had begun absorbing moisture. Because the cans are sealed while the powder is heated to  $290^\circ\text{C}$ , it was decided to measure only the moisture that was retained at  $290^\circ\text{C}$ . We placed the samples in our moisture analyzer furnace and heated them to  $290^\circ\text{C}$ . The samples were then heated to  $1000^\circ\text{C}$ , and the moisture release was measured. The amount of moisture released between these temperatures was about 0.02%.

#### Upgrade of Hot-Cell Operations

Equipment needs for the Building 2026 hot cells were examined, and priorities were set. We plan to update a few critical items immediately and later to replace and automate all equipment in the hot cells and glove boxes. The status of each of the items is as follows:

**Automatic titration assembly.** The Reactor Programs Group evaluated the Mettler titrator, using the Davies and Gray procedure for uranium and using a back titration of excess EDTA with copper for thorium. This instrument will be set up first as a titrator for uranium.

**Parr density meter.** Two (a conventional and a remote model) density meters have been purchased. The remote model will be installed in a hot cell, and the other instrument will be used for routine laboratory measurements.

**Spectrophotometer.** A Spectronic 20 instrument has been installed in the hot cell. Instrumentation and Controls Division personnel have purchased fiber optics for evaluation, and the radiation testing has begun.

**Fluorometer.** A fiber optic fluorometer has been constructed and will be used to determine the precision and accuracy of uranium measurements in the 1–300  $\mu\text{g}/\text{ml}$  range.

**Pipet for weighed aliquots.** Several commercial pipets of the "Eppendorf" type have been evaluated, and all were found to be too heavy for weighing by difference. Typical weights were 75–150 g. A plastic disposable syringe (weight 3 g) was tested to determine its suitability as a dispensing tool. Aliquots of acid solution ranging in size from 100–1000  $\mu\text{l}$  were

measured by weight difference and titrated with standard base. Relative standard deviations for the weighing and titrating ranged from 0.14 to 0.59%, decreasing with increasing aliquot size. This type of syringe appears to be a suitable candidate for the pipet system.

#### Testing of Coatings

The number of requests for testing of paints, coatings, and other materials used in nuclear reactor primary containment areas continued to increase this year. Sample specimens, including coated steel panels and concrete blocks as well as other miscellaneous materials, were submitted by a total of 28 companies. Over 200 coating systems were tested and evaluated. Included among the more than 1800 test specimens were 40 systems for ease-of-decontamination testing, 750 specimens for radiation resistance testing, and the remainder, including the irradiated specimens, for simulated loss-of-coolant accident (LOCA) tests. Highly specialized radiation testing involving a large number of unrelated samples was carried out for two additional companies as well as for several ORNL facilities. Decontamination tests are conducted in Building 3019. Irradiation testing is done using the spent fuel assemblies at the HFIR fuel storage pool. The environmental test autoclave is located in Building 2026. ORNL still remains the only installation with qualified personnel, equipment, and expertise to conduct all three tests at one laboratory as required by the test specifications. (*G. Goldberg*)

#### GENERAL ANALYTICAL LABORATORY

R. R. Rickard, Group Leader

Most of the analytical service provided by the General Analytical Laboratory was in support of programs administered by the Chemical Technology and the Metals and Ceramics divisions. To a lesser extent, a wide variety of analyses were performed for other programs within ORNL and for some outside institutions. Selected topics covering the analytical effort in support of the above activities are discussed below. Steps taken to upgrade the instrumental capabilities of the laboratory, in keeping with a standing objective, are also mentioned.

Basic studies of the Purex and Thorex solvent extraction processes required analyses not only for uranium and thorium but also frequently for ruthenium and zirconium in both aqueous and

tributyl phosphate (TBP)-dodecane organic solutions. Degradation products of TBP, namely, monobutyl phosphate (MBP) and particularly dibutyl phosphate (DBP), necessitated the abandonment of weak acids as stripping agents in favor of solutions of ammonium carbonate or potassium carbonate. Ruthenium was determined by atomic absorption spectrophotometry. Zirconium concentration was determined in the sample as received by x-ray fluorescence.

Solvent extraction studies relating to the Alternate Fuel Cycle Technology Program used extensively a mixer-settler system. Consequently, hundreds of samples were taken principally for uranium and free acid analyses. Uranium concentrations in the samples ranged from milligram-per-milliliter to milligram-per-liter levels. Likewise, the free acid levels varied widely. Spectrophotometric and fluorometric techniques were employed to determine uranium in the samples. A servo-type titrator was used for the free acid measurements.

In the Fuel Recycle Program some basic equilibrium studies were made of thorium in nitric acid-hydrofluoric acid solutions. These studies required numerous thorium analyses employing spectrophotometric (Arsenazo III) and volumetric (EDTA) techniques. Total fluoride was measured using a fluoride ion-selective electrode. An important parameter in these studies was temperature; at elevated temperatures special sampling precautions were often required to obtain meaningful analytical data.

An interest in optimizing the conditions of dissolution for thorium oxide in the presence of Zircaloy prompted some experiments to elucidate the interaction of nitric acid, aluminum nitrate, and small amounts of hydrofluoric acid in a weak zirconium salt solution. These studies required analyses for thorium and zirconium, but, since both of these were to be determined using a common chromogenic agent (Arsenazo III), it was necessary to separate them. A xylene solution of TTA was chosen as an extractant for zirconium. Thorium was then analyzed in the raffinate solution, and zirconium was determined following wet ashing of the organic extractant.

The UO<sub>2</sub> microsphere sphere-pac work carried out in the Metals and Ceramics Division required considerable analytical effort. In particular, density gradient measurements, particle inspections, porosity, and mercury density determinations were made on hundreds of samples. High density (>10 g/cm<sup>3</sup>) materials of low porosity required a more refined

technique to get meaningful density data. Likewise, special steps had to be taken to determine the mercury density of powdered materials. These steps included the use of a modified penetrometer to handle <1-g-size samples.

A study of the precipitation of carbides in low-alloy steels as a function of chromium and molybdenum content has been under way for months. Over this period, numerous chromium and molybdenum analyses were performed on the dissolved carbides using atomic absorption spectrophotometry and thiocyanate-spectrophotometry, respectively.

Aerosol release and transport studies of uranium and sodium were carried out by the Engineering Technology Division using the facilities in the Nuclear Safety Pilot Plant. The nature of these studies dictated the use of a relatively large number of sampling points. Consequently, over the past year thousands of samples consisting of filters, filter holders, and deposition plates have been analyzed for uranium and sodium. Uranium was determined using a fluorometric method, and sodium was measured using atomic absorption spectrophotometry.

Our laboratory has been working with 11 other institutions through an ASTM committee network to establish sample handling protocol for refuse-derived fuel (RDF being burnable industrial waste) and to refine applicable analytical methodology. This work involves, in addition to ASTM committee work, an infrequent but sizable analytical effort directed toward the analysis of industrially prepared wastes distributed to the participating institutions.

The following improvements in instrumentation were made: An automatic Karl Fischer titrator, a Brinkman Metrohm recoding titrator, an ash fusion system, a Leco sulfur determinator, and a Perkin-Elmer Sigma 10 data acquisition system have been put into productive use. In addition, the vacuum fusion system has been upgraded with a new electronics package and the addition of a new chromatograph, complete with a dual readout option through coupling to the Sigma 10 system. This upgraded vacuum fusion system is more stable and reliable than the old system.

## REACTOR PROGRAMS

D. A. Costanzo, Group Leader

### Gas-Cooled Reactor Program Studies

**Time-of-flight mass spectrometry studies.** A time-of-flight mass spectrometer (TOFMS) was used to analyze effluents from HTGR fuel processing

reactions.<sup>3</sup> Studies included the effect of helium as the levitating gas for the carbonization of uranium weak-acid resin (U-WAR) in fluid-bed processes, the pyrolysis of "matrix slug" material used in the fabrication of fuel rods, the determination of pyrolysis products during "green stick" burning, the efficiency of the perchloroethylene scrubber to remove decomposition products from the effluent gas stream from fuel microsphere coating processes, and efficiency of molecular sieves to trap perchloroethylene vapors from the effluent gas stream.

In studying the effect of the nature of the levitating gas on the fluidized-bed carbonization of U-WAR, it was found that helium was less efficient than argon or nitrogen. More time was required to complete the carbonization process when helium was used, which may have been caused by the fact that helium has a higher thermal conductivity than argon or nitrogen.

"Matrix slug" material M-162, which is used to bind fuel microspheres into fuel rods, was pyrolyzed in argon and vacuum. The volatile gaseous decomposition products were monitored by mass spectrometry throughout the heating cycle from ambient to about 800°C. Twenty profiles of gas evolution curves for significant masses were determined for each experiment. To help identify the fragments produced during the pyrolysis, each component in M-162, octadecanol, "pitch," and polystyrene was pyrolyzed individually in the same manner as for M-162.

Pyrolysis products in the effluent gases from the burning of "green stick" (unfired fuel rods) in 70% argon-30% oxygen were determined by mass spectrometry. Complete burning of the organic materials in the effluent gas stream was demonstrated after the path length of the effluent stream in the heated zone was extended.

A report<sup>4</sup> was issued on the efficiency of the perchloroethylene scrubber in the fuel particle coating facility to remove pyrolysis products from the effluent gas stream in microsphere coating processes.

The mass analysis of effluent gas components before and after a molecular sieve trap in the effluent

gas stream from the fuel particle coating facility showed that molecular sieves will efficiently remove perchloroethylene vapors from the stream. Other hydrocarbon gases not removed by the perchloroethylene scrubber were also trapped by the molecular sieves.

A Columbia Scientific Industries model CSI-260 digital data system and a Digital Equipment Corporation model LA36-DE DECwriter II hard-copy terminal have been installed on the TOFMS. The CSI-260 measures peak heights and identifies mass numbers coming from the TOFMS and will also normalize the peaks relative to the largest peak. This equipment has greatly reduced the amount of time used for data processing. (*D. A. Lee*)

**Acid in perchloroethylene scrubber solutions.** A detailed study has been made on the problem of acid in perchloroethylene scrubber solutions collected from HTGR fuel preparation processes. Used scrubber solutions are corrosive and difficult to process for reclamation and recycle. Hydrochloric acid was found to be concentrated on the carbon particles suspended in perchloroethylene. Filtration of carbon from the scrubber solution removed the acid corrosion source in the process equipment. Corrosion products chemisorbed on the carbon particles were identified. Filtered perchloroethylene from used scrubber solutions contained practically no acid. The completed study<sup>5</sup> has been prepared for publication. (*D. A. Lee*)

**Distribution and transport of tritium in the Peach Bottom HTGR.** We continue to collaborate with the Chemical Technology Division in studies of the behavior of radionuclides in high-temperature gas-cooled reactors. During this reporting period, we made a study of the distribution and transport of tritium in the Peach Bottom HTGR. A report describing this study and its results was written and is in the process of being published.<sup>6</sup> Two reports describing prior work concerning the examination of fuel elements from the Peach Bottom HTGR were

3. D. A. Lee, "Monitoring of Gaseous Effluents from HTGR Fuel Preparation Reactions by Time-of-Flight Mass Spectrometry," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, pp. 35-36.

4. D. A. Lee and D. P. Stinton, *Perchloroethylene Scrubber Effectively Removes Hydrocarbons from the Effluent Stream of the HTGR Fuel Particle Coater*, ORNL/GCR-78/21 (September 1978).

5. D. A. Lee, *Acid in Perchloroethylene Scrubber Solutions Used in HTGR Fuel Preparation Processes. Analytical Chemistry Studies*, to be published as an ORNL/TM report.

6. F. F. Dyer and R. P. Wichner, *Distribution and Transport of Tritium in the Peach Bottom HTGR*, to be published as an ORNL report.

published.<sup>7,8</sup> Additionally, a report that presented highlights of the computer program ANGEL, which was used to process gamma spectra in the fission product surveillance studies, was prepared.<sup>9</sup>

A main objective of the study of tritium in the Peach Bottom HTGR was to arrive at a balance between the amount formed and the amount that remained in components of the reactor plus the amount that was released in gaseous and liquid wastes. Quantities of tritium were expressed as activities (curies) referenced to the final shutdown date (October 31, 1974) of the reactor. In arriving at the tritium balance, the activities of tritium formed in the fuel by ternary fission, those formed in the fuel matrix and graphite from <sup>6</sup>Li impurities, and those formed in the coolant from <sup>3</sup>He were estimated by simplified neutronics calculations. Tritium formed from <sup>10</sup>B in the control rods was estimated from the change in reactor excess reactivity. The tritium remaining in the fueled and reflector regions of the core was estimated from activities measured at ORNL in six fuel elements and one radial reflector element. Lithium impurity was determined in all major parts of the fuel elements and in the reflector element by SSMS. The amounts of tritium released from the reactor as liquid and gaseous wastes and shipped offsite in solid wastes were accounted for from reports published by the Philadelphia Electric Company and General Atomic Company. For a list of these reports, see ref. 6.

Although a few of the sources and sinks of tritium in this reactor (e.g., the control rods) were not experimentally analyzed, it is believed that our study has accounted for about 90% of the tritium formed. The reader is referred to a report by Dyer et al.<sup>6</sup> for a more complete account of the methods and results of this study. (F. F. Dyer)

7. F. F. Dyer, R. P. Wichner, W. J. Martin, and L. L. Fairchild, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element F03-01*, ORNL/TM-5996 (May 1978).

8. R. P. Wichner, F. F. Dyer, W. J. Martin, and L. L. Fairchild, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element E01-01*, ORNL/TM-6353 (October 1978).

9. F. F. Dyer, "ANGEL: A Conversational Program for Nuclear Fuel Element Scanning by Ge(Li) Gamma Spectroscopy," presented to American Nuclear Society Topical Conference on Computers in Activation Analysis and Gamma-Ray Spectroscopy, Mayaguez, Puerto Rico, Apr. 30-May 4, 1978, to be published in the proceedings.

**The effect of steam corrosion on the structural properties of reactor graphite.** Laboratory experiments have been initiated to study the effect of moisture on the structural properties of reactor-grade graphites using a closed-loop apparatus. The operating conditions of temperatures, gas flows, and moisture in the sweep gas will be varied to simulate the secondary coolant in an HTGR. Graphite species will be characterized for density, surface area, and porosity before and after treatment.

The construction of two corrosion apparatuses has been completed. Each is a closed system and contains a quartz reaction tube. Reaction zone temperatures are provided by a standard three-zone Lindberg model 54377 tube furnace. The moisturized helium is circulated over the graphite by a gas circulating pump. The apparatuses are quite similar; one will be set up to accept brittle-ring specimens, whereas the other is designed for a range of solid cylindrical specimen sizes of various dimensions. A Perkin-Elmer Sigma 1 gas chromatograph equipped with an automatic gas sampling valve has been installed on-line to monitor the corrosion products generated during the experiment. These products include H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>. A water saturator, to supply a constant amount of moisture to the closed loop, was constructed of copper. The efficiency of saturation was checked in the laboratory, and the amount of water in the helium was found to be about 99% of the theoretical partial pressure of water over the range of temperatures studied (0 to 20°C).

Experiments were done to determine when structural damage in untreated graphite occurs during pore size measurements by high-pressure mercury penetration. The porosity measurements were made using an Aminco model 5-7121 porosimeter. After the pore size measurements, the graphite sample was removed from the porosimeter, and the mercury that was retained by graphite was removed by vacuum distillation at elevated temperatures. The porosimetry measurement was then repeated and the results compared to the original data. The first indication of damage was evident when the pressure exceeded 2000 psig.

The assembly of a BET-type surface area apparatus for the measurement of surface area and gas porosities of oxidized and unoxidized graphite is near completion. When assembled, the system will be fully automatic, using a Hewlett-Packard 9825A for control and data acquisition. Pressure/vacuum changes will be monitored by an MKS Baratron solid-state manometer system. The system will

provide an absolute pressure sensing range of 0–100 torr with an accuracy of  $\pm 0.08\%$ . The range of the surface-area measurement will be 0.1–100  $\text{m}^2/\text{g}$ , using at least three absorption gases.

A helium densitometer has been set up and evaluated. The apparatus used is a modified version of that described by Pearson, Harrar, and Gutmacher.<sup>10</sup> The constant-temperature water bath has been eliminated because all measurements are to be made at ambient temperature with temperature and pressure corrections incorporated into the calculations. The precision and accuracy of the densitometer were determined by comparing the measured density of mercury with the theoretical value. Precision and accuracy were found, using this method, to be within  $\pm 0.5\%$ . Reactor-grade graphite samples (helium density  $2.06 \text{ g/cm}^3$ ) and powder samples (helium densities between  $1.35 \text{ g/cm}^3$  and  $1.50 \text{ g/cm}^3$ ) were measured with a precision of better than  $\pm 0.7\%$ .

For highly porous samples, care must be taken to allow time for the helium to penetrate the pores and reach equilibrium. The sample cells were designed to accommodate solids of 6-mm and 12-mm diam, having lengths up to 25 mm. The cells can also hold up to  $5 \text{ cm}^3$  of powder. The densitometer can effectively measure the densities of powders and porous solids. (R. F. Apple, J. L. Botts, J. D. Kintigh)

#### Advanced Fuel Recycle Program Studies

**Chromatographic separation studies.** Gas and liquid chromatographic separation capabilities were established for analytical development studies related to advanced fuel reprocessing. The liquid chromatograph was previously described.<sup>11</sup> Feasibility studies were concluded on the separations of nitrate-nitrite and nitrate-azide mixtures that can exist in hydrazine stabilized solutions of plutonium(III) during Purex processing. Good separations of nitrite and azide species from nitrate media were obtained on an Aminex A-25 strong-base anion exchange resin with  $0.5 \text{ M KCl}$  as the eluant. At a flow rate of  $1.76 \text{ ml/min}$  (400 psi pressure), retention times for nitrite, azide, and nitrate ions are about 13, 30, and 38 min, respectively. The pH of the solutions

injected onto the column should be within the range 2–7 for optimum results. A report describing this work was published.<sup>12</sup>

A gas chromatographic study was carried out on several selected organophosphorus compounds that are widely used as extractants in nuclear fuel technology. Dexsil-300, which is noted for its thermal stability at high temperatures, was used as the stationary phase. Hydrogen flame ionization detection was employed. The substances chromatographed are representative of the trialkyl phosphate, dialkylalkyl phosphate, organophosphorus acid, and trialkylphosphoric oxide classes of compounds. Dexsil-300 appears to be well suited as a stationary phase for the separation of a wide variety of high-boiling organophosphorus compounds. A report of this work was published.<sup>13</sup> (D. L. Manning)

#### Infrared spectra of organophosphate compounds.

As part of our continuing effort on the characterization of organophosphorus compounds of interest in nuclear fuel technology,<sup>13,14</sup> Fourier transform infrared (FTIR) spectra were recorded of several compounds of the types listed above including also dodecane, a commonly used diluent. The spectral region studied included the frequency range  $625\text{--}300/\text{cm}$ , which contains useful information not examined previously. Differences among the trialkyl phosphate spectra are rather subtle; however, differences between tributyl phosphate and triisobutyl phosphate and between trioctylphosphine oxide and tri(2-ethylhexyl)phosphine oxide are sufficient for spectral identification. Similar comparisons may be made for the other compounds. The spectra obtained should prove useful for screening studies as well as for liquid and gas chromatographic applications involving infrared detectors. A report of this work is in preparation. (D. L. Manning)

**Time-of-flight mass spectrometry studies of LWR fuel preparation processes.** A TOFMS was used to analyze the effluents from the thermal reactions of gel-sphere-pac  $\text{UO}_2$  fuel for thermal reactors. These

10. R. K. Pearson, J. E. Harrar, and R. G. Gutmacher, *Some Recently Developed Chemical and Physical Analytical Methods*, UCRL-6639 (April 1961).

11. D. L. Manning, "Reactor Projects," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 39.

12. D. L. Manning, *Separation of Nitrate-Azide and Nitrate-Nitrite Mixtures by Liquid Chromatography*, ORNL/TM-6335 (August 1978).

13. D. L. Manning, *Gas Chromatographic Studies of Organophosphorus Compounds Using Dexsil-300 as a Stationary Phase and a Hydrogen Flame Ionization Detector*, ORNL/TM-6423 (September 1978).

14. C. S. MacDougall, *Determination of Monobutylphosphoric Acid and Dibutylphosphoric Acid in Tributylphosphate Dodecane Extracting Solutions*, ORNL/TM-6268 (April 1978).

studies included an evaluation of urania gel pyrolysis for the production of high-density fuel microspheres, analyses of urania gel decomposition products, a kinetic study of the dehydration and deamination of urania gel microspheres, and the conversion of urania gel microspheres from  $\text{UO}_3$  to  $\text{UC}_2$ .

In one study, a series of pyrolysis experiments was performed to determine optimum thermal conditions for the production of high-density gel urania fuel microspheres. Microspheres made with and without organic binders were heated in either air,  $\text{CO}_2$ , 96% Ar-4%  $\text{H}_2$ , or vacuum; mass spectra of the evolved gaseous decomposition products were recorded over a temperature range of 200–750°C. Peak heights of significant masses were plotted against temperature. The product gas evolution curve profiles were used to determine plausible decomposition mechanisms. A report describing this work in detail has been written.<sup>15</sup>

In a second study,  $\text{UO}_3$  microspheres prepared by an internal gelation process<sup>16</sup> were pyrolyzed, and the gaseous products were monitored by the TOFMS. The gel was heated from 25 to 800°C at various heating rates. Evolution profiles were made for each product by plotting ion current vs temperature. From the shape of the profile and the peak temperature of evolution, several hypotheses about the decomposition mechanism could be formulated. Estimates of the activation energy for the dissociation processes for removal of water and ammonia from the spheres were made; the values were 9 kcal/mol and 20 kcal/mol, respectively. A report that summarizes this work is in preparation.<sup>17</sup> (D. A. Lee, M. C. Burrell<sup>18</sup>)

**Thorium assay in process solutions.** Several techniques for the precision analysis of thorium in nitrate solutions by potentiometry were evaluated. A direct titration of thorium with fluoride produced an average recovery of  $99.85 \pm 0.23\%$  (one standard deviation). An Orion specific-ion-indicating electrode was employed. Four pM electrode systems

were tested for application to the thorium assay by an EDTA titration. Rhodium-rhodium (EDTA), palladium-palladium (EDTA), copper-copper (EDTA), and mercury-mercury (EDTA) were tested as indicating electrodes. Only the mercury electrode system exhibited usable response to thorium. Using an EDTA titration of  $\text{Th}^{4+}$  with the mercury-indicating electrode system, an average thorium recovery of  $99.32 \pm 0.06\%$  (one standard deviation) was achieved.

A precise and accurate potentiometric technique for the assay of thorium fuels and process solutions for thorium was developed. Thorium is separated from fission product impurities by anion exchange from nitrate and chloride solutions. This combination effectively eliminates such materials as the alkalis, alkaline earths, lanthanides, zirconium, molybdenum, iron, and ruthenium. Theoretically, the actinides should be separated, although this has not been done. Uranium(VI) need not be separated from thorium for the assay. After the separation, thorium is analyzed by a potentiometric technique. The  $\text{Th}^{4+}$  is reacted with an excess of EDTA, and the unreacted EDTA is then titrated with standard  $\text{Cu}^{2+}$  using an Orion specific-ion electrode. The precision of the assay (entire process) was  $+0.40\%$  (one standard deviation). For thorium fuels not containing fission products (and thus no ion exchange and no fuming), a precision of  $\pm 0.10\%$  can be routinely expected. In either case, the method is unbiased within the limits of precision for the assay. An ORNL/TM report is in preparation. In conjunction with this work, a literature search concerning the analysis of thorium was performed.<sup>19</sup> (C. S. MacDougall)

**Solvent extraction study.** A solvent extraction study to determine equilibrium conditions of the system thorium nitrate–nitric acid–30% tributyl phosphate in normal dodecane has been completed. Experimental conditions studied were 30 to 60°C, 0.05 to 1.5 M  $\text{Th}(\text{NO}_3)_4$ , and 0.0 to 3.0 M  $\text{HNO}_3$ . Extractant concentration was constant at 30% tributyl phosphate. Thorium nitrate concentration, free acid, and density were measured for the aqueous and organic phases and the boundary condition established for third-phase formation.

The data demonstrate the interactions of the components of the Thorex system, and they can be used to improve the mathematical description of

15. D. A. Lee and D. P. Stinton, *Evaluation of Urania Gel Pyrolysis by Mass Spectrometry*, ORNL/TM-6538, to be published.

16. J. B. W. Kanij, A. J. Noothout, and O. Votoček, "The KEMA U(IV) Process for the Production of  $\text{UO}_2$  Microspheres," p. 185 in *Proc. Panel Sol-Gel Process for Fuel Fabrication*, IAEA-161, Vienna, May 1973.

17. M. C. Burrell and D. A. Lee, *Analysis of  $\text{UO}_3$  Gel Microsphere Decomposition Products by Mass Spectrometry*, ORNL/TM-6649, to be published.

18. ORAU Summer Research Participant, Bloomsburg State College, Bloomsburg, Pa.

19. C. S. MacDougall, unpublished data, April 1978.

equilibrium in the SEPHIS-Thorex computer program.<sup>20</sup> A report summarizing the results of this work is in preparation.<sup>21</sup> (*J. L. Marley*)

**Reference sample plan.** A reference sample plan for the proposed Advanced Fuel Recycle Program Hot Engineering Facility (AFRP-HEF), a pilot-scale demonstration facility, has been formalized. The plan is based on the Purex flow sheet described in the HEF Interim Design Report, FY 1977. The objective is to provide a means to assess the analytical chemistry research and development necessary and to provide a basis for assignment of development task priorities. As the AFR Program progresses, the plan will be used for cost estimation. With the sample rate known, precise allocation of personnel and funding of analytical chemistry support of plant operation can be made. The following information is provided on analytical chemistry requirements (form UCN-13137): sample number and origin; purpose, form, and level of radioactivity; sample frequency and size; attributes required; expected concentration of each attribute and the precision required for each; reference procedure to be used and the established precision (1 S) of the procedure; and notes giving status of development efforts and the types of methodology being developed. (*J. L. Marley*)

### Methods Development

**Determination of zirconium in tributyl phosphate-dodecane solutions.** A method for the direct determination of zirconium in degraded TBP solutions from the Purex process has been developed. Stripping zirconium from organic solutions has caused analytical errors because of polymerization and insolubility of zirconium compounds. Therefore, a method has been developed in which the chromogenic complex was formed directly in the presence of 30% TBP-70% dodecane. Acetone together with the aqueous reagents caused the zirconium-Arsenazo-III complex to form quantitatively in the aqueous phase. The molar absorptivity ( $2.84 \times 10^3$  liters  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ) was the same as that found for all aqueous solutions of zirconium without acetone. Beer's law

was obeyed up to 0.5  $\mu\text{g}$  of zirconium per milliliter. (*D. A. Lee*)

**Stripping thorium and zirconium from TBP solutions containing DBP and MBP.** Several chemicals were tested for stripping thorium and zirconium from Purex solutions of TBP, DBP, and MBP in dodecane. The highest stripping coefficient found for thorium was 600 when 5 M  $\text{K}_2\text{CO}_3$ -4% ethanol was equilibrated with the organic solution. Zirconium was completely stripped from a similar TBP solution using 5 M  $\text{K}_2\text{CO}_3$ -1 to 2%  $\text{H}_2\text{O}_2$ . Zirconium phosphate precipitate at the interface of the immiscible solutions was soluble in 5 M  $\text{K}_2\text{CO}_3$ -1 to 2%  $\text{H}_2\text{O}_2$ . Other ineffective chemicals tested for thorium and zirconium stripping from the organic phase were: 6 N HCl, 6 N  $\text{HNO}_3$ , 6 N  $\text{H}_2\text{SO}_4$ , 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , 0.2 M  $\text{KIO}_3$ , 0.2 M ammonium citrate, 0.2 M EDTA in 0.2 M  $\text{K}_2\text{CO}_3$ , and 11.5 N  $\text{H}_2\text{SO}_4$ -5.8 N HF. (*D. A. Lee*)

**The determination of free acid in uranium and thorium.** Free acid, the amount of acid that would remain if hydrolyzable ions were removed from the solution,<sup>22</sup> is usually performed at ORNL by titration to a predetermined pH, using a pH-adjusted oxalate solution to complex the hydrolyzable cations. The procedure can be adversely affected by the presence of cations (e.g., Pu or Zr) that are not adequately complexed at the optimum pH for uranium. A new approach to the problem was investigated: thermometric titration using a Sanda model DVR thermotitrator. Potassium fluoride was selected as the most effective complexing agent; sodium hydroxide was used as the titrant. A satisfactory analysis for acid was established, using a constant amount of KF (30 ml of 4.5 M KF) and open-top Dewar containers. Sample closure to prevent heat loss was unnecessary.

Free acid, as standard nitric acid, varied from 0.4 to 4.0 meq  $\text{HNO}_3$  and has been measured in the presence of uranium (238 mg U) and then thorium (232 mg Th) to demonstrate that interference from hydrolysis does not occur. Slopes of curves obtained were coincident within experimental error, and correlation was good ( $>0.999$ ). The precision was 0.01 meq (1 S). It was also demonstrated that the analysis was satisfactory in the presence of uranium up to 952 mg (4 mmol) and thorium up to 464 mg (2 mmol). (*J. L. Marley*)

20. W. S. Gronier, *Calculations of the Transient Behavior of a Dilute Purex Solvent Extraction Process Having Application to the Reprocessing of LMFBR Fuels*, ORNL-4746 (April 1972).

21. A. J. Weinberger, J. L. Marley, and D. A. Costanzo, *A Solvent Extraction Study of the Thorium Nitrate, Nitric Acid, Tributyl Phosphate-Dodecane System*, ORNL/TM-6334, to be published.

22. G. L. Booman, M. C. Elliott, R. B. Kimball, F. O. Cartan, and J. E. Rein, "Determination of Free Acid in the Presence of Hydrolyzable Ions," *Anal. Chem.* **30**, 284 (1958).

**Gas chromatographic determination of monobutyl phosphoric acid and dibutyl phosphoric acid in 30/70 TBP-dodecane extracting solution.** Dibutyl and monobutyl phosphoric acid are determined in 30% TBP-70% dodecane Purex solvents by gas chromatography. The DBP and MBP are derivatized using methyl-8. The volatilized species are separated on a 305 × 0.32 cm stainless steel column containing 60-80 mesh Chromosorb W coated with 15% Carbowax 20-M and measured by an FID detector. Limits of detection are 0.001 M for both MBP and DBP with a relative standard deviation of ±5% at the 0.15 M concentration level. Systems containing varying concentrations of H<sup>+</sup>, Fe<sup>3+</sup>, Th<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup> are analyzed successfully. This work has been reported.<sup>23</sup> (C. S. MacDougall)

**Determination of uranium in nuclear fuels.** A Mettler automatic titrator was evaluated using the modified Davies and Gray titration for uranium. This system is modular in design and is capable of performing any volumetric operation—from simple dispensing to fully automated titrations. Fifty-milligram quantities of uranium were determined with a recovery of 100.07% and a precision of ±0.16% (1 S). This work has been described.<sup>24</sup> (C. S. MacDougall)

**The determination of uranium in Robinson reactor fuels.** The determination of uranium in dissolver solutions of H. B. Robinson LWR reactor fuels irradiated to 30,000 MWd per metric ton of uranium was investigated. Following an extraction of the uranium into TOPO, the organic layer is removed from the hot cell, and the uranium is determined by the modified Davies and Gray potentiometric titration method.<sup>25</sup> Initial results indicated a recovery of about 90% of the calculated uranium value based on fuel burnup. On solution standing, subsequent uranium values showed a positive bias and were not reproducible. This positive bias was eliminated by taking the test aliquot to fumes of H<sub>2</sub>SO<sub>4</sub> prior to its extraction. At this time, the interference has not been identified, but it could be caused by fission products of technetium or ruthenium. (R. F. Apple)

23. C. S. MacDougall, *Determination of Monobutyl Phosphoric Acid and Dibutyl Phosphoric Acid in Tributyl Phosphate-Dodecane Extracting Solutions*, ORNL/TM-6268 (April 1978).

24. C. S. MacDougall, unpublished data, May 1978.

25. C. D. Bingham, "New Brunswick Laboratory Titrimetric Method for the Determination of Uranium—Basic Method," *Annu. Prog. Rep. July 1973–June 1974*, NBL-272, USAEC New Brunswick Laboratory, October 1974, pp. 113–115.

**Characterization of UO<sub>2</sub> fuel materials.** Analytical capabilities have been established and methods evaluated according to ASTM method C 696 for the chemical characterization of nuclear-grade UO<sub>2</sub> powder, microspheres, and pellets. In support of the Thermal Reactor Fuel Refabrication Development Program, an evaluation of the gravimetric method for uranium content and oxygen-to-uranium atomic ratio has been completed. The accuracy and precision of the method was determined using a UO<sub>2</sub> powder material containing 88.15% uranium with an O:U of 2.002. Replicate determination of this material gave a mean uranium value of 88.15 wt % with a standard deviation of 0.036 wt %. The oxygen-to-uranium ratio calculated from each individual uranium value gave a mean O:U of 1.999 with a standard deviation of 0.007. In addition to uranium content and O:U, UO<sub>2</sub> sol-gel microspheres are analyzed for carbon, gas content, moisture, and impurities. (J. L. Botts)

**Disintegration of HRB 14 irradiation test specimens.** Irradiation test specimens consisting of 31% BISO-coated ThO<sub>2</sub> fuel particles in H-481 graphite flour and A240 petroleum pitch were fired at 1800°C and formed into small planchettes with diameters of about 12 mm and thicknesses of about 3 mm. After irradiation, the planchettes must be deconsolidated without damage to the fuel particles so that postirradiation experiments can be performed on individual fuel particles.

A chemical procedure for deconsolidating the planchettes was evaluated. The procedure consisted of immersing the planchette in a solution containing 20 wt % (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 98% H<sub>2</sub>SO<sub>4</sub> at room temperature. After 5–10 min, the planchette began to disintegrate. Placing the planchette-containing solution in an ultrasonic bath for 2–3 min further disintegrated the planchette, with the coated fuel particles settling to the bottom of the solution and the carbon matrix material floating on its surface. The fuel particles were immediately separated, washed, and dried. No damage of the particle surface was detected by microscopic examination. The method can easily be adapted to remote handling operation for irradiated specimens. (F. L. Layton)

**Multisample chlorination of HTGR fuel particles.** The determination of porous carbon coatings of HTGR fuel particles is accomplished by high-temperature chlorination and x-radiographic examination of the chlorinated particles.<sup>26</sup> Because up to

26. D. E. LaValle et al., *The Determination of Defective Particle Fraction in HTGR Fuels*, ORNL/TM-5483 (November 1976).

18 h of chlorination per sample is required to detect particles with porous carbon coatings, a sample holder was designed for simultaneous chlorination of up to eight samples. The holder is a cylinder of high-density graphite and contains up to eight porous carbon cups; each cup has a capacity of about 2 g of fuel particles. Chlorine gas, at a flow rate of 75 cm<sup>3</sup>/min, is introduced through an orifice at the bottom of the holder so that it passes up through the porous cups and the fuel particles. The maximum temperature gradient from the bottom to the top sample holder is 1290 to 1450°C.

Eight test portions of a BISO fuel particle batch were carried through the chlorination procedure and then x radiographed. Microscopic examination of the radiographs revealed that all eight batches were similarly affected by the chlorination. The amount of kernel migration and the extent of kernel attack by the chlorine were essentially the same for all eight portions. (*F. L. Layton*)

**Separation of chlorinated BISO fuel particles by density.** Long-term chlorination (72 h) of several batches of BISO-coated ThO<sub>2</sub> fuel particles was carried out. Chlorine penetrates to the kernels of particles that have porous low-temperature isotropics (LTIs) and either partially or completely removes the kernels. The kernels of particles with nonporous LTI pyrocarbon coatings remain unaffected. Therefore, particles with porous LTIs are less dense after undergoing chlorination. This variation in density is used as a means of separating the particles.

The actual separation is effected by placing the chlorinated particles in 1,1,2,2-tetrabromoethane ( $d \cong 2.95 \text{ g/cm}^3$ ). Those particles whose densities are greater than 2.95 g/cm<sup>3</sup> sink to the bottom and are removed. By diluting the tetrabromoethane with toluene, particles of varying densities may be separated. The separated particles are thoroughly washed with acetone, dried, and weighed. After being radiographed, the particles are returned to the Metals and Ceramics Division for characterization of the LTIs. (*F. L. Layton*)

**Determination of defective silicon carbide coating fraction.** A procedure for the determination of defective SiC coatings of TRISO fuel particles by helium intrusion at 1200°C was investigated. Previously evacuated TRISO particles are exposed to 1 atm of helium at 1200°C for 1 h. After exposure, the particles are cooled to room temperature and then reevacuated. On subsequent heating to 1200°C, the intruded helium is released and measured manometrically. Because pyrocarbon is permeable to

helium and SiC is not, only in those particles with defective SiC coatings will the helium penetrate to the kernel and fill the voids in it and in the buffer carbon coating surrounding it. The amount of helium released in addition to that normally released from the outer pyrocarbon coatings is correlated with the number of particles having defective SiC coatings.

Difficulty in finding a suitable material to contain the fuel particles during induction heating was encountered. Carbon, because of its porosity to helium, was ruled out initially. Several metals, including Pt, Mo, Ta, and Ir, were tried. At the outgassing temperature of 1400°C, all of these metals reacted with SiC, and all except iridium reacted with carbon. Vitreous carbon was considered as a container but was ruled out because of its poor resistance to thermal shock and its relatively high specific resistivity. In the method currently being investigated, particles are contained in one carbon crucible during exposure to helium at 1200°C and then transferred to a new carbon crucible for outgassing at room temperature and subsequent outgassing at 1200°C for the collection of the intruded helium. (*F. L. Layton*)

**Automated x-ray fluorescence analyzer.** A joint project with the Physicochemical Analysis Group is to specify, purchase, set up, and use an automated x-ray fluorescence (XRF) system. This project is a part of our responsibility in the Advanced Fuel Recycle Program. The XRF system will be capable of handling both radioactive and cold samples. In addition to visiting other laboratories to observe existing equipment, some experiments were performed to simulate future work. For example, the existing Y-12 Plant Laboratory energy-dispersive and wavelength-dispersive analyzers were used to confirm that both were suitable for determination of elemental distribution coefficients between TBP and aqueous extraction phases. This was important in choosing a candidate instrument because wavelength-dispersive instruments are more expensive. A detailed series of qualitative and quantitative tests was then performed using commercial vendor energy-dispersive equipment. The tests included detection of 10-ppm concentration levels of multiple elements, quantitative analysis of simulated fission product solutions, and demonstration of the detection of 50-ppm levels of uranium and thorium using the 100-keV energy lines excited by a <sup>57</sup>Co source.

Early reports from the Karlsruhe analytical laboratories recommended a filter paper technique for analysis of fission product solutions. This was

evaluated and found to be less precise and accurate than a direct solution analysis technique. Later Karlsruhe reports confirm ORNL data, and the solution analysis technique will be used in their laboratories unless the radiation level is very high.

Purchase specifications for the high-volume XRF system have been completed; bid responses are expected in late January 1979. (*J. H. Stewart, L. D. Hulett, D. A. Costanzo*)



## 4. Bio-Organic Analysis

M. R. Guerin

Programs constituting the Bio-Organic Analysis Section continue to focus on biologically significant components of complex natural mixtures. Tobacco smoke, coal- and shale-derived liquids, ambient environmental samples, and physiological fluids are receiving principal attention. Sampling and sample handling, chemical class separation, quantitative chromatographic and instrumental analysis, and spectroscopic examination constitute the principal analytical chemical activities of the section.

Research into the biological properties of coal-derived crude oils has confirmed the contribution of nitrogenous constituents to bacterial mutagenicity. The further purification of the highly mutagenic alkaline fraction of synthetic oils and the synthesis of a model compound have demonstrated the importance of polyaromatic nitrogen heterocyclics to this biological activity. Infrared spectroscopy, derivatization gas chromatography, and preparative adsorption column chromatography have, however, identified polyaromatic primary amines as the major constituents of the mutagenically enhanced fraction of the synthetic oils. Both the nitrogen heterocyclics and the amines are present as a complex mixture of alkylated derivatives, which is in agreement with other studies in which we find a predominance of multialkylated derivatives in the polycyclic aromatic hydrocarbon isolate of a synthetic crude oil.

Class fractionation methods developed to prepare materials for biological testing have been compared, and a method has been selected for routine bioassay support. The method, combining the advantages of acid-base partitioning and gel chromatographic separation, is being optimized for routine use. An in-depth study of fractions derived solely from gel chromatographic fractionation has demonstrated the strengths and limitations of the method. Fractionation schemes and quantitative analytical methods developed in the course of these studies are being readied for application to process- and site-specific environmental and health assessment programs for the Office of Health and Environmental Research of the Department of Energy.

The analysis of cigarette smoke using chemiluminescence suggests that 40-70% more "oxides of nitrogen" is delivered by a cigarette than was previously thought and that nitrogen dioxide deliveries are substantial rather than trace. A trapping material was discovered in the course of these studies that effectively removes hydrogen cyanide and simultaneously reduces nitrogen dioxide to nitric oxide. Our Tobacco Smoke Chemistry Group has provided quantitative analytical services to the National Cancer Institute Smoking and Health Program by analyzing a wide variety of foreign and domestic commercial cigarettes in support of international epidemiology studies. Smoke-related research, increasingly addressing human dosimetry, has led to methods for the sampling and quantitative analysis of physiological fluids for nicotine and its metabolites. Methods have also been established for the preparation of urines for mutagenicity testing and the analysis of the urines for volatile organic content. Subfractionation of cigarette smoke condensates suggests that harmene and/or norharmene are major contributors to the mutagenicity of cigarette smoke.

Environmental programs have produced a sampling device and analytical protocol for the determination of organic pollutants in air and a protocol for the collection and analysis of organics in dilute aqueous solution. Methods for the analysis of aqueous samples are being applied to the determination of polycyclic aromatic hydrocarbons in stream waters and of priority pollutants in aqueous extracts of solid wastes. Bioassay preparation and quantitative analytical methods developed to characterize solid waste extracts are being considered for incorporation into the Resource Conservation and Recovery Act regulations by the Environmental Protection Agency.

Procedures and analytical methods that cut across program lines have also advanced during this report period. Glass capillary column gas chromatography, typically capable of providing 500,000 theoretical plates of separating power, is now available for routine use. Polymer adsorbent sampling and sample preparation methods have been developed for air sampling and analysis, physiological fluids analysis, and aqueous extract concentration. Sample oxidation is now routinely applicable to the direct determination of residual carbon-14 or tritium in the class fractionation and isotope dilution quantitation of organics in complex mixtures. A central facility for the maintenance and preparation of research materials for biological study has been recognized as a potential management tool for basic bioassay and chemistry research. Acquisition in this report period of a Fourier transform infrared spectrometer and a gas chromatograph-mass spectrometer-data system promises to provide the Analytical Chemistry Division with an enhanced capability for organic structural identification problems.

## ENERGY TECHNOLOGIES

**Introduction.** Energy-related work in this section is concerned with the organic characterization of fossil-derived materials. Attention has centered on the development of separations methods and the elucidation of biologically important classes of compounds. Collection of samples and analysis of organic components from by-product streams in conversion or combustion processes has also been of primary interest.

**Comparative class composition of synthetic and natural crude oils.** Our Sephadex LH-20 separation procedure is now established for routine bench-scale use. A number of fossil-derived oils have been processed, and sufficient quantities of the materials examined have been collected so that biological (mutagenesis) and chemical characterization studies can be carried out.

The fractions designated in Table 4.1 are defined by the operations. The volatile fraction is the material that is lost by azeotropic distillation with benzene and ethanol and by evaporation to a reasonably constant weight under reduced pressure. The hexane-insoluble material is self-defined matter that does not pass through a 5- $\mu$ m filter. The other fractions have been described previously<sup>1</sup> except for the residue, which is material that cannot be eluted from the gel with

acetone. Portions of the intermediate fractions that are hexane soluble, lipophilic, and sieved are starting materials for subsequent steps and are collected for biological and chemical characterization so that material balances might be obtained for each stage of the fractionation procedure.

The data presented in Table 4.1 compare the compositions of the crudes examined. The first four oils were fractionated earlier by an acid-base extraction procedure followed by chromatography of the neutral portion on Florisil.<sup>2,3</sup> One can see that the aliphatic fraction is largest in all materials except Synthoil, in which case the largest fraction is in the hexane-soluble portion. The aromatic fractions total about 13% of these materials. Polyaromatic fractions, which would be expected to contain the highest

1. A. R. Jones, M. R. Guerin, and B. R. Clark, "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale," *Anal. Chem.* **49**, 1766 (1977).

2. J. L. Epler, J. A. Young, A. A. Hardigree, T. K. Rao, M. R. Guerin, I. B. Rubin, C.-h. Ho, and B. R. Clark, "Analytical and Biological Analyses of Test Materials from the Synthetic Fuel Technologies. I. Mutagenicity of Crude Oils Determined by the *Salmonella typhimurium*/Microsomal Activation System," *Mutat. Res.* **57**, 265 (1978).

3. I. B. Rubin, M. R. Guerin, A. A. Hardigree, and J. L. Epler, "Fractionation of Synthetic Crude Oils from Coal for Biological Testing," *Environ. Res.* **12**, 358 (1976).

Table 4.1. Comparative compositions of fossil fuel product oil fractions from gel partition chromatography

Fraction	Weight percent						
	Shale oil	COED syncrude	Synthoil	Mixed crudes	HC 21	HC 24	HC 26
Volatiles	1.1	7.0	0	10.7	4.0	27.9	20.7
Hexane insoluble	1.3	0.2	51.2	2.5	33.6	46.4	52.7
Hydrophilic	7.0	3.4	11.0	0.8	17.8	8.4	7.0
Polymeric	2.3	7.4	0.4	3.4	10.5	0.3	0.1
H-bond	5.2	8.2	5.7	14.9	0	1.6	5.2
Aliphatic	59.8	55.0	21.8	39.2	9.8	4.8	5.5
Monoaromatic	4.9	6.8	3.3	2.5	15.2	1.7	1.1
Di + triaromatic	6.1	6.7	6.3	4.1	12.3	4.5	2.6
Polyaromatic	2.0	1.0	3.9	6.7	12.8	3.0	1.7
Residue <sup>a</sup>	0	0	2.6	12.9	<i>b</i>	1.8	0.5
Total	89.7	95.6	106.0	97.7	116.0	100.4	97.1

<sup>a</sup>Eluted with acetone.

<sup>b</sup>Not determined.

specific biological activity of the three aromatic fractions, vary significantly among samples. The sums of the hydrophilic and the H-bond (polar) fractions range from 12 to 17%. These fractions also would be expected to show high biological activity.

The last three materials listed in Table 4.1 are derived from samples obtained from the ORNL bench-scale hydrocarbonization unit. Compositions of these products differ considerably, both from the first four and from each other. The large amount of volatile fraction of HC-24 and HC-26 is attributed to water associated with the samples. All hydrocarbonization samples have a large hexane-insoluble content. The aliphatic fraction is small, and the aromatic content is proportionately higher. The sum of the polar fractions ranges from 10 to 18%.

Currently, an evaluation is being made of the data in Table 4.1 and their associated bioassay results to relate them to comparable data obtained from chemical extraction.<sup>2,3</sup> This is difficult because gel and solvent partitioning do not provide fractions that are exactly analogous. The correspondence between fractions produced by the two procedures is currently under investigation.

In this production-scale work, sample sizes range from 40 to 60 g; this quantity of oil can be handled in one pass through the initial stage. In the second and third stages of the procedure, however, samples of only 4 to 5 g can be chromatographed in one passage, and multiple runs must be made to complete a sample. Accordingly, we have investigated a scale-

down of the procedure in which oil samples ranging from 0.05 to 1.0 g are processed. Recovery values for both the lipophilic and hydrophilic fractions over this sample range are essentially the same as for the large-scale sample procedure. (*I. B. Rubin, B. R. Clark, M. R. Guerin*)

**Compositions of Sephadex LH-20 fractions.** A study was undertaken to examine the fractions from the Sephadex LH-20 separation scheme described in the preceding section. At this stage the primary interest is in knowing how the chemical classes are distributed. A shale oil that had been used in the developmental work was chosen for this study because of favorable experience with this material in the LH-20 separation scheme.

The approach taken was to divide each of the Sephadex fractions into acidic, basic, and neutral compounds via a solvent partitioning scheme. Neutral subfractions were further separated by alumina adsorption chromatography into aliphatic, aromatic, and polar components. Some of the subfractions were analyzed by infrared and nuclear magnetic resonance spectroscopy and gas chromatography-mass spectrometry. A vast amount of data was produced and is still being reduced to interpretable form, but some generalizations can be made from the interpretation of data thus far.

From the gravimetric data obtained following the separations, a most obvious conclusion is that *all* the Sephadex fractions contain at least small amounts of acidic, basic, and neutral components. The relative amounts vary in a manner that one would expect for

the type of fraction being considered. For instance, the hydrophilic fraction composition is 12.9% acidic and 10.8% basic, whereas the aliphatic fraction has <1% total basic and acidic components (the lowest in these components). Surprisingly, however, the hydrophilic fraction is 64% "neutral" when sub-fractionated, and the aliphatic fraction is 97.8% neutral. Clearly, the Sephadex separation of the hydrophilic from the lipophilic components only parallels the solvent distribution (separation) of the acids-bases and the neutrals and separates on a sharply different basis. A solvent distribution separation scheme would place many more components in the neutral category than Sephadex places in the lipophilic category. This behavior is probably explained by functional group-gel interactions that are strong in the gel separation scheme but are not important in a solvent distribution, which separates more or less entirely on the polarity of molecules in acidic and basic aqueous media. The hydrogen bonding fraction (13.2% acidic/basic; 55.4% neutral) parallels the hydrophilic fraction, whereas the one-ring aromatic fraction (2.3% acidic/basic; 91.7% neutral) and the two- and three-ring aromatic fractions (1.8% acidic/basic; 93.5% neutral) parallel the aliphatic fraction. So the trends are consistent and expected.

All the spectroscopic and elemental analytical data are consistent with expectation for the classes of compounds postulated in each fraction. The hydrophilic fraction has the highest nitrogen content, little aromatic hydrogen [from nuclear magnetic resonance (NMR)], and the lowest H:C ratio (1.23) of all the fractions. The polymeric fraction has the highest sulfur content, the lowest nitrogen content, a high H:C ratio (1.77 by NMR and 1.67 by elemental analysis), and about 100% aliphatic hydrogen (NMR). The hydrogen-bonding fraction has an H:C ratio similar to the hydrophilic fraction (1.28) and a high nitrogen content but only about half as many heteroatoms as the hydrophilic fraction. The aliphatic fraction has the highest C:H ratio (1.74) and about 100% aliphatic hydrogen. The aromatic fractions have progressively decreasing H:C ratios (one-ring, 1.41; two-ring, 1.25; polycyclic, 1.02).

Our current evaluation of the Sephadex LH-20 scheme is that it is highly reproducible for the materials repeatedly separated. The class separations proceed essentially as expected, although they are not directly comparable to more classical separations via solvent partitioning.

This scheme was devised primarily to separate complex, fossil-derived materials for biotesting.

Current plans for a generalized sample separation use part of the LH-20 scheme but include a pre-distillation for highly volatile materials and some acid-base solvent partitioning. The contribution of this work toward the goals of the Synthetic Fuels Life Sciences Program has been large. Sephadex LH-20 gel separations have been incorporated into nearly all of the liquid chromatographic separations procedures that we have developed and are developing to meet the needs in the isolation of bioactive components from synthetic fuel-related materials. (B. R. Clark, N. A. Goeckner,<sup>4</sup> I. B. Rubin)

Separation and analysis of parent and multi-alkylated polycyclic aromatic hydrocarbons (PAHs) in a synthetic crude oil. The extreme complexity of PAH isolates from some synthetic crude oils hinders the identification and quantification of their constituents. As shown by the first trace in Fig. 4.1, even the high resolving power of glass capillary column gas chromatography (GC) is insufficient to completely separate the many constituents present in a complex PAH isolate from a coal-derived crude oil.<sup>5</sup> Further, many such isolates contain large amounts of material that do not elute by GC and cannot be accounted for by this analytical method. Successful analysis of such PAH isolates requires further purification and division into smaller and, we hope, simpler fractions prior to GC.

The PAH isolate shown in Fig. 4.1 was subjected to further purification and subdivision. Because a gas chromatographic-mass spectrometric (GC-MS) examination of the PAH isolate suggested that the complexity resulted from the presence of many chromatographically overlapping multialkylated derivatives of PAHs, a Biobeads SX-12 gel filtration system<sup>6</sup> capable of resolving parent-plus-simple-alkylated PAHs from multialkylated PAHs was applied to the PAH isolate. Three eluting fractions were collected: a preliminary non-PAH fraction, a multialkylated PAH fraction, and a parent-plus-simple-alkylated PAH fraction. The multialkylated PAH fraction was found to constitute

4. Sabbatical professor, Western Illinois University, Macomb.

5. M. R. Guerin, J. L. Epler, W. H. Griest, B. R. Clark, and T. K. Rao, "Polycyclic Aromatic Hydrocarbons from Fossil Fuel Conversion Processes," p. 21 in *Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons*, P. W. Jones and R. I. Freudenthal, eds., Raven Press, New York, 1978.

6. B. F. Severson, M. E. Snook, R. F. Arrendale, and O. T. Chortyk, "Gas Chromatographic Quantitation of Polynuclear Aromatic Hydrocarbons in Tobacco Smoke," *Anal. Chem.* **48**, 1866 (1976).

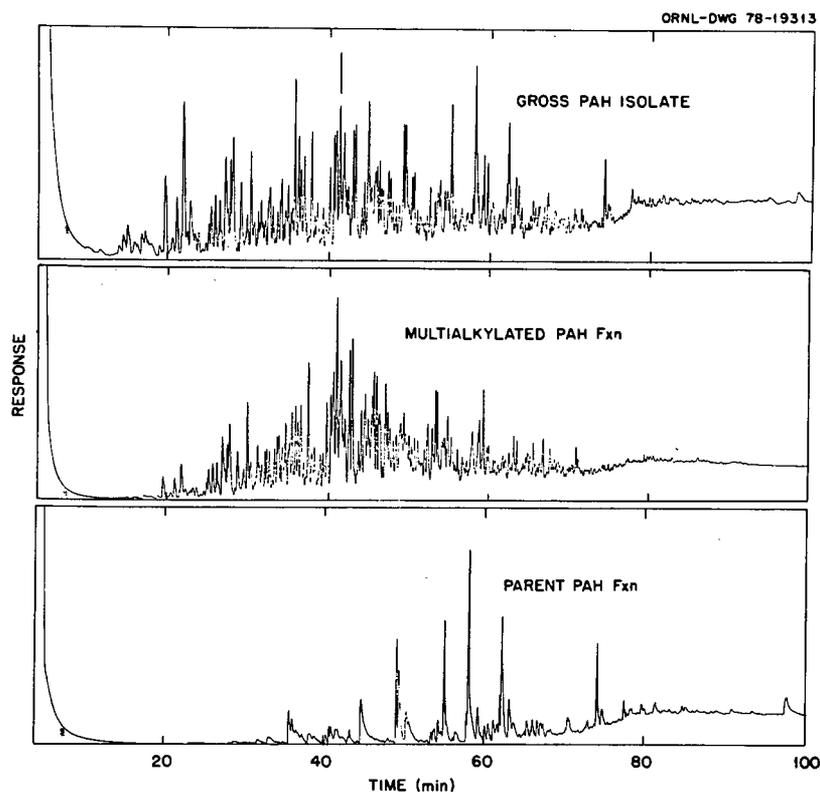


Fig. 4.1. Glass capillary column gas chromatographic profiles of coal-derived crude oil, PAH isolate and its parent, and multialkylated PAH fractions.

about 47 wt % of the original PAH isolate, whereas the parent-plus-simple-alkylated PAH fraction contributed about 13% of the isolate. The initial non-PAH fraction had negligible mass. Forty percent of the isolate was not recovered. Although small losses of the more volatile two-ring PAHs would be likely during solvent removal, the bulk of the unrecovered material may correspond to highly polar and/or polymeric compounds in the PAH isolate which would not elute during GC analysis. Consistent with this polar/polymeric hypothesis was the observation of the slow elution in very broad bands of unidentified material when the Biobeads gel columns were eluted with toluene and methylene chloride.

Glass capillary column GC of the multialkylated and parent-plus-simple-alkylated PAH gel fractions (Fig. 4.1) indicated that the multialkylated PAH fraction was still too complex for direct GC analysis. GC-MS of the multialkylated PAH fraction revealed the presence of more than 270 multialkylated PAH derivatives ranging from C<sub>2</sub>-indane through C<sub>5</sub>-pyrene. In contrast, the parent-plus-simple-

alkylated PAH fraction was a comparatively simple mixture that could be analyzed with reasonable success even by packed column GC. Nineteen major components (66%) of this fraction consisted of parent PAHs and their C<sub>1</sub>-derivatives. Alkyl substitution never exceeded C<sub>2</sub> in this fraction. The parent-plus-simple-alkylated PAH fraction contained several bioactive PAHs, including the carcinogens benzo[*a*]pyrene and benzo[*b*, *j*, or *k*]fluoranthene and the cocarcinogens fluoranthene, pyrene, and benzo[*ghi*]perylene. The specific microbial mutagenic activity of this fraction was very high. Interestingly, the multialkylated PAH fraction exhibited only slightly less *specific* mutagenic activity but a much greater *total* mutagenic activity because of its greater percentage weight in the original PAH isolate.

Because of its complexity, the multialkylated PAH fraction was next subfractionated according to PAH ring size by gel filtration on Sephadex LH-20 with isopropanol. Subfractions corresponding to the elution of naphthalene, phenanthrene, and benz[*a*]anthracene and containing PAHs with

two, three, and four-plus-larger rings were collected. The two-ring subfraction accounted for 39% of the multialkylated PAH fraction; the three-ring subfraction amounted to 19%; and the four-plus-larger-ring subfraction, 5%. About 36% of the multialkylated PAH fraction was not recovered. A significant portion of the two-ring subfraction may have been lost during solvent removal.

In spite of the subdivision of the multialkylated PAHs into three subfractions, the components of each subfraction were still too complex to be properly resolved, even by glass capillary column GC. Just as the multialkylated PAH subfraction contributed to the complexity of the original PAH isolate, the "naphthalene" subfraction of the multialkylated PAH fraction similarly contributed most of the complexity of the latter. Somewhat lesser, but still significant, complexity existed in the other two subfractions, indicating the intricate nature of the multialkylated PAH of this coal-derived crude oil. Obviously, improved ring-size resolution is needed to successfully separate the subfractions. Microbial mutagenic bioassay of the subfractions indicated that the mutagenicity of the multialkylated PAHs was concentrated in the larger PAH ring systems. This result suggests that the diaromatics, which make up the bulk of the multialkylated PAHs, can be disregarded and that future attention should be directed at methods of analysis of the larger PAHs.

Research is now focusing on improving the methods for separating the multialkylated and parent-plus-simple-alkylated PAHs and for subfractionating the multialkylated PAHs. Recent results suggest that a simple dimethyl sulfoxide/pentane partitioning of the PAH isolate can effectively separate the multialkylated and parent-plus-simple-alkylated PAHs. Sterically hindered sulfoxides also are being investigated for achieving an even cleaner separation. (*B. A. Tomkins, W. H. Griest*)

**Nitrogenous polycyclic aromatic compounds in synthetic fuels.** During the last 2 years, we have taken a special interest in the identification of nitrogen-containing aromatic compounds found in crude synthetic fuels. Compounds of this type are present in relatively large quantities in coal-derived and oil shale-derived crude oils compared with the natural petroleum crudes. Furthermore, nearly all bioassay data accumulated on fractions of synthetic crudes have implicated nitrogen-containing compounds as having the greatest specific activities (activity per unit of mass) among all the classes present. The focus of interest on nitrogen-containing

aromatic compounds has resulted from a very close collaboration between members of the Biology Division, performing bioassays, and members of this division, performing separations and analyses. Elucidation of the likely health/environmental importance of these nitrogen-containing compounds is a clear demonstration of the usefulness of an integrated chemical analysis-bioassay approach in screening complex mixtures.

In general, three classes of nitrogen-containing compounds are important: (1) neutral aza-arenes with a pyrrole-type nitrogen(s), (2) basic aza-arenes with a pyridine-type nitrogen(s), and (3) basic aromatic amines with an aniline-type nitrogen(s). The relative proportions of any of these types can vary considerably among crude oils, but collectively they constitute 1-2 wt % (N) of the whole crudes. This compares with a figure of 0.05-0.20 for natural petroleum crudes.<sup>7</sup> A substantial amount of the nitrogen-containing compounds may be removed through hydrogenation steps in upgrading the crudes; residuals will always remain, however, and there is a potentially serious hazard when the likely size of a synfuels industry is factored into the calculations.

The greatest challenge in this work so far has been the development of separations methods to isolate and concentrate each of the aforementioned classes. Although some methods for the separation of basic and neutral nitrogen-containing compounds from complex mixtures have appeared in the literature, no previous work has involved the isolation of the bioactive (mutagenic in this case) components of each of these classes. Throughout the development of current separations schemes, fractions were bioassayed to observe the effectiveness of the separation, using the bioassay as the criterion. This approach has resulted in isolation of the basic nitrogen-containing bioactive components into a fraction of about 0.1 wt % of the whole crudes. The neutral nitrogen compounds have also been separated from the neutral fraction and typically constitute about 2 wt % of the PAH fraction.

Basic fractions from the oils were obtained by first dissolving the oils in diethyl ether and extracting the acidic components with 1 M NaOH. A second extraction with 1 M HCl partitioned the basic components in the HCl phase, and these were

7. H. L. Lochte and E. R. Littmann, p. 291 in *The Petroleum Acids and Bases*, Chemical Publishing Co., Inc., New York, 1955.

back-extracted into ether at a pH of 11. Further details of this procedure are reported elsewhere.<sup>8</sup> The basic fraction thus isolated is about 100% nitrogen-containing compounds. Of these, only about 10% have been proven bioactive, using the Ames mutagenesis test. This "10% subfraction" was isolated, using a combination of basic alumina and Sephadex LH-20 gel with a sequence of solvents. The alumina column was eluted with benzene to give an inactive fraction (~70 wt %), followed by ethanol to remove the active components. The ethanol subfraction was placed on the Sephadex column and eluted with isopropanol, followed by acetone. The acetone subfraction contains about 90% of the activity of the original basic fraction, but is only about 10% of the weight of the whole basic fraction. Preliminary analyses of the acetone subfractions show that the bulk of the constituents are polycyclic aza-arenes (ring nitrogens) and amino-substituted PAHs. Specific component analyses are difficult because of the small amounts that are finally isolated and the lack of standard compounds for comparison of spectroscopic properties. Nevertheless, further work is aimed toward the determination of exact structures of the isomers, which is important in uncovering the identity of especially biologically active compounds.

Neutral aza-arenes appear to be generally less important, from a biological viewpoint, than are the basic nitrogen compounds. However, some compounds of this class are known carcinogens; consequently, this class cannot be disregarded. Neutral aza-arenes are separated from the total neutral fraction (resulting from an acid-base solvent partitioning) with the combination of a Sephadex LH-20 column and a silicic acid column. The Sephadex column separation removes aliphatics (eluted with isopropanol) and leaves the aromatic hydrocarbons and their heteroatomic analogues together (eluted with acetone). The latter two classes are separated on a silicic acid column with a gradient elution scheme starting with a benzene/hexane (1/3) mixture and ending with a benzene/hexane (2/1) mixture. The most polar constituents can be removed from the column with ethanol. The benzene/hexane cut using a 2/1 mixture contains the neutral nitrogen compounds with yields of 50 to 90%, the lower figure indicating the approximate yields for low-molecular-weight compounds, for example, indole.

This work has received significant attention. Quite obviously a great deal remains to be done, especially with regard to specific compound identification. An immediate utility of the results of this work is that the fledgling synthetic fuels industry can learn in advance the kinds of biologically active materials with which it must cope. The long-range utility is that basic information on the bioactivities vs chemical compositions of these kinds of compounds may help increase our understanding of what constitutes a chemical carcinogen. (C.-h. Ho, B. R. Clark, M. R. Guerin, C. Y. Ma,<sup>9</sup> T. K. Rao,<sup>10</sup> J. L. Epler<sup>10</sup>)

**Synfuels combustion testing.** Two years ago we began to develop a program in the combustion of synthetic fuels, the purpose of which was to learn about combustion behaviors and combustion products of synthetic fuels. Such studies, carried on concurrently with process development, should yield information useful to the process development and to the development of advanced combustion devices (both stationary and mobile). The proposed program required a variety of technical skills; and, because the Pittsburgh Energy Technology Center (PETC) had both combustion engineering expertise and combustion facilities, we discussed with them a series of joint simple experiments. Synthetic fuel materials are quite limited in amount; one most readily available in quantities suitable for a small-scale combustion test is shale oil. From a 100,000-bbl production run at the Paraho retorting facility in Anvil Points, Colorado, the U.S. Navy agreed to supply us with about 1600 gal. We also obtained some crude oil from the Laramie Energy Technology Center. Plans to test lightly hydrotreated versions of each oil were never realized because of a fire that destroyed the oils at the hydrotreating facility. Objectives of the shale oil combustion tests were: (1) to qualitatively examine the normal combustion products in the boiler facility being used and (2) to measure in the flame and in the stack those engineering parameters that determine combustion behavior.

A 100-hp, four-pass, dry-back, Cleaver-Brooks firetube boiler facility was used for the tests. Normal combustion conditions (~3% excess O<sub>2</sub> in the stack) were chosen to allow comparison with conventional No. 6 fuel oils. Oxygen, CO<sub>2</sub>, CO, NO/NO<sub>x</sub>, SO<sub>2</sub>, and total hydrocarbons (gas phase at STP) were measured with permanent on-line instrumentation;

8. I. B. Rubin, M. R. Guerin, A. A. Hardigree, and J. L. Epler, "Fractionation of Synthetic Crude Oils from Coal for Biological Testing," *Environ. Res.* 12, 358 (1976).

9. Visiting faculty member, University of Mississippi, Oxford.

10. Biology Division.

a flue gas opacity monitor measured the particulate density in the flue gas; and a cascade impactor sampled the particulates for size classification. During these runs, however, very little particulate was produced, and analysis of the impactor plates was thus inconclusive.

We designed a gas sampling apparatus for collecting organic volatile constituents. A sampling manifold used for the first test collected organic volatiles by adsorption onto beds of solid adsorbent; both Tenax-GC polymer and XAD-2 resin were used. The apparatus was simple but limited the information obtainable. The flue gas water was removed in a condenser between the stack probe and the adsorbent bed; this caused some of the organic volatiles at flue gas temperatures to condense out as well, and only the most volatile compounds could be expected to reach the trap. In subsequent tests, a more elaborate sampling train was used. A Tenax-GC collection apparatus designed by Jones et al.<sup>11</sup> was used to sample flue gas during an entire 6- to 8-h run. By heating the sample line from the probe to the Jones sampling apparatus at a temperature high enough to maintain the flue gas above the dew point and prevent condensation in the Tenax bed itself, we made the best compromise between sampling too hot a gas (with resultant inefficient adsorption) and the problem of water condensation that prevents adsorption.

Small glass columns packed with Tenax were also used to collect compounds volatile enough to pass through an upstream moisture condenser (as in the first tests). These columns were designed to fit in the injector port of a gas chromatograph and to be thermally desorbed onto the head of a cryogenically cooled column. Both flame ionization and flame photometric detectors were used in the analysis on packed columns. A few samples were chromatographed on a capillary column. Resin (XAD-2, cleaned with several solvents in a Soxhlet extractor) was packed into a stainless steel piece of tubing, used to sample flue gases, and then reextracted with the same sequence of solvents used for cleaning. Analyses were carried out using GC-MS and GC.

Results of the analyses were somewhat surprising. Virtually no PAHs were detected in any of the samples; nor were heteroatomic aromatic com-

pounds, other than a few sulfur compounds, detected. The absence of nitrogen compounds was the most surprising because nitrogen makes up about 1.5–2.0% of the oils. Apparently, nearly all of the nitrogen is oxidized; flue gas NO/NO<sub>x</sub> was very high (360–600 ppm) relative to other fuels. As mentioned above, a wide variety of sulfur compounds were detected at trace levels; in samples obtained during start-up or upset conditions, high-molecular-weight sulfur compounds (e.g., benzothiophene) were detected.

Although these tests were not run systematically enough to make a quantitative comparison between the Paraho and Laramie shale oils, no striking differences were observed in the combustion products; both contained a number of different saturated hydrocarbons at trace levels. These largely reflect the hydrocarbon types found in the shale oils, that is, *n*-alkanes, cycloalkanes, steranes, and terpanes. Very little olefinic material was detected. The oils had very similar elemental compositions and combustion behaviors. The Btu/lb was 18.5 kcal. The nonoil (API classification) fraction was about 0.0% for the Laramie oil and only about 1% for the Paraho oil. Both of these burned about like a No. 2 diesel fuel and had boiler efficiencies comparable to a No. 6 fuel oil.

No further tests are currently planned. The PETC has been funded to set up a small-scale, commercially available combustion unit to test small amounts of coal liquids. We may participate in a formal combustion test program at some later date. (*B. R. Clark, A. D. Horton, C. E. Higgins, M. R. Guerin*)

**Trapping and determination of volatile sulfides.** A surprising number of sulfur-containing compounds were found in the Tenax traps used in the combustion tests just described. This result has led to a short-term study to determine the efficacy of trapping organosulfur compounds on Tenax for quantitative analysis. Compounds of this class are usually quite labile and cannot be stored or transported in the gaseous state.

To determine the efficiency of Tenax-GC for trapping volatile sulfides, the glass insert of a capillary column injector was packed with about 20 mg of 60–80 mesh Tenax-GC. The insert was conditioned in the injector port for 1 hr at 250°C. A glass trap was fabricated from a glass tee, with a sealed bulb on one leg, a nylon S/L tee with an injector cap and carrier gas inlet attached to the second leg, and the Tenax trap attached to the third leg. The sample was injected into the nylon tee, from

11. P. W. Jones, R. D. Giammar, P. E. Strup, and T. B. Stanford, "Efficient Collection of Polycyclic Organic Compounds from Combustion Effluents," *Environ. Sci. Tech.* 10, 806 (1976).

which it passed through a tapered inner tube and impinged on the closed end of the tee, from which it passed to the Tenax trap. The bulb could be heated if desired to facilitate the passage of the less volatile compounds.

A solution of sulfur compounds in methylene chloride was prepared that contained diethyl, dipropyl, dibutyl, and dihexyl sulfides; diethyl and dibutyl disulfides; thiophene; 2-methyl, 3-methyl, and 2,5-dimethyl thiophenes; secondary and tertiary butyl sulfides; benzothiophene; and benzothiazole. A 1- $\mu$ l aliquot was injected into the tee with 20 ml of helium per minute sweeping the sample into the Tenax trap. The Tenax was desorbed in the injector port for 10 min at 250°C, with a carrier flow of 2 ml/min onto a 30-M UCON 50 HB 2000 capillary column cooled to -75°C. The column was heated rapidly to +75°C after the desorption period and temperature programmed at 4°/min to 175°C. All of the compounds listed above were completely separated by this column in 32 min.

Trapping, desorption, and determination of these compounds were repeated with and without heating the sealed bulb on the glass tee. Without heat, the less volatile dihexylsulfide, benzothiophene, and benzothiazole were about 25% below the values obtained with direct injection into the GC, whereas the more volatile compounds [except dipropylsulfide (50%), tert butyl sulfide (80%), and dibutyl sulfide (50%)] were recovered quantitatively. As expected, when the bulb was heated, the less volatile compounds were quantitatively recovered, but the most volatile compounds recovered from the Tenax averaged only 50% of the original values.

Aging studies of samples transferred to the Tenax trap without heating showed essentially quantitative recovery of all components after 17 h. After 88-h storage, there was a 50% loss each of dipropyl sulfide, 2,5-dimethyl thiophene, and dibutyl sulfide; a 75% loss of tert butyl sulfide; and a 30% loss of benzothiazole. Other component recoveries were essentially quantitative.

Trapping of volatile sulfur compounds on Tenax-GC with transportation and later analysis seems to be feasible for most compounds expected from gasifiers or combustion processes. Efforts to trap sulfur compounds on XAD-2 with subsequent thermal desorption or with desorption with polar-nonpolar solvents was unsuccessful. (*A. D. Horton, B. R. Clark*)

**Gasifiers in industry program.** The Department of Energy is studying the practicality of using

small-scale, low-Btu coal gasifiers directly in conjunction with and onsite with the facility consuming the product gas. The study has involved the submission of proposals by private industry and public institutions; six of the proposals have been accepted. The first gasifier, located at the University of Minnesota, Duluth (UMD), is nearly operational, with two others scheduled for construction in the next 2 years. The UMD gasifier will provide heat for the entire campus. All facets of operation are to be studied, which include dependability, economics, and the health and environmental impacts of prolonged operation. ORNL was asked by DOE to undertake the assessment of the UMD gasifier during a 3-year operating period. Plans to do similar assessments are being prepared for the next gasifier at Pike County, Kentucky, and, following that, one at the Land O'Lakes Corporation plant in Minnesota.

The Analytical Chemistry Division plays a central role in this program because we are responsible for the preparation and distribution of samples, the analysis of samples, the collection of the analytical data, and the dissemination of those data to the team responsible for making the assessment. In the first year of the UMD gasifier operation, process samples will be collected and analyzed qualitatively and quantitatively for specified compounds and elements. The current plan for process characterization specifies about 30 different analyses (some are multielement or multicomponent) of samples taken from 20 different locations in the plant, beginning with the bunker coal feed and ending with stack gases from the boilers. Gaseous samples from the occupational environment will be collected on adsorbents and analyzed using standard methods. Two mobile trailer units with equipment for continuous monitoring will record atmospheric concentrations of EPA criteria pollutants outside the plant. This aspect of the work has been subcontracted by the Environmental Sciences Division.

We will be using an EPA level I type of approach during the first year of operation. This approach provides mostly qualitative data with quantitation limited to approximations of a factor of about 3. Identifications are important at this stage, as is semiquantitation of classes of compounds, that is, organosulfur, organonitrogen, and PAH classes of compounds. Using toxicity data in conjunction with the approximate amount of a compound or element determined, it is possible to evaluate the need for more careful (or discontinued) measurement of a

compound or element during the remainder of the study. This approach is economical and useful whenever a study continues over a sufficient time to allow evaluation in stages as described.

A sample management system is being established to record sample location, to check on the progress of an analysis, and to record the results. There may be as many as 1000 analytical results during the first full year of operation of one gasifier. Present plans are to incorporate the sample-data management function into the current Sample Transaction System used by other sections of the division.

A quality assurance program is being formulated. In initial stages, the reproducibility of sampling will be a primary concern. Gasifier ashes, coal feeds, and cyclone separator fines pose the most difficult problems. Most of the samples that we will analyze will be composited from samples taken on a daily basis, a shift basis, or a schedule to be determined from experience. Sample collection and shipment is being handled through a subcontract with UMD personnel under our technical supervision. Some gaseous samples are too labile for shipment and will be analyzed onsite by the same UMD personnel trained by us at onsite visits.

Quality assurance of analysis will be handled in the usual way, that is, replicate analyses, analysis in different laboratories, analysis using different methods, incorporation of "knowns" or standard reference materials, etc. This can be done fairly easily and economically for elemental analyses, routine coal analyses, etc., but analyses of organic constituents are more difficult to assure. This will become a major concern when the quantitation of specific compounds becomes necessary. Analytical results will be all important in answering the ultimate assessment question: is this gasifier safe to operate from a health and environmental viewpoint? (*B. R. Clark, M. R. Guerin*)

## ENVIRONMENTAL ANALYSIS PROGRAM

The projects in the Environmental Analysis Program emphasize the development and application of methodology for sampling and analysis of atmospheric and aqueous organic pollutants and the support of health and environmental effects research with materials from synthetic fuels production.

**Examination of electrostatic precipitator ash as a surrogate for fly ash.** Fly ash is difficult and expensive to collect from the ductwork or stack of a coal-fired electric power generation plant, whereas electrostatic precipitator hopper ash (ESP ash) can be obtained

readily in large quantities. The suitability of ESP ash as a convenient chemical surrogate for fly ash was examined through a comparison of the particle morphology and size distributions, elemental compositions, extractable organics, and PAH contents of the two ashes.

Particle morphology and size analyses were carried out on fly ash, unsized ESP ash, and a respirable size fraction of ESP ash prepared with a Bahco microparticle classifier. Scanning electron microscope photographs of the three ashes indicated similar particle morphology. The geometric size distributions of the three ashes were found to approximate a logarithmic normal distribution with median geometric diameters of 1.4  $\mu\text{m}$  (fly ash), 1.6  $\mu\text{m}$  (sized ESP ash), and 1.8  $\mu\text{m}$  (unsized ESP ash). The ESP is known to be less effective in collection of very small particles; thus the sized fraction of ESP ash would be expected to more closely resemble fly ash. Comparison of elemental data for the three ashes indicated small, but apparently real, differences in their composition. However, neither ESP ash stood out as an obviously better surrogate of the elemental composition of fly ash. The sized fraction of ESP hopper ash was chosen for further chemical comparison with fly ash because of its greater similarity in particle size distribution.

Organic analysis required the development of special methods optimized for the small (3-g) quantity of fly ash available for study. Ultrasonic agitation in benzene was found to be the most rapid and efficient method of ash extraction, but, even with this method, quantitative recovery of all PAHs was not achieved. The PAH extraction recoveries decreased with increasing PAH ring size and were lower than recoveries of saturated hydrocarbons of greater carbon number, implying a  $\pi$ -complex binding mechanism. These results indicate that current extraction methods may not accurately reflect the actual composition of organics adsorbed on fly ash, although they may indicate those accessible species that could exert a chemical or biological influence. For this comparative study of ESP ash vs fly ash, carbon-14-labeled benz[*a*]anthracene was chosen as the most suitable single PAH tracer for monitoring extraction recoveries because its extraction behavior is intermediate between that of the small- and large-ring PAHs.

Organic extracts of stack ash and sized ESP ash were prepared by ultrasonic extraction in benzene after spiking with carbon-14-labeled benz[*a*]anthracene. The extracts were concentrated with dry flowing nitrogen under reduced temperature and

pressure and were analyzed by Dexsil 400 glass capillary column gas chromatography. The major feature of the extracts of both the sized ESP ash and the fly ash was a series of *n*-paraffins from *n*-C<sub>17</sub>H<sub>36</sub> to *n*-C<sub>36</sub>H<sub>74</sub>. The paraffin concentrations slowly increased with chain length up to *n*-C<sub>22</sub>H<sub>46</sub> and then slowly decreased in the sized ESP ash. A more even distribution of concentrations was apparent in the fly ash paraffins, but above *n*-C<sub>29</sub>H<sub>60</sub> the fly ash was not significantly different from a blank. The ESP ash contained 3.6 ppm total *n*-paraffins; almost four times more than the 0.86 ppm on the fly ash.

Before PAH analyses were performed, the extracts were purified of gross organic material that would streak the thin layer chromatography (TLC) plate and interfere with spectral analysis. Purification was accomplished with small alumina columns constructed from disposable Pasteur pipettes, using hexane to elute paraffins and other relatively nonpolar organics and benzene to elute the PAHs. The concentrated, purified ash extracts, PAH standards, and blanks were analyzed by TLC with *in situ* fluorescence and by liquid scintillation counting. PAHs were identified using TLC mobility *R<sub>f</sub>* and fluorescent emission spectra. Five PAHs were identified by both criteria; two PAHs were identified by only one of the criteria because of interferences or weak spectra.

Quantitation of the PAHs was achieved by comparing PAH fluorescence emission intensity at a spectral peak maximum with standards of similar concentration. However, measurements were hampered by the trace levels of PAHs and the significant PAH background in the blank. Benzo[*a*]pyrene (0.69 ppb), benz[*a*]anthracene (3.5 ppb), pyrene (1.4 ppb), and fluoranthene (tentative identification; 5.1 ppb) were measured in the fly ash, but only pyrene (23 ± 6.4 ppb) and fluoranthene (tentative identification; 19 ± 0.59 ppb) were measured in the sized ESP ash. The other identified PAHs were not significantly different in concentration from the blank, and thus their presence in the ash samples was not proved.

Some evidence was found for the presence of alkylated PAHs in the ash samples. Often, weak "shoulders" were observed on the higher *R<sub>f</sub>* side of the PAH TLC spots, and their fluorescent spectra were shifted by 2–3 nm. Comparison of authentic 1-methylpyrene and pyrene indicated that simple methylation results in a slight increase in TLC mobility and a small positive shift in the fluorescent peak wavelength, consistent with the tentative identification of the shoulders as methylated deriva-

tives of PAHs. The lack of sufficient authentic standards prevents positive identification and quantification.

Although limited fly ash sample availability prevented rigorous, statistical comparison of ESP ash with fly ash, the results suggest that a respirable size fraction of ESP hopper ash can act as a qualitative surrogate for fly ash. (*W. H. Griest, L. B. Yeatts, Jr.*)

Sampling system for vapor phase organic pollutants. An improved vapor phase sampling unit has been developed for the Environmental Protection Agency. The system, shown in Fig. 4.2, is designed to be mounted on the side of existing EPA high-volume air particulate samplers. The vapor phase is sampled from a point just below the particulate filter and is pulled through the traps by a separate vacuum pump, allowing both particulate and vapor phase samples to be collected simultaneously. The modules consist of a flow control and monitoring unit mounted permanently to the Hi-Vol samplers and demountable traps. The entire system is constructed of stainless steel, glass, and Teflon to minimize spurious contamination.

The vapor phase collection traps are constructed of 15.24-cm lengths of 1.27-cm-ID conical-ended glass pipe. About 20 cm<sup>3</sup> of adsorbent is held in place with stainless steel screens and Teflon retainer rings. Each end of the glass pipe is fitted with a specially designed threaded bushing, which permits the traps to be mounted in series on the control module as shown in Fig. 4.2 and to be hermetically sealed for shipment using Teflon end-caps.

The control unit accommodates two sets of traps so that duplicate samples can be taken. Traps may be mounted individually or as pairs (Fig. 4.2). The second trap of each set is a backing trap used primarily to detect breakthrough losses of poorly absorbed compounds. Adjustable flow controllers regulate the flow through the traps independently of the downstream (suction) pressure. A single flow meter is provided so that the actual flow in either set of traps can be periodically monitored during a sampling experience. The valving is designed so that one set of traps can be removed from the system without interrupting the collection in a second set.

The choice of adsorbent resin for the sampling unit traps, the sampling protocol, and the analytical protocol to be used for the Yugoslavian gasifier study were determined in a cooperative effort with EPA personnel. For these purposes, the EPA conducted a sampling trip to the Chapman gasifier in Kingsport,

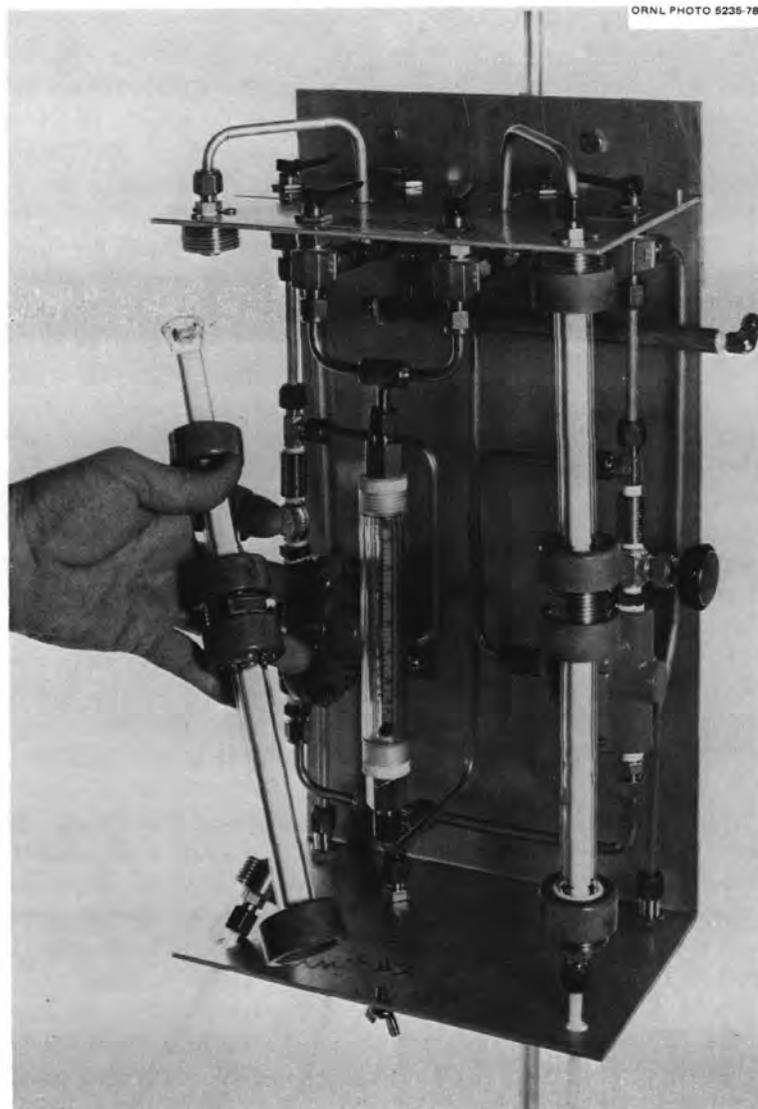


Fig. 4.2. Sampling system for vapor phase organic pollutants.

Tennessee. Series traps packed with Tenax-Tenax, Tenax-XAD-2, or XAD-2-XAD-2 combinations for the primary and backup traps were employed in side-by-side 24-h sample collections at 3 to 4 liters/min. Particulates were collected on Microquartz filter pads. The vapor phase passing through these filters was sampled for organic content. The exposed traps were returned to us to determine the types of vapor phase compounds collected and to ascertain which resin was the best collector.

Exposed resins from the gasifier sampling were subjected to two types of analyses: thermal desorption and solvent extraction. In the latter, the entire

contents of the traps were spiked with carbon-14-labeled benzo[*a*]pyrene and were Soxhlet-extracted with either pentane (Tenax) or benzene methanol (XAD-2) until the tracer was quantitatively recovered. The gross extract was then concentrated and analyzed by gas chromatography with a Dexsil 400 packed column. We observed that neither the Tenax nor the XAD-2 traps collected sufficient vapor phase material in the retention index range of 1200 to 3800 for GC analysis. In contrast, a large amount of such material was found on the air particulate pads, including at least 31 PAHs. Thus under these sampling conditions the bulk of such

compounds was retained on the particulate filter pad and was not transferred to the vapor phase traps. A 24-h particulate sample of about 90 mg was sufficient for solvent extraction/concentration and GC analysis.

Thermal desorption analysis of the vapor phase traps, however, was quite successful. Seventy to ninety milligrams of resin from each trap was packed into glass tubes and thermally desorbed at 250°C onto a cryogenically cooled glass capillary column coated with OV-330. The column was then temperature programmed, and the eluting components were detected by flame ionization. Gas chromatography profiles containing over 100 peaks with retention indices from 600 to 1800 were obtained from the Tenax traps. Blanks from unexposed Tenax traps were very low. In contrast, the thermal instability of XAD-2 resin caused very intense backgrounds and prevented its use for thermal desorption analysis even at much lower desorption temperatures.

Because only a small quantity of the Tenax trap resin is required for thermal desorption analysis, replicate analyses or a battery of several different analyses can be performed on each sample. For repeated analyses conducted on a single day, the precision appears to be better than  $\pm 10\%$ , and reproducibility from day-to-day is closer to  $\pm 15\%$ . Analysis of the Tenax backup trap in the series dual-trap combination indicated that a small (practically negligible) amount of sample breakthrough occurred from the primary Tenax trap during the 24-h collection. Thus the primary traps and only a few representative backup traps from a large-scale sampling trip need to be analyzed.

A 24-h sample collection with Tenax on the newly designed sampling device plus thermal desorption analysis has been adopted by the EPA as the primary method for characterizing the vapor phase organic emissions near the Yugoslavian gasifier. Five sampling modules and 200 traps were constructed and delivered to the EPA for this sampling trip. (*J. H. Moneyhun, C. E. Higgins, W. H. Griest, R. W. Holmberg*)

**Analysis of stream waters for polycyclic aromatic hydrocarbon content.** The Environmental Sciences Division is studying the environs of a large coking plant in Pennsylvania because aqueous effluents from this type of operation might resemble those from coal conversion plants. We are participating in this study. The overall project is concerned with the

distribution, persistence, and fate of PAHs in the aqueous environment and their potential ecological impact.

Analytical studies required the collection of PAHs from 4- to 20-liter quantities of water from each of 30 stream and river sampling sites near the coking plant. A total of about 370 liters of water was to be sampled. A sampling system was needed that was simple to operate, rugged in construction, efficient in collection of aqueous PAHs, and amenable to mass production. Readily available XAD-2 resin was chosen for the PAH collection medium. A column was constructed from 30 cm  $\times$  2 cm OD glass tubing tapered to 5 mm at the tip and fitted with a bored-out rubber stopper at the opposite end. The stopper fits into the mouth of a standard 1-gal jug. Upon inversion, water in the jug percolates through the column. A 20-gauge hypodermic needle inserted through the rubber stopper acts as an air bleed into the jug and allows more uniform water flow. The amount of XAD-2 resin required to collect PAHs from 3.8-liter quantities of water was estimated with both distilled and natural water samples spiked with carbon-14-labeled benzo[*a*]pyrene ( $^{14}\text{C}$ -BaP). Thirty grams of XAD-2 resin provided the best compromise between collection efficiency and flow rate.

The design was further evaluated by spiking 3.8 liters of distilled water with 34 PAHs at a concentration of approximately 3  $\mu\text{g}$ /liter each and passing the water through the XAD-2 column. Five percent of the  $^{14}\text{C}$ -BaP passed through the column, 1% was retained on the water jug walls, and 95% was recovered in the eluting organic solvent. The eluted PAHs were next subjected to Florisil and alumina adsorption chromatography and were analyzed by gas chromatography. No contamination problems from the rubber stopper were experienced. The two- and three-ring PAHs were not recovered, probably because the water samples passed through the XAD-2 columns too rapidly for efficient resin/water equilibration of these more water-soluble PAHs. Some losses of these more volatile PAHs do occur during isolation, but, if they had been collected by the resin, the analysis would have at least indicated their presence. Corrected recoveries (relative to  $^{14}\text{C}$ -BaP) of larger PAHs rapidly rose with increases in PAH ring size and were essentially 100% for five- and six-ring PAHs. Improved collection recoveries of smaller PAHs might be achieved by adjustment of the pH and ionic strength of the stream water prior to

percolation through the XAD-2 columns. However, such measures are not practical in a large-scale field-site water collection. The effectiveness of extended batch-wise prepurification of the XAD-2 resin also was investigated. Extended extraction of the resin with acetone was sufficient to eliminate any blank correction problems.

About 110 XAD-2 resin columns were prepared for the field site sampling. Two columns, spiked with both labeled and unlabeled PAHs, were included as controls. Radiolabeled PAH tracer solutions were prepared in small glass vials to allow each water sample to be spiked with a tracer for recovery corrections. In the field, the water samples were collected in amber jugs from a boat and were carried to shore for spiking and percolation through the XAD-2 columns. The exposed sample columns and unexposed control columns were shipped back to ORNL on dry ice. Before PAH isolation, the XAD-2 resin in each column was repacked into a slightly larger glass column for elution with organic solvents in a direction opposite to that of the water collection. The samples were carried through the same isolation and analysis procedure as before.

One complicating problem was degradation of the PAH tracer solution, apparently by exposure of the unprotected vials to sunlight in the field. The tracers could not therefore be used to correct for PAH recoveries. However, spiking experiments with natural water samples from two local sources approximating the organic carbon and particulate content of the coking-plant-site water indicated an average  $^{14}\text{C}$ -BaP collection efficiency of about 88%. This estimate was used in subsequent calculations. The essentially quantitative PAH recoveries and "clean" appearance of the GC profiles of the control samples suggested that the isolation and analytical procedures were executed properly and that the XAD-2 columns were not contaminated during shipment and storage.

The major PAHs in the coking plant effluent channel wastewater discharge were found to be unsubstituted PAHs. Fluoranthene ( $18\mu\text{g/liter}$ ) and pyrene ( $14\mu\text{g/liter}$ ) were the major aqueous PAHs. Substantial concentrations of benzo[*a*]pyrene ( $2\mu\text{g/liter}$ ) and benzo[*b*, *j*, or *k*]fluoranthene ( $5\mu\text{g/liter}$ ) also were present. PAH concentrations dropped off sharply downstream of the point of discharge into the creek, where multialkylated PAHs and several unidentified organic compounds complicated the GC analyses. Several phthalates also were present in relatively high concentrations in the PAH

isolates from the creek. (*W. H. Griest, R. R. Reagan, S. H. Watson, S. E. Herbes,<sup>12</sup> G. R. Southworth<sup>12</sup>*)

**Determination of priority pollutants in aqueous extracts of solid wastes.** We are developing and validating analytical techniques for the removal, concentration, and quantitation of EPA priority pollutants in aqueous extracts obtained from a standard toxicant extraction procedure (TEP) extract of solid wastes. The TEP has been selected by the EPA to provide estimates of solid waste leachate characteristics; it is to be used to meet regulatory requirements of the Resource Conservation and Recovery Act (RCRA). The extracts are to be subjected to biological and chemical analysis. Chemicals of first concern are those designated by the EPA as "priority pollutants."

Attempts to assay chemically and biologically the aqueous extracts directly were unsuccessful. Therefore, an investigation of methods to concentrate organic constituents from the TEP extracts was carried out. Cyclohexane and methylene chloride were investigated as partitioning organic solvents and compared with resin extraction on Amberlite XAD-2, as described by Junk et al.<sup>13</sup> Careful control of both pH and ionic strength is imperative if a meaningful comparison is to be made. The pH of the aqueous system was therefore adjusted to 6.8 with  $\text{Na}_3\text{PO}_4$ , and the conductance was subsequently adjusted to  $20\text{ mmho/cm}$  with  $\text{NaCl}$ . Blank TEP extract solutions were prepared as indicated, and then spiked with known activities of  $^{14}\text{C}$ -labeled compounds representing the various chemical classes found in the priority pollutant list. The aqueous material was subjected to both solvent partition and resin extraction. Although methylene chloride gave the most efficient extraction, its use in various bioassays is questionable because of its positive mutagenic response. It should be noted that, although both solvent partition and XAD-2 provide reliable extraction, XAD-2 provides, in addition, a direct 100-fold concentration. Furthermore, as many as 15 aqueous samples may be extracted simultaneously with the use of a simple peristaltic pump, thus eliminating considerable

12. Environmental Sciences Division.

13. G. A. Junk, C. D. Chriswell, R. C. Chang, L. D. Kissinger, J. J. Richard, J. S. Fritz, and H. H. Svec, "Applications of Resins for Extracting Organic Components from Water," *Z. Anal. Chem.* **282**, 331 (1976).

technical bench time. Organic concentrates obtained from XAD-2 extraction of urine have been shown to be appropriate materials for short-term bioassays. Therefore, we have chosen XAD-2 as the method of extraction.

Fractionation of the concentrate is required, as indicated by the complex profiles obtained from earlier waste extracts. Because a sizable number of the priority pollutants are PAH in nature, the fractionation scheme previously developed in this laboratory for isolating PAHs was applied to the organic extracts obtained from the solvent/resin study. The recoveries of the representative  $^{14}\text{C}$ -labeled compounds were traced through this scheme. Nonpolar materials are separated from polar organics by column chromatography on Florisil. The nonpolar organics are further fractionated on alumina into a PCB/pesticide/mono- and diaromatic fraction, a polyaromatic fraction, and possibly a heteroatomic fraction. The PCBs and pesticides may be further fractionated on charcoal; this procedure is currently under investigation. To test further the validity of this procedure a 0.1-ppm solution of benzo[a]pyrene, benz[a]anthracene, and polychlorinated biphenyls (PCB 1242) was also carried through the resin extraction and concentration procedure. The recoveries proved to be accurate and precise. The XAD-2 concentration method and the Florisil-alumina fractionation scheme are now in routine use. Examination of the TEP extracts of the first four solid wastes provided by EPA and a TEP extract blank have revealed only a small PCB contamination (~8 ppb) attributable to the TEP extraction apparatus or solvents.

We have also evaluated the purge-and-trap method for the determination of volatile organics in water.<sup>14</sup> A manual version<sup>15</sup> of this method has been adopted. External standard analysis is performed by purging 1 ml of aqueous sample containing 1 ppm volatile pollutants with  $\text{N}_2$  into a precolumn packed with 2 mg Tenax and 1 mg Florisil in series. The volatiles are desorbed in the injector of a GC and cryogenically collected at the head of a 0.2% DEGS glass capillary column. The

volatiles are then eluted via temperature programming and detected by flame ionization. The pollutants are spiked into the aqueous solution just before purging. The standard solutions are made up in ethylene glycol at the 1 mg/ml level. Sixteen volatile brominated and chlorinated compounds have been tested. The average precision is estimated to be  $\pm 20\%$ , but the recovery is unknown; the sensitivity is about 0.1 ppm for a 1.0-ml sample. Lower concentrations may be determined by using larger samples.

Several of the TEP extracts generated so far have been analyzed for purgeable volatiles. None could be detected at the 0.1-ppm level, even when the leachate was frozen immediately after generation. This is not surprising in view of the fact that the current TEP requires that the solid wastes be extracted in open containers for 24 h. Any volatiles present in the waste are probably lost to the atmosphere during the TEP. To obtain meaningful data on the volatile content of solid wastes, it will be necessary to analyze the waste directly or to modify the TEP apparatus to purge continuously the system during extraction.

Fourteen EPA priority pollutant and primary drinking water standard metals have been chosen for the metals determination protocol. Joint studies with other Analytical Chemistry Division sections compared the results obtained by atomic absorption spectrophotometry, spark-source mass spectrometry (with isotope dilution where applicable), inductively coupled plasma emission spectrometry, optical emission spectroscopy, and neutron activation analysis. Comparative analytical results were in good agreement, validating atomic absorption spectrophotometry as a reliable analytical method for TEP extracts. Further comparison in a collaborative study with the Illinois State EPA and analysis of an EPA Laboratory Performance Standard solution provided additional validating evidence. The metals protocol is now routine. In contrast to the organic analyses, most of the 14 metals have been detected and measured in each TEP extract, suggesting that such extracts are predominantly inorganic (or ionic) in content.

The research and development phase of this work has given way to an almost routine handling of the TEP extract samples. We will continue to suggest and evaluate changes in the TEP, in the analytical methods for priority pollutant measurement, and in the isolation of pertinent material for bioassay. (M. P. Maskarinec, E. M. Burnett, W. H. Griest, R. W. Harvey)

14. T. A. Bellar and J. J. Lichtenberg, "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," *J. Am. Water Works Assoc.* **65**, 739 (1974).

15. K. Grob, "Organic Substances in Potable Water and Its Precursor: Part I. Methods for Their Determination by Gas-Liquid Chromatography," *J. Chromatogr.* **84**, 255 (1973).

**Synthetic fuels research sample repository.** The EPA/ORNL Chemical Repository provides physical and chemical support to health and environmental effects research addressing alternate fossil energy technologies. Support centers around the preparation, distribution, and maintenance of materials related to coal conversion and shale oil recovery processes. The primary objective of the effort is to make samples available for basic research programs in the chemistry and biology of synthetic fuels. Judicious selection of samples allows for interlaboratory comparisons and interrelation of basic research efforts.

Activities in this report period have centered on special services while scoping the utility of the central sample supply concept. About 331 samples have been provided to a total of 52 researchers over the past year. Interest in acquiring samples is at a new high, largely caused by the new availability of materials of greater relevance and/or interest to technology developers. Storage, handling, and data-recording facilities are now being upgraded to provide the special care and documentation required by these more relevant materials.

An example of special studies undertaken in the past year is the sampling assistance, preparation, and characterization of particulates from oil shale retorting. A suite of samples was collected by an experienced subcontractor for the repository at various process points in an oil shale retorting facility. Onsite supervision of the sampling was conducted by repository personnel because available process information was insufficient for proper design of the entire sample collection. EPA's interest in these samples centers on bioassay of the respirable particulates. Several companies were considered for preparation of a respirable size fraction from over 200 kg of retorted shale particulates for bioassay by other EPA contractors. Two 2-kilogram quantities of fly ash provided by the EPA were furnished to each of two companies for preparation of a respirable size fraction. The returned particulate fractions were compared with respirable fractions prepared in-house. Examination of scanning electron microscope (SEM) photographs of each particulate fraction indicated that the product of one company was superior to that of the other. This company was chosen subsequently for subcontracting preparation of the respirable size fraction of the retorted shale particulates. About 14 kg of respirable particulates was separated from over 200 kg of retorted shale.

Chemical and physical characterization is being conducted on two bulk retorted shale particulate samples, the respirable size fraction of one particulate sample and an air particulate sample collected in the vicinity of the point where the retorted shale particulates are dumped from a conveyor. Particle size analysis with our Bahco particle size classifier indicated that both bulk particulate samples followed a logarithmic normal distribution and that about 40 wt % of the material was in a respirable size range. The amount of the airborne sample was insufficient for an aerodynamic particle size analysis.

The morphology and geometric particle diameter distribution of the particulates were determined with an SEM. An examination of SEM photographs showed that the airborne material had a larger fraction of finer particles than did the other two samples, leading to the conclusion that wind currents did not carry the larger particles to the high-volume sampler. In agreement with the Bahco aerodynamic diameter analyses, the photographs did not show gross differences in particle sizes between the two bulk particulate samples. There was visual evidence of crystal formation in all cases, especially in the airborne sample.

Elemental analysis of the retorted shale particulates was conducted by the Mass and Emission Spectrometry Section, using inductively coupled plasma emission spectroscopy and spark source mass spectroscopy with isotope dilution where applicable. No significant differences in elemental composition were observed with the possible exception of potassium and boron, which were about three times more concentrated in the air particulates than in the other samples. This result suggests that the elemental composition of retorted shale particulates is not dependent on particle size as it is in fly ash from coal combustion.

The major organic compound content of the retorted shale particulates was determined by solvent extraction, concentration, gas chromatography, and radiolabeled tracer recovery measurements. The bulk of the extractable organics from all samples consisted of a series of *n*-paraffins. These hydrocarbons ranged from *n*-C<sub>10</sub> to *n*-C<sub>36</sub> in the retorted shale particulates and the respirable size fraction, but the airborne sample lacked the *n*-C<sub>10</sub> to *n*-C<sub>15</sub> paraffins. This effect may have resulted from sublimation losses to the air being drawn through the air particulate sampling pad. The most concentrated species were *n*-C<sub>12</sub> and *n*-C<sub>13</sub>

paraffins in the particulate samples, but  $n\text{-C}_{31}$  to  $n\text{-C}_{33}$  paraffins predominated in the airborne samples. The total paraffin concentration in the particulates ranged from 27 to 47 ppm and was somewhat higher in the airborne sample, 58 ppm. In comparison, ash from one coal-fired electric power generation plant contained only 9 ppm of  $n$ -paraffins of about the same range and relative distribution as the retorted shale particulates. These data have been furnished to the EPA to support their biotesting of retorted shale particulates.

Facilities and procedures developed in support of the basic research program are being examined for their use in supporting site-specific assessment programs. The practicality of developing a suite of reference research materials to support both types of programs is also under study. (*L. B. Yeatts, Jr., W. H. Griest*)

### TOBACCO SMOKE PROGRAM

Our tobacco smoke studies are funded by the National Cancer Institute's (NCI) Smoking and Health Program (S&HP) and by the Council for Tobacco Research, USA, Inc. (CTR). Close collaboration with other NCI and CTR contractors is required. Our studies take three primary directions: (1) chemistry of both gas and particulate phases of tobacco smoke as it is generated under highly defined conditions, (2) delivery of reproducible doses of smoke to experimental animals for inhalation bioassay, and (3) the analytical chemistry associated with the biological impact of smoke on the experimental animal.

**Chemical analysis of smokes of foreign commercial cigarettes.** The S&HP of the NCI has been directing increasing attention to the association of smoking and cancer on a worldwide basis. Because of differences among nations in the epidemiology of cancers in smoking populations, NCI has been investigating the differences in the chemistry of smokes of various foreign cigarettes. ORNL, at the request of S&HP management, has been providing the analytical chemistry support for this project. During the past reporting period, we have analyzed the smokes from 160 brands of various foreign commercial variants. Some of the nations surveyed include Kenya, the Philippines, Italy, Austria, Sri Lanka, the United Kingdom, France, and South Africa.

Generally, constituents for which we have analyzed have been limited to those thought to have the greatest biological impact: "tar," nicotine, and

carbon monoxide. Both nicotine and carbon monoxide have been implicated in cardiovascular disease. Nicotine is a toxic alkaloid, whereas carbon monoxide is a respiratory enzyme poison and is thought to be important in the development of atherosclerosis. The tar contains most of the carcinogenic constituents in tobacco smoke and a number of toxic and irritating materials. For these analyses and for the first time, we obtained gas phase samples for carbon monoxide analysis from the exact cigarettes smoked to acquire tar and nicotine deliveries. This practice has been a significant step in improving the precision and accuracy of the data we report. Because commercial smoking products are involved, our work is closely scrutinized by the tobacco companies.

Because of the wide assortment of cigarettes that have been analyzed, some interesting tentative conclusions are now possible concerning the nature of smoking materials around the world. For example, although most American cigarette brands manufactured in the United States for export are essentially the same as those consumed in the United States, such is not always the case for cigarettes exported from the United Kingdom. Generally, the smokes of cigarettes with American or English brand names manufactured in lesser developed countries under licensing agreements have much greater tar and nicotine contents than their counterparts in the nation of the parent company. And, interestingly, filter cigarettes in some countries deliver *more* tar, nicotine, and CO than their nonfiltered counterparts. This work is currently being prepared for both an ORNL/TM report and open literature publication.

An assumption critical to the use of tar deliveries as a relative rating of the potential health impact of a cigarette is that the chemical differences among tars is known, but it is not clear how important (or unimportant) these differences are from a health-impact standpoint. During the current contract year, we are beginning to develop high-resolution, semi-quantitative profiling methodologies that should make the routine screening of tar from both commercial and experimental cigarettes more cost effective. The intent is to answer questions concerning the overall chemical composition of tobacco smoke particulate matter. (*R. B. Quincy, R. A. Jenkins*)

**Determination of oxides of nitrogen in cigarette smoke by chemiluminescent analysis.** The use of chemiluminescence for the determination of oxides of nitrogen has been spurred by interest in characterizing atmospheric pollution. In this technique, ozone

is reacted with nitric oxide to produce  $\text{NO}_2^*$ , which is in an excited electronic state (about 10% yield). The  $\text{NO}_2^*$  relaxes to a ground state, emitting a photon that is registered on a photomultiplier tube. Total oxides of nitrogen  $\text{NO}_x$  are measured by first flowing the gas sample through a reaction chamber that reduces  $\text{NO}_2$  to  $\text{NO}$ . The quantity of  $\text{NO}_2$  is determined as the difference in response between the  $\text{NO}$  and  $\text{NO}_x$  "modes" of the analyzer. There are many commercial chemiluminescent analyzers; they differ in the nature of the reductive converter, that is employed in the  $\text{NO}_x$  mode.

Analysis of cigarette smoke must be carried out rapidly to reduce the possibilities of both the conversion of  $\text{NO}$  to  $\text{NO}_2$  (which would yield artificially large  $\text{NO}_2$  values) and the reaction of  $\text{NO}$  and/or  $\text{NO}_2$  with organic gas phase constituents of the smoke. The method must also allow a puff-by-puff analysis for oxides of nitrogen content. In the final procedure, the gaseous effluent from a single-puff smoking machine is introduced as a bolus into a large-bore stand tube. The chemiluminescence analyzer with its built-in pump continually sweeps the contents of the stand tube. Thus, because the smoke is rapidly mixed with incoming air, it is analyzed as a dilute puff. Dilution of the smoke in the stand tube acts to reduce artifactual conversion of  $\text{NO}$  to  $\text{NO}_2$ . The integrated voltage output of the analyzer is related to the absolute amount of  $\text{NO}$  and/or  $\text{NO}_2$  introduced into the stand tube.

Other workers have reported<sup>16</sup> varying degrees of quenching of the chemiluminescent reaction by such species as carbon dioxide, water, carbon monoxide, and hydrogen. This was of special concern to us because of the high concentrations of  $\text{CO}$  (5% v/v) and  $\text{CO}_2$  (10% v/v) in most fresh cigarette smokes. Thorough studies have been conducted on most of these potential quenchers. Because of rapid dilution of the smoke in the stand tube, the response of the analyzer to  $\text{NO}_x$  mixtures (at levels simulating those in cigarette smoke) was found to be reduced less than 1% by "puffs" of 10%  $\text{CO}_2$ . Hydrogen, methane, and carbon monoxide have also been found to be unimportant quenching agents for the present system configuration.

16. R. D. Matthews, R. F. Sawyer, and R. W. Schefer, "Interferences in Chemiluminescent Measurement of  $\text{NO}$  and  $\text{NO}_2$  Emissions from Combustion Systems," *Environ. Sci. Tech.* 11, 10912 (1977).

Another potential problem in chemiluminescent analysis is one of false positives; that is, the analyzer responds to something that is not  $\text{NO}$  or  $\text{NO}_2$ . Since many low-molecular-weight organic compounds will emit photons (albeit at shorter wavelengths than those from  $\text{NO}_2^*$ ) upon reaction with ozone or oxygen, we investigated potential positive interferences from many of the constituents present in significant quantities in the vapor phase of cigarette smoke, such as nicotine, methane, nitromethane, methanol, acrolein, and hydrogen sulfide. Although all of the more plausible candidates yielded no response from the analyzer, the system was found to respond to hydrogen cyanide ( $\text{HCN}$ ) when operated in the mode of the analyzer in which the sample is routed through the converter assembly. Preliminary evidence suggests that the  $\text{HCN}$  "interferes" by displacing trace amounts of adsorbed  $\text{NO}$  or  $\text{NO}_2$  from the converter assembly, to which the analyzer responds in the usual fashion. Because the gas phase of cigarette smoke can contain up to a few hundred micrograms of  $\text{HCN}$ , several methods were investigated for the selective removal of  $\text{HCN}$  from diluted cigarette smoke. Of course, any selective trapping material would have to pass oxides of nitrogen quantitatively. Many trapping systems were evaluated, including absorbants, chemical reactors, and ion exchangers. One material, Amberlyst 15 cation exchange resin, loaded with  $\text{Ag}^+$  and then reduced with hot (220°C) hydrogen gas has proved particularly useful. A small tube filled with this material (~3 ml volume) placed in the inlet to the analyzer nearly completely removes  $\text{HCN}$  from the smoke stream. In addition, the resin apparently quantitatively reduces  $\text{NO}_2$  to  $\text{NO}$ , obviating the need to run the sample through the converter assembly and thereby bypassing the portion of the analyzer that is most susceptible to interferences. Thus, to measure  $\text{NO}_x$  in smoke, the sample is analyzed with the trap in place. To measure just  $\text{NO}$ , the trap is removed from the analyzer stream.

Analysis of smoke delivered by the Kentucky Reference 1R1 cigarette yielded values of 11.5  $\mu\text{mol}$  of  $\text{NO}_x$  per cigarette, of which about 8.5% was present as  $\text{NO}_2$ . This proportion is significantly greater than had been anticipated (although literature values for  $\text{NO}_2$  in smoke are virtually nonexistent because of the great difficulty in performing a direct measurement of  $\text{NO}_2$ ). In addition, the quantity of  $\text{NO}_x$  from the 1R1 cigarette determined by chemiluminescence is about 70% greater than

amounts determined by two of the more popular methods for oxides of nitrogen: the Saltzman colorimetric method<sup>17</sup> and the acidified hydrogen peroxide trapping nitrate selective electrode method.<sup>18</sup> Careful investigation in our laboratory revealed that these methods are too slow to prevent side reactions of the NO<sub>x</sub> with organic gas phase constituents in smoke and are not effective in trapping NO<sub>x</sub> from the smoke in a quantitative manner.

Comparison of results using chemiluminescence with those determined by the Saltzman method revealed a high degree of correlation ( $R = 0.995$ ) between the two sets of values. This suggests that, while less accurate, the colorimetric procedure remains useful for determining relative levels of NO<sub>x</sub> in cigarette smokes. For a selected group of experimental cigarettes, we found NO<sub>x</sub> values to range from a low of about 3  $\mu\text{mol}$  per cigarette (for a cigarette made from reconstituted tobacco sheet) to a high of about 40  $\mu\text{mol}$  per cigarette (for a variant made entirely of burley leaf); these NO<sub>x</sub> values were 30 to 300% greater than those determined via the colorimetric method. Nitric oxide values ranged from 8 to 30% of the total oxides present. The fraction of NO<sub>x</sub> that NO<sub>2</sub> represents is unexpectedly large, and potential explanations for this are being investigated. (*R. A. Jenkins, B. E. Gill*)

**Operational and chemical monitoring of inhalation bioassay experiments.** The S&HP of the NCI is involved in part with developing and employing inhalation bioassays to determine the relative biological impact of tobacco smokes from experimental cigarettes. The complexity and developmental nature of a tobacco-smoke inhalation bioassay requires sophisticated chemical and instrumental methods to define exposures adequately. It has been our responsibility to provide this support and to monitor the bioassay studies.

The National Cancer Institute is currently sponsoring several inhalation bioassay projects. The study at Battelle Pacific Northwest Laboratories, Richland, Washington, has recently concluded its chronic exposure phase. Three bioassays, one at Beth Israel Hospital, Boston, Massachusetts, one at Borriston

Research Laboratories, Temple Hills, Maryland, and one at Hazleton Laboratories, Reston, Virginia, are now in the chronic exposure phase. An additional study is scheduled to begin shortly at the Veterans Administration Hospital, East Orange, New Jersey. These bioassays employ various animal models, including rats, pigeons, and beagle dogs. The relative importance of nicotine dose, the efficacy of respiratory measurements in detecting smoke-related pulmonary dysfunction, the importance of carbon monoxide in tobacco-smoke associated atherogenesis, and the development of potentially less hazardous cigarettes are being investigated.

The primary objective of our monitoring effort is the chemical documentation of exposure conditions and smoke dose to permit a confident interlaboratory comparison of bioassay results. This documentation provides the chemical basis for determining relationships between observed pathology and chronic smoke exposure. Specifically, inhalation bioassay monitoring seeks answers concerning the magnitude of the smoke dose that the animals receive, the sources and/or the extent of variability of the dose, and whether or not the smoke reaching the animals is truly representative of that which the cigarette produces.

Each bioassay laboratory in the chronic-exposure phase of the study is visited periodically by at least two ORNL staff members. Data are obtained to estimate the average smoke dose offered to the experimental animals. This dose can vary over the course of the exposure, and many factors (machine, cigarette type, exposure personnel, and environmental) influence this variation. Several tests are conducted on each site visit to evaluate these factors. While on site, inhalation exposures are observed, measurements are made on smoke-generation devices, both gas- and particulate-phase smoke samples are taken, and discussions are held with laboratory personnel regarding identified or anticipated problems. Cigarettes scheduled for use in bioassay studies are sampled and returned to ORNL for analysis. Results of the site visits are reported to both bioassay laboratory personnel and NCI management through informal topical reports.

Data gathered from onsite measurements during the past year have led to some important findings concerning the smoke doses that the animals are offered in these several chronic studies. For example:

1. In a study designed to evaluate the physiological impact of different concentrations of nicotine in smoke, three animal exposure groups are being

17. B. F. Saltzman, "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," *Anal. Chem.* **26**, 1949 (1954).

18. C. H. Sloan and G. P. Morie, "Determination of Nitrogen Oxides in Cigarette Smoke with a Nitrate Ion Electrode," *Tob. Sci.* **18**, 98 (1974).

offered nicotine levels that are being maintained at a fairly constant 1:3:9 ratio.

2. In one study, rats received a whole-body smoke dose that, on a body weight normalized basis, was twice as large as the dose received by dogs smoking similar cigarettes.
3. Preliminary evidence suggested that pigeons may inhale much more smoke than might have been predicted from measured breathing patterns.
4. For a group of beagle dogs exposed to the smoke of one particular cigarette, variation in the offered dose of gas phase smoke constituents was found to be caused by the nonuniformity in cigarette filter construction.
5. The gross chemistry of the particulate matter of the smoke of a cigarette containing an anti-ciliastatic additive was found to be very similar to the smoke of an identical cigarette that did not contain the additive.

To define better the exposure in a chronic inhalation bioassay, it is necessary to obtain data more frequently than is now possible with occasional visits by ORNL personnel. Although techniques developed by ORNL to define the exposures are available to all bioassay laboratories, the techniques cannot always be cost-effectively applied, even if laboratories have the facilities to perform the chemical analyses. One solution to this problem is the use of monitoring instrumentation to obtain data for routine characterization of the exposures. Ideally, such instrumentation could be used easily by a nonprofessional bioassay laboratory staff with only minimal or no chemical analyses. This year, we report on progress made in the application of such instrumentation, both for routine characterization of the exposures and for use as a noninvasive dosimeter in single animal (dog) inhalation bioassays.

Developed under a contract with CTR, the optical particulate sensor has been described in detail previously.<sup>19</sup> Infrared light backscattered from smoke particulates is registered as instantaneous smoke concentration. Thus the integrated output of the sensor is proportional to the amount of total particulate matter (TPM) flowing past it in a given time at a constant flow.

For field testing at bioassay laboratories using beagle dogs as an animal model, a prototype monitoring unit was constructed at ORNL. The particulate sensor itself is mounted inside a small tube that can be affixed to the end of the cannula of a dog exposure system. While the exposure system is operating (without the dog being present), smoke is withdrawn from the cannula past the sensor at constant flow by a small vacuum pump built into the electronics package. Particulates are collected on a filter pad mounted immediately downstream of the sensor for purposes of calibration. Evaluation under carefully controlled conditions at ORNL indicated that integrated sensor response was directly proportional to the weight of the TPM or the amount of nicotine collected to within cigarette-to-cigarette variability and was independent of cigarette type. Under field trials at the Veterans Administration Hospital and Borriston Research Laboratories, it was shown that TPM or nicotine delivery could be accurately measured by the particulate sensor with only a daily four-point calibration of the system.

Use of the sensor system during actual exposure of animals to tobacco smoke indicated that there are important differences in patterns of smoke withdrawal from the exposure systems which are a result of cannula design. Certain types of intertracheal cannulas (uncuffed) permit smoke to remain as a concentrated bolus in the exposure system for quite some time. During this time, aerosol particle size can increase; this could alter the site of deposition in the lung of the smoke particulates.

Field trials at bioassay laboratories indicated that the sensor would respond quite rapidly to changing smoke concentrations; we therefore thought that the sensor could serve as the basis for an instrumental approach to a noninvasive measurement of the amount of smoke actually inhaled by a dog under chronic exposure conditions. Because response of the particulate sensor is linear with the smoke particulate concentration signal, we speculated that multiplication of the concentration signal and a linear flow signal followed by integration would result in a system output that would be proportional to the total amount of particulates passing by a fixed point, regardless of flow rate. Thus, with a smoke sensor installed at the entrance to the tracheal cannula and the flow sensor installed at the inspiration valve at the head of the stand tube of a smoke exposure system, the total amount of particulates inhaled by the animal would be proportional to the integrated signal. For such a system to be feasible, the smoke sensor must respond to rapid changes in smoke

19. R. A. Jenkins et al., "Monitoring the NCI Inhalation Bioassay Exposures," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 67.

concentration, and the responses of both flow and sensor systems must be "in phase."

To determine if both smoke and flow sensor systems are adequately in phase to perform analog multiplication and integration in real time, an experimental assembly of available components was constructed. Tests were performed simulating regular and irregular rapid breathing patterns in dogs. The particulate sensor was located in a small tube between the end of the exposure system stand tube and the entrance to the cannula. A pneumotachograph flow meter with a maximum capacity of 60 liters/min was installed in place of the inspiration valve on the front of the exposure machine such that all air inhaled by the animal (simulated) is routed through the pneumotach. The pneumotach is a flow meter of the laminar type, which produces a small differential pressure drop that is linear with flow rate. In preliminary tests, the experimental assembly has performed quite well. The response of the system varies within about  $\pm 6\%$  for the total TPM output of a cigarette under widely ranging flow conditions, which is within the range of expected cigarette-to-cigarette variability. For simulated constant smoke concentrations, integrated responses for a given volume of air were within  $\pm 2\%$  for both simulated rapid irregular breathing and slow steady breathing. The results indicate that this instrumental approach to noninvasive dosimetry is feasible. We currently have under construction a prototype system that can be tested in the field. We expect that this unit will be capable of noninvasively determining the amount of smoke inhaled by an animal during the bioassay exposure. (R. A. Jenkins, T. M. Gayle,<sup>20</sup> R. B. Quincy, B. E. Gill)

**Monitoring instrumentation for large-scale tobacco smoke inhalation exposures of mice.** As part of an ongoing effort for the CTR, we have developed instrumentation to monitor tobacco smoke inhalation exposures. In work described in a previous report,<sup>21</sup> the basic instrumentation to accomplish this effort was described. During the past year, this instrumentation has been expanded into a comprehensive monitoring system and has been installed at the inhalation exposure facility operated for CTR by Microbiological Associates (MA) of Bethesda, Maryland. The purposes of this monitoring system

are to document the level and duration of exposure to the cigarette smoke and to detect and prevent overexposure conditions that could lead to accidental death of test animals.

At MA hundreds of mice are exposed simultaneously with an SEM II exposure system. The SEM II smokes 30 cigarettes every 10 min and delivers smoke to the animals via a complex multichannel, multianimal containment assembly. Thus the first stage of the instrumentation development was to design, fabricate, and install for testing a prototype to monitor a single exposure channel. This unit continuously monitored both the particulate matter in the smoke (using the ORNL-developed optical particulate sensor)<sup>22</sup> and the carbon monoxide (CO) in the gas phase using a commercial analyzer that selectively detected the CO infrared adsorption. Both instantaneous and time-integrated quantities were displayed. To prevent overexposure of animals caused by operator error or smoking machine malfunction, alarm circuitry was tied to both detectors. The alarms responded to overly high levels of particulate matter and CO and also responded to exposures that were prolonged beyond prescribed limits. This unit operated quite successfully and was extensively tested under exposure conditions. It was found that optically detected TPM correlated quantitatively with that collected and determined gravimetrically on filter pads. Further, CO levels were found to parallel particulate levels.

As a result of this testing, a monitoring unit for a multichannel (four) exposure rack has been designed, fabricated, and installed at MA in cooperation with Process & Instruments Company (P&I), Brooklyn, New York. In view of the demonstrated accuracy and reliability of the optical particulate sensor, only these detectors were used for smoke concentration measurement. Readout from the four exposure channels was made on four two-pen recorders. One pen of each recorder shows the instantaneous TPM being delivered to the animals, and the second pen of each recorder gives the integrated value for each run. The same general concept of high smoke level alarms coupled with exposure duration alarms as used in the test monitor was incorporated into the equipment. The system was installed, tested, and calibrated in late 1977. During initial calibration, over 60 runs were made and weights of particulate matter

20. Instrumentation and Controls Division.

21. T. M. Gayle, C. E. Higgins, and J. R. Stokely, "Design and Testing of a Smoke Monitoring Unit for the SEM II Exposure System," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 70.

22. C. E. Higgins, T. M. Gayle, and J. R. Stokely, "Sensor for Detection of Tobacco Smoke Particulates in Inhalation Exposure Systems," *Beitr. Tabakforsch.* 9(4), 185 (1978).

collected on filter pads carefully compared with integrated readings from the optical detector. The results showed good correlation, with an overall relative standard deviation of less than 5%. The four-channel system has been in daily use since its installation, and periodic recalibration has verified long-term stability of the sensors.

A portable monitoring "cart" was also designed and fabricated at ORNL and placed in service at MA in 1978. This unit provides for CO and CO<sub>2</sub> measurements of the smoke gas phase from a single stream and contains an auxiliary optical particulate detector for use on any part of an exposure system. Digital displays and recordings of the integrated values are possible. Although TPM measurements are adequate for routine monitoring, the periodic measurement of CO and CO<sub>2</sub> is quite important. Specific tests have established a correlation between the CO and TPM offered the animal and the uptake by the animal of CO (as carboxyhemoglobin) and TPM (<sup>14</sup>C-DTC deposition).

The monitoring cart also incorporates a puff volume calibration system for SEM II exposure machines. The SEM II is a constant-pressure rather than a constant-volume smoking machine. Its puff pressure must be periodically adjusted to provide the standard 36-ml, 2-s puff. Variations arise due to differences in resistance-to-draw (pressure drop) among individual cigarettes and among different cigarette types. The calibration system provided by ORNL measures the flow rate of the whole smoke produced during a 30-cigarette-10-puff run and provides a digital readout of the integrated total volume. The machine operating (purr) pressure may then be readjusted to correct the puff volume. The flow meter employed for this work is a laminar differential-pressure device (pneumotachograph). Heating of the pneumotach prevents accumulation of tobacco smoke particulates that would otherwise affect both accuracy and reliability of the flow measuring system. (*T. M. Gayle,<sup>20</sup> R. W. Holmberg*)

**Sampling and determination of nicotine in physiological fluids for tobacco smoke dosimetry.** To determine cigarette smoke dose by performing a simple analysis on a sample obtained nondestructively from the smoking subject has long been the goal of smoking and health studies. The quantities of nicotine and/or its metabolites in physiological fluids are promising potential indicators of dose because nicotine is unique to tobacco, nicotine is a major component of both the tobacco and the smoke aerosol, and nicotine is readily absorbed into the

biological system. Serious complications result, however, because nicotine is rapidly metabolized and redistributed throughout the body and is present at trace levels as a result of extensive dilution. A careful sampling regimen must therefore be followed if the results are to mirror dosimetry, and a rapid, reliable method for determination of nicotine at trace levels in serum and/or urine is necessary. Consequently, a collaborative effort between Borriston Research Laboratories and ORNL was established to determine the utility of analyzing either the serum or urine from a smoking dog for nicotine and/or its metabolites as a method of estimating cigarette smoke uptake by the animal.

The experimental approach involved exposing a dog to the smoke of two successive cigarettes labeled with <sup>14</sup>C-nicotine bitartrate and continuously sampling the blood and urine both during and for some time after the smoke exposure. Continuous blood samples were obtained by attaching a peristaltic pump to a cannula surgically implanted in the jugular vein. For several hours following exposure, continuous urine samples were obtained via bladder catheterization. Afterwards, the animal was placed in a metabolic cage to collect urine at 12-h intervals.

A generalized pattern of <sup>14</sup>C clearance could be discerned from the results of experiments performed on several dogs. The <sup>14</sup>C activity (and thus the sum of nicotine and its metabolites) in the blood increased rapidly after initiation of the exposure and reached a maximum after exposure to the second cigarette. The activity then decreased rapidly until about 12 min after exposure, after which time the decline slowed significantly. In contrast, <sup>14</sup>C activity began to appear in the urine about 1 h after the initiation of the exposure. Elimination was very rapid over the next 3 h, but significant amounts of <sup>14</sup>C activity were eliminated over a 3-d period.

These findings are important for dosimetric measurements. They indicate that serum levels of nicotine (and cotinine, its major metabolite) may be too transient for obtaining meaningful samples but that a large fraction of the nicotine/cotinine is eliminated from urine in the first few hours following exposure. For a chronic exposure situation, animals are often exposed over a 10- to 12-h period each day. The data from this study suggest that, to obtain a meaningful sample, all urine voided during the day, including that eliminated during smoke exposure, must be collected. Additionally, our results suggested that nicotine/cotinine may be lost from metabolic cage sampling through bacterial action, volatility, or

chemical reaction. Additional experiments are now under way to test this observation, which, if confirmed, may dictate modifications in classic urine collection procedures for dosimetry.

For the routine chemical determination of nicotine/cotinine in physiological fluids, a method is required that (1) is capable of isolating the nicotine/cotinine in a simpler chemical matrix than the physiological sample itself and (2) is sufficiently sensitive to determine nicotine/cotinine at very dilute concentrations. Previous methods for determination of nicotine and cotinine in urine and serum have relied mainly on solvent partition schemes for isolation and purification, whereas the final determination is made by gas<sup>23-29</sup> or liquid<sup>30</sup> chromatography. Although the sensitivity of these methods has been entirely sufficient, the isolation schemes have been generally nonreproducible and tedious. In addition, total analysis times have been rather long. Earlier work on the screening of urine for basic drugs of abuse by adsorption onto Amberlite XAD-2 (ref. 31) led us to investigate the practicality of this approach for the rapid quantitative isolation of nicotine and its metabolites from body fluids while relying on high-pressure liquid chromatography (HPLC) for the final determination. We have

recently developed and reported<sup>32</sup> a new method that is based on this approach. Briefly, the procedure involves concentration of urine or serum organics on XAD-2 resin, followed by elution with methanol/chloroform. Because of prior resin treatment, the eluate is biphasic, and the chloroform layer contains the tobacco smoke alkaloids. The layer is concentrated, and an aliquot is analyzed by HPLC. Carbon-14 tracer studies have indicated that recoveries are both high and reproducible. The method is sufficiently sensitive to determine quantitatively nicotine in the urine of a nonsmoker (at 7 ng/ml).

This work is only part of a larger collaborative effort between Borriston Research Laboratories and ORNL to study tobacco smoke dosimetry in chronically exposed animals. Sacrificial tissue samples are currently being analyzed at ORNL to determine tar distribution patterns in the lung, whereas presacrifice urine samples are being analyzed for nicotine/cotinine. We expect to report on our joint findings within the coming year. (M. P. Maskarinec, J. E. Caton, R. A. Jenkins, G. M. Henderson, R. W. Harvey, P. Buhl,<sup>33</sup> A. G. Manus,<sup>33</sup> R. Weichbrod<sup>33</sup>)

**Nomograph for predicting smoke particulate deposition in mice.** To assess the biological activity of inhaled cigarette smoke, one must have available some estimate of the amount of smoke reaching the target organs of the exposed animal. Two important parameters in the exposure of any animal to cigarette smoke are (1) the length of time during which the test animal is exposed to the smoke aerosol and (2) the concentration of the smoke aerosol to which the animal is exposed. In our joint studies with MA over the past 3 years, a significant effort has been devoted to the development of quantitative cigarette smoke inhalation dosimetry measurements in mice. This effort has resulted in data that thoroughly characterize the quantity and distribution of cigarette smoke particulate matter deposited in mice exposed for different time intervals to different cigarette smoke concentrations on the Walton horizontal smoking machine (P&I). Data from both the time- and concentration-dependent studies have been used to develop a model that predicts the quantity of

23. M. S. G. Clark, M. J. Rand, and S. Vanov, "Comparison of Pharmacological Activity of Nicotine and Related Alkaloids Occurring in Cigarette Smoke," *Arch. Int. Pharmacodyn. Ther.* **156**(2), 363 (1965).

24. A. H. Beckett and E. J. Triggs, "Determination of Nicotine and Its Metabolite, Cotinine, in Urine by Gas Chromatography," *Nature* **211**, 1415 (1966).

25. H. Schievelbein and K. Grundke, "Gas-Chromatographische Methode zur Bestimmung von Nicotine in Blut und Geweben," *Z. Anal. Chem.* **237**, 1 (1968).

26. I. E. Burrows, P. J. Corp, G. C. Jackson, and B. F. J. Page, "The Determination of Nicotine in Human Blood by Gas-Liquid Chromatography," *Analyst* **96**, 81 (1971).

27. P. F. Isaac and M. J. Rand, "Cigarette Smoking and Plasma Levels of Nicotine," *Nature* **236**, 308 (1972).

28. C. Dumas, R. Badre, A. Viala, J.-P. Cano, and R. Guillermin, "Micromethode de Determination de la Nicotine et de la Cotinine dans le Sang et l'Urine par Chromatographie en Phase Gazluse. Resultats Obtenus Chez Divers Fumeurs," *Eur. J. Toxicol.* **8**(5), 280 (1975).

29. L. Neelakatan and H. B. Kostenbauder, "Electron Capture Derivative for Determination of Nicotine in Sub-Picomole Quantities," *Anal. Chem.* **46**(3), 452 (1974).

30. I. D. Watson, "Rapid Analysis of Nicotine and Cotinine in the Urine of Smokers by High-Performance Liquid Chromatography," *J. Chromatogr.* **143** 203 (1977).

31. M. P. Kullberg and C. W. Gorodetsky, "Studies on the Use of XAD-2 Resin for Detection of Abuse Drugs in Urine," *Clin. Chem. (Winston-Salem)* **20**(2), 177 (1974).

32. M. P. Maskarinec, R. W. Harvey, and J. E. Caton, "A Novel Method for the Isolation and Quantitative Analysis of Nicotine and Cotinine in Biological Fluids," *J. Anal. Toxicol.* **2**, 124 (1978).

33. Borriston Research Laboratories, Temple Hills, Md. 20031.

particulate matter deposited in the mouse respiratory tract as a function of exposure time and cigarette smoke concentration.

The mouse dosimetry studies had shown that smoke particulate deposition increased linearly with increasing smoke concentration but exponentially with time of exposure. Thus observed deposition was found to fit the following equation:  $D = A \cdot C \cdot P \cdot T^B$ , where  $D$  is the smoke particulate deposition expressed as  $\mu\text{g}$  TPM per animal,  $C$  is the smoke aerosol concentration in  $\mu\text{g}$  TPM per milliliter,  $P$  is the number of smoke puffs to which the animal is exposed, and  $T$  is the time of exposure to each puff.  $A$  and  $B$  are constants. Data for total internal cigarette smoke particulate deposition, for deposition in the lung, and for deposition in the total respiratory tract (lung, skinned head, and larynx) have been fitted to this expression with the resulting values for  $A$  and  $B$  being 0.014 and 1.3 for deposition in the lung, 0.015 and 1.34 for deposition in the total respiratory tract, and 0.021 and 1.26 for total internal deposition.

By expressing the above equation logarithmically, it can be adapted to the nomographic form:  $U + V = W$ , which is illustrated in Fig. 4.3. The relative standard deviation of deposition values read from the nomograph compared with deposition measured in mouse lungs is about 15%. Such variation for animal studies is quite acceptable. Thus this model and nomograph should be quite useful because quick estimates of particulate deposition can be made for a

given exposure, conditions can be quickly chosen that will approximate a given dose, and the range of exposure conditions that will result in the same dose can be quickly ascertained. The nomograph reduces many thousands of analytical data points to a form that may be conveniently used by bioassay practitioners. This work is representative of our attempts to produce information rather than data only and to consider our collaborators' needs in treating and formatting analytical chemical results. (*J. E. Caton*)

**Mutagenic component of ether-soluble base fraction of cigarette smoke condensate.** An important part of the NCI's S&HP has been the development of candidates for the "less hazardous cigarette." Hazard is assessed with some form of biological testing, either long-term skin painting bioassay or chronic inhalation exposure of experimental animals. Although these bioassays are important for understanding the mechanisms of potential health impact, they are quite expensive to conduct and are not particularly cost effective for routine screening of large numbers of experimental cigarette smokes or smoke condensates. The Ames bacterial mutagenicity assay<sup>34</sup> has appeared very

34. B. N. Ames, J. McCann, and E. Yamasaki, "Methods for Detecting Carcinogens and Mutagens with the *Salmonella*/Mammalian-microsome Mutagenicity Test," *Mutat. Res.* 31, 347 (1975).

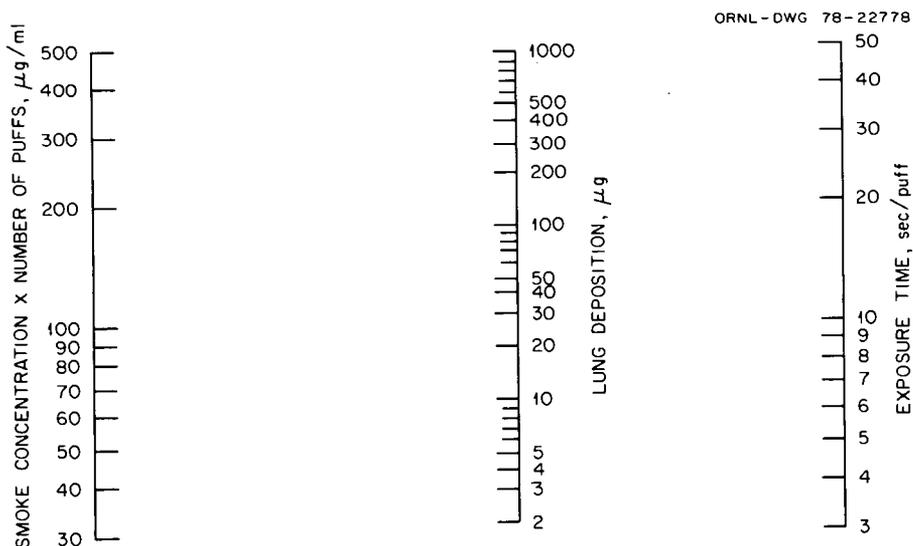


Fig. 4.3. Nomograph relating cigarette smoke exposure conditions for mice on the Walton horizontal smoking machine to resulting deposition of cigarette smoke particulate matter in the lungs.

promising for the cost-effective screening of potentially mutagenic (carcinogenic) materials, but complex organic matrices often contain substances that are toxic to the bacteria. Our approach to this problem has been the class fractionation of complex materials such that toxic materials can be segregated and biologically active constituents can be concentrated into chemically simpler mixtures. The purpose of this work has been to determine if fractionation and subfractionation procedures developed for chemical characterization and biological testing as part of other programs could be applicable to smoke-related matrices. The focus of the work has been on the fraction that contains the ether-soluble basic constituents (the ESB) because ESBs from synfuel materials have been shown to contain most of the mutagenic activity of the overall matrix.

The ESB fractions and subfractions of smoke condensates from three cigarette types made from widely differing tobacco blends were obtained. For all three condensates, both the benzene and isopropanol subfractions exhibited little or no mutagenic activity. The major constituent in both subfractions is nicotine. Thus the lack of biological activity of the two subfractions is not surprising, inasmuch as nicotine is known to be mutagenically inactive. These results parallel those of related synthetic fuel studies. Nicotine is a substituted pyridine, and pyridine analogs have been shown to be major constituents in the benzene subfraction of synfuels. Generally, such subfractions have exhibited little or no mutagenic activity.

Virtually all of the mutagenic activity of the ESB fraction resides in the acetone subfraction (which comprises 8–21% of the weight of the ESB). Tentative GC-MS identification suggests that the major constituents in the acetone subfraction are harmaline and norharmaline, which are nitrogen heterocyclics. Although more detailed chemical characterization of this subfraction is now under way, these results also parallel the findings of the synthetic fuel studies. In addition, although the number of condensate samples is small, the specific mutagenicity of the ESB fraction correlates well with biological activity as measured by the long-term skin-painting bioassay, suggesting that the fractionation-short-term bioassay procedure may be an effective indicator of the tumor-producing activity of cigarette smoke condensate. (C.-h. Ho, G. Mamantov, R. A. Jenkins, M. R. Guerin)

## METHODOLOGY AND SPECIAL PROJECTS

Several new or special techniques are under study for use in the Bio-Organic Analysis Section. Methodology developed in these efforts finds application in a number of projects.

**Aerosols for inhalation bioassay studies.** The CTR supports studies relating to the health aspects of cigarette smoking. Part of this effort is realized in large-scale inhalation bioassay experiments being carried out by MA. The Bio-Organic Analysis Section has been involved for several years in providing research and development support to this project, particularly in the areas of chemistry and instrumentation.

Recently the efforts of this project have expanded to more basic studies of biological response to aerosols that are better defined and simpler in a chemical sense than cigarette smoke. At present, work is under way to develop systems allowing controlled exposures to aerosols of nicotine, benzo[*a*]pyrene, and tetradecanoylphorbolacetate (TPA). Last year the development of a nebulizer<sup>35</sup> for the production of TPA aerosols for biological exposures was reported. This work has culminated in the delivery of a complete system for exposure and monitoring to MA. It consists of a compressed air-driven nebulizer designed to work with solution volumes of the order of 1 ml, a monitoring system based on the Gayle light-scattering particulate sensor for continuous measurement of the aerosol concentration,<sup>36</sup> and a module for controlling operation of the system and allowing the aerosol stream to be sampled onto filter pads for direct aerosol analysis.

The particle size characteristics of a typical aerosol delivered by this system have been determined. For these measurements 1% methylene blue dissolved in ethanol was used as a stand-in for TPA. Particles were collected on Nucleopore filters and observed and photographed at magnifications of about 20,000 $\times$ , using scanning electron microscopy. Measurements and data reduction were made using

35. R. W. Holmberg and J. H. Moneyhun, "Aerosolization of Bioactive Chemicals for Inhalation Testing," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, p. 60.

36. C. E. Higgins, T. M. Gayle, and J. R. Stokely, "Sensor for Detection of Tobacco Smoke Particulates in Inhalation Exposure Systems," *Beitr. Tabakforsch.* **9**, 185 (1978).

techniques previously discussed.<sup>37</sup> The distribution of sizes was found to be adequately described by a logarithmic normal distribution with number median diameter  $d_g = 0.13 \mu\text{m}$  and geometric standard deviation  $\sigma_g = 1.8$ . The mass median diameter derived from these results is  $0.40 \mu\text{m}$ . More than 90% of the mass of the particulates is in sizes of less than  $1 \mu\text{m}$ .

Analytical methods necessary to establish both the quantity and chemical integrity of a TPA aerosol are being studied. Chromatographic methods are the methods of choice and have been applied to TPA and to those derivatives currently available: 20-OXO-TPA, phorbol (P), phorbol-13-acetate (P-13-A), and phorbol-12-myristate (P-12-M). Gas chromatography has not proved useful because most of the compounds are nonvolatile. High-pressure liquid chromatography has been reported<sup>38</sup> to provide a sensitivity of  $0.05 \mu\text{g}$  TPA but required gradient elution and was slow. We examined isocratic HPLC techniques using a variety of sorbent-solvent combinations and obtained excellent performance with respect to both analysis time and chromatographic efficiency. Zorbax<sup>R</sup>-ODS (DuPont), a reverse-phase column material, was used with 10% water in methanol as the eluting solvent. Separation of the entire range of phorbols was possible in  $< 8$  min. Retention times (s) are: P, 70; P-13-A, 80; P-12-M, 320; TPA, 380; and 20-OXO-TPA, 420. This method has been employed for analysis of TPA stock solutions used by MA for intertracheal inoculations.

Thin-layer chromatography (TLC) is also an attractive analytical method for these phorbol derivatives. Although it is considerably less quantitative than HPLC, it is rapid and requires minimal equipment. We have found that TPA and some of its degradation products can be separated on aluminum-backed silica gel strips, using a number of different developing solutions. Elution with dilute solutions of methanol or acetic acid in chloroform gives excellent separations. For example, using 7% methanol in chloroform, the  $R_f$  value for TPA was 0.5–0.6; for 20-OXO-TPA, 0.8; for 12-O-tetradecanoylphorbol and P-13-A, 0.3; and for P,  $\leq 0.1$ . Plates are exposed successively to vapors of phosphoryl chloride, water, and pyridine or other volatile amines and then heated

to develop the color. The entire TLC process, including developing the strip and fixing the spots, requires only 15 min. Less than  $0.5 \mu\text{g}$  per spot can be detected. (R. W. Holmberg, J. H. Moneyhun, M. P. Maskarinec, C. E. Higgins)

Thin-layer chromatographic separation and direct fluorometric determination of benzo[a]pyrene. Thin layer chromatography is a rapid and sensitive technique for separating and isolating a desired component from a complex matrix of other compounds. Benzo[a]pyrene is a compound with an unusual and intense fluorescence emission spectrum. Thus the TLC separation of BaP and its subsequent fluorometric determination offer a particularly attractive means for analysis of large numbers of samples that have relatively small total solids concentrations. We have found this method to be useful for the analysis of BaP in air samples as part of a routine monitoring program.

The following procedure has been adopted for the analysis of BaP in air samples: The filter from the air sampling unit is extracted with benzene, using ultrasonic agitation to enhance the extraction rate. The extract is concentrated or diluted to a given volume (10 ml), and its fluorescence spectrum is examined, using an excitation wavelength of 484 nm and scanning the emission spectrum from 370 to 450 nm. This scan is performed at high sensitivity where the Rayleigh solvent absorption effect can be observed. Absence of the Rayleigh effect indicates that quenching is taking place. Samples that do not show BaP absorption and that show no appreciable quenching are eliminated from further treatment at this stage and reported to have less than detectable levels of BaP.

Any sample exhibiting a pure BaP spectrum is analyzed directly by comparison of the spectrum with the spectrum of a standard. The relative absorption intensity can be used to calculate the concentration. The absorption intensity does not vary linearly with concentration once a concentration level greater than  $0.1 \mu\text{g}/\text{ml}$  is attained, and it is necessary to make an appropriate dilution or prepare a working curve beforehand.

Samples with impure fluorescence spectra or exhibiting quench behavior are subjected to thin-layer purification. A thin-layer glass plate of  $20 \times 20$  cm dimensions coated with a  $250\text{-}\mu\text{m}$  layer of acetylated cellulose is scored to provide 20 channels, each 1 cm wide. Each channel of the plate is spotted with  $50\text{--}80 \mu\text{l}$  of sample or a suitable standard solution. The prepared plate is then placed in a developing bath with the spotted edge at the bottom.

37. R. W. Holmberg, "Particle Size Characteristics of Tobacco Smoke," *Anal. Chem. Div. Annu. Prog. Rep.* Nov. 30, 1975, ORNL-5100, p. 64.

38. D. L. Berry, "Separation of a Series of Phorbol Ester Tumor Promoters by LC," *Chromatogr. Rev.* 3(2), 5 (1977).

Developing solvent is placed in this bath to provide an immersion depth of 1–1.5 cm. Ethanol and methylene chloride in a 2:1 volume ratio have been found suitable for this particular development. The development time is 1 h.

The developed plate is examined under a black light to locate the BaP marker spot and then scanned over the appropriate distance, with the excitation wavelength set at 384 nm and the emission wavelength at 402 nm. The emission intensity of each sample is measured and compared with that of an appropriate standard solution. Total time required for processing one plate is about 3 h. A plate represents the analysis of at least 12 different samples and a suitable number of standard solutions. The  $R_f$  value of BaP is of the order of 0.4 while that of benz[*a*]anthracene (BaA) is about 0.75 and that of phenanthrene about 0.85. Precision of about 5% can be realized with samples containing 1–100 ng/ml of BaP.

We are currently applying this technique to small-scale preparative separations. The plate is not scored, and the sample is applied as a thin band at the origin. The band corresponding to the desired material is then recovered and extracted. Separations of a few milligrams of desired material are possible in this manner. (*H. Kubota*)

**Oxidation of radiolabeled materials prior to liquid scintillation analysis.** Labeled chemicals are employed extensively in the Bio-Organic Analysis Section to estimate the recovery of organic compounds after separations processes. The amount of tracer that remains associated with the solid phase involved in a separation process has generally been determined by difference. The recent acquisition of a sample oxidizer (model B-306, Packard Instrument Company, Downers Grove, Illinois) has made possible the direct determination of residue tracer associated with several different solid phases. The sample oxidizer converts all organic carbon present in the sample to CO<sub>2</sub> and all hydrogen present to H<sub>2</sub>O by ignition in a platinum/rhodium basket maintained at a potential difference of 4 to 12 V (ac) under an oxygen atmosphere. The liberated CO<sub>2</sub> and water containing carbon-14 and tritium, respectively, are then separated, trapped, and delivered to scintillation vials along with the appropriate liquid scintillator solution. Such sample treatment allows liquid scintillation analysis to be carried out on insoluble, highly colored, or highly quenched samples.

Several operating parameters must be optimized to obtain reliable results. These parameters include the

burn time, the amount of easily combustible material that must be added to the sample to achieve complete ignition, and the volume of absorbing solution used to trap the liberated CO<sub>2</sub>. Ignition time for samples that can be completely burned is readily determined by simple observation. However, the proper amount of combustible material and the amount of CO<sub>2</sub>-absorbing solution for a given type of sample must be determined experimentally because excess combustible material generates additional CO<sub>2</sub>, which in turn requires a greater volume of CO<sub>2</sub>-absorbing solution. Because counting efficiency decreases with increasing amounts of the CO<sub>2</sub>-absorbing solution, the ideal experimental parameters are: (1) a minimal amount of combustible material, (2) a minimal amount of CO<sub>2</sub> absorbing solution, and (3) the shortest burn time consistent with complete recovery of activity (95% or better) and maximum counting efficiency. A generalized "Simplex design"<sup>39</sup> has been developed for optimizing these experimental parameters for a given type of sample. At this writing the procedure has been optimized for fly ash, XAD-2 resin, and a fossil-derived liquid generated by the COED process.

The fly ash sample was the most difficult because the sample cannot be completely burned. However, it was found that better than 95% of the activity could be liberated by a 3-min ignition of a fly ash sample prepared by blending four parts fly ash with three parts of powdered cellulose and then adding 1 μl of Combustaid (Packard Instrument Company, Downers Grove, Illinois) for each milligram of fly ash. Subsequent ignition of the remaining ash liberated no additional activity, and the residual ash showed no activity when added directly to the scintillation solution and analyzed. Apparently the burning cellulose in intimate contact with the fly ash aids the destructive oxidation of all organic material associated with the fly ash.

Both the XAD-2 resin and the fossil-derived liquid can be burned completely (no visible residue). Recovery of activity is 98% or greater, and counting efficiency is at least 50% for both samples. (*J. E. Caton, Z. K. Barnes,<sup>40</sup> G. M. Henderson*)

**Glass capillary column gas chromatography.** The use of wall-coated open-tubular columns in gas chromatography has increased dramatically over the

39. D. E. Long, "Simplex Optimization of the Response from Chemical Systems," *Anal. Chim. Acta.* **46**, 196 (1969).

40. Student participant, Western Kentucky University, Bowling Green.

last 5 years. Several reasons for this increase are: (1) The permeability of open-tubular columns allows the use of much longer columns (up to 150 m), greatly increasing total efficiency. (2) The Van Deemter curve for open-tubular columns has a smaller contribution from the "C" or "resistance to mass transfer" term. Higher carrier gas velocities may therefore be used, with a significant decrease in analysis time. (3) Open-tubular columns may be coated with much lower levels of stationary phase (usually <0.5%). Lighter loading produces an increased boiling range of compounds that can be eluted from a given column as well as decreased analysis time, decreased column bleed, and increased separation efficiency. (4) Materials from which open-tubular columns are made, especially glass and nickel, are relatively inert, making possible the analysis of labile compounds without degradation in the chromatographic system.

Glass capillary columns may be made from standard glass tubing (1.22 m × 7.5 mm × 2.5 mm ID), using glass drawing machines. Either soda lime glass or borosilicate glass may be used. Additional surface treatments are performed, depending on the nature of the column desired. Several treatments are used routinely at this laboratory. Etching of soda-lime glass with HCl gas at 400°C produces a surface of NaCl crystals that may be observed by electron microscopy. The roughness of this surface provides the proper contact angle for the coating of polar phases such as polyglycols. In addition, the NaCl layer serves to deactivate the surface. Leaching of the surface of borosilicate capillaries with 12 N HCl at 100°C removes many of the trace metal oxides and also liberates many Si-OH groups. This treatment results in a high surface concentration of Si-OH groups (which can be further modified chemically) and decreases the activity of the surface.

Reaction of a leached surface with chemical modifiers such as trialkylorganosilanes may produce surfaces similar to the stationary phase; for example, hexamethyldisilazane/trimethylchlorosilane (5/1) may be used to produce a surface with a good wettability for polydimethylsiloxanes (OV-101, SE-30, SF-96, SP-2100, etc.). Further deactivation may be achieved by dissolving ionic surfactants in the stationary phase prior to coating the column. Two such agents currently in use are (bis)triphenylphosphoryl chloride (cationic) and tetraphenylboron sodium (anionic). These agents serve to cover surface ionic groups with bulky hydrophobic groups and are especially useful for the analysis of acidic and/or basic compounds. These agents suffer from the

limitation that they are somewhat volatile and cannot be used above 220°C. However, for many applications, high temperatures are not required, and these materials have good utility.

We have studied various techniques for the uniform deposition of the stationary phase on the glass surface. These techniques fall into two general classes: dynamic methods and static methods. Dynamic coating involves pressurizing the column with a concentrated solution (10% wt/wt) of the stationary phase and leaving behind a phase on the surface. The amount of phase left behind depends on the velocity of the solvent/phase plug. A slow-moving plug leaves behind less phase than a fast-moving plug. Therefore, variations in plug velocity cause deposition of a nonuniform film of stationary phase. In practice, it is difficult to maintain a constant velocity, especially with viscous stationary phases.

Static methods, on the other hand, involve filling the column with a dilute solution of stationary phase in a volatile solvent, sealing one end of the column, and applying vacuum to the other end. The solvent is evaporated, and the stationary phase is left behind. This method provides careful control of the phase ratio; columns can therefore be prepared with highly reproducible retention characteristics. We have used this method almost exclusively for this reason.

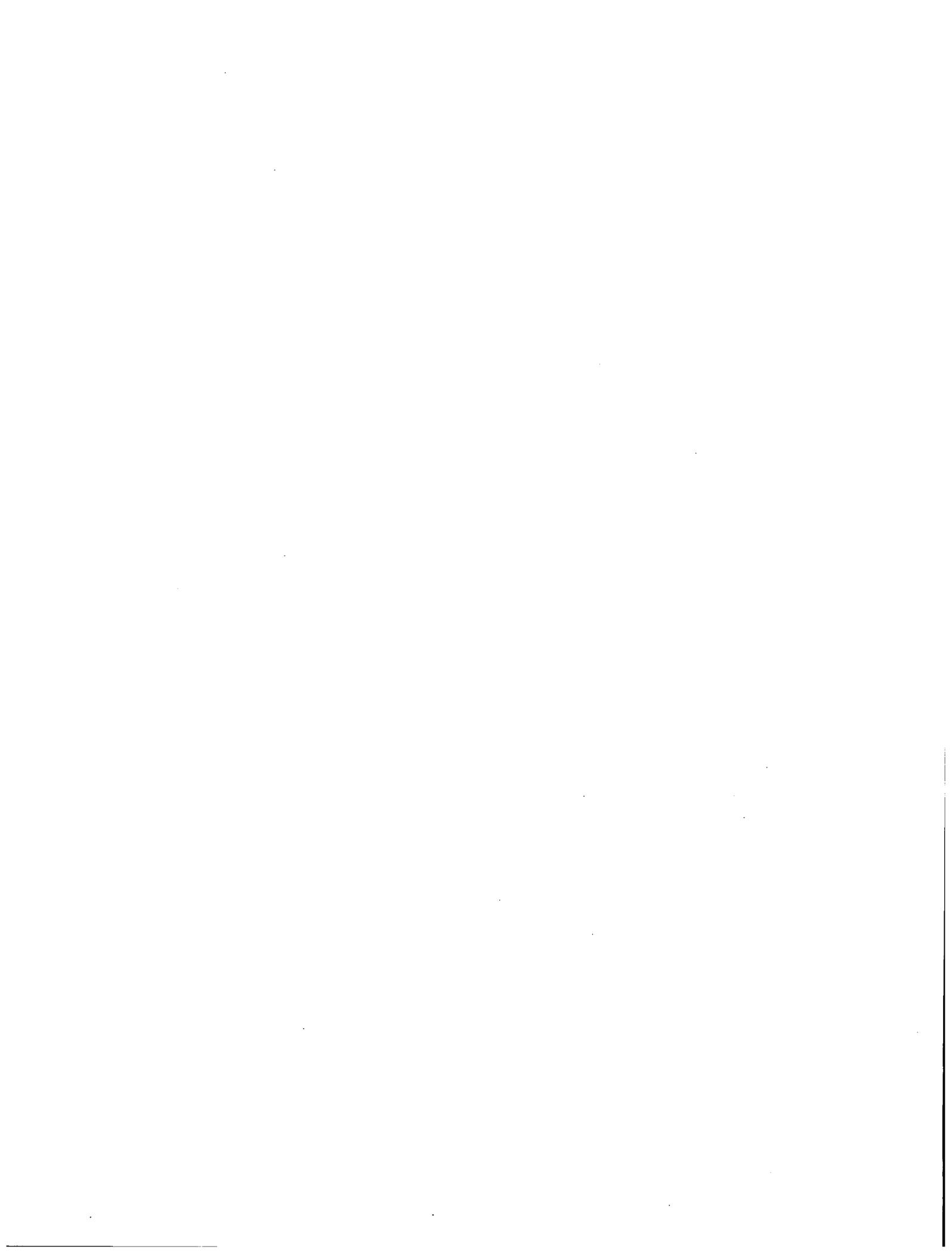
Assuming that high-efficiency columns can be reproducibly prepared, care must be taken to ensure that the gas chromatograph maintains the efficiency inherent in the column. Although newer gas chromatographs have the main features important for the proper use of high-resolution columns, older instruments must be extensively modified to incorporate these features. Crucial to the maintenance of chromatographic efficiency are a low dead volume (<100 μl), an all-glass injection system, and a line-of-sight column-to-detector interface. Therefore, we have constructed and installed several splitless injection systems that meet the above criteria. We have also altered the detector manifold on our Perkin-Elmer chromatographs for line-of-sight connections. This arrangement is now being used by Perkin-Elmer in the new Sigma series instruments. Currently, nine gas chromatographs are available for the use of capillary columns, five of which have been modified in-house and four of which have been purchased for capillary column work. In addition, the new HP-5985A GC/MS/DS is equipped with a capillary inlet and a mass spectrometric interface.

Since the introduction of capillary column technology into this section, virtually every program area has benefited from the increased separation power and

inertness. The analysis of PAHs by capillary column gas chromatography has been particularly successful. Whereas a complete PAH analysis (naphthalene to coronene) formerly required 4 h on a Dexsil 400 packed column, the analysis can now be done in about 2 h, with superior separation. Carbowax-20 M and UCON-50-HB-2000 glass capillary columns have been successfully applied to analysis of complex mixtures of polar organics such as volatile urinary constituents, shale oil retort water, cigarette smoke gas phase constituents, and extracts of solid wastes. OV-101 and other nonpolar stationary phases have been applied to the analysis of jet fuel, crude oils,

hydrotreated oils, and polychlorinated biphenyls. In addition, trimethylsilylated extracts from cigarette smoke TPM, acidic urinary constituents, and resin-extracted urinary constituents have been analyzed on such columns.

Continuing research in this area includes development of columns of unique selectivity, improved resolution, and increased capacity. In addition, standard analytical methods based on packed column techniques are being replaced by capillary column methods. (*M. P. Maskarinec, A. D. Horton, G. Olerich*)



## 5. Nuclear and Radiochemical Analysis

J. R. Stokely

The Nuclear and Radiochemical Analysis Section provides radiochemical and activation analysis services and support for ORNL and UCC-ND programs. Developmental activities are carried out in the section to upgrade existing analysis capabilities and to make scientific contributions in nuclear and radiochemical analysis. The section is organized into three groups: The Low-Level Radiochemical Analysis Group provides sample analysis and general radioanalytical support to programs involved with the behavior and monitoring of low levels of radionuclides in the environment and in effluents from ORNL facilities. General radiochemical analyses and activation analyses are performed by the Radiochemical and Activation Analysis Group. A Special Projects Group conducts nonroutine analyses, provides developmental support for programs, and carries out radiochemical development.

During the past year several improvements in section operations have resulted from the acquisition of new laboratory facilities, counting instrumentation, and miscellaneous laboratory equipment. Because of an expanding work load, improvements and expansion of facilities and capabilities for low-level radiochemical analysis have received the highest priority. Three new chemical laboratories and a counting facility for low-level work were placed in operation this year. A multiinput spectrometer system (Nuclear Data 6603) and alpha- and gamma-ray detectors have been acquired, and full implementation of the system in the coming months will alleviate deficiencies in low-level spectrometry capabilities. Two new high-resolution, high-efficiency lithium-drifted germanium detectors were put into service in the intermediate-level analysis group for routine analysis. Addition of these detectors allows faster turnaround on a large volume of routine analyses requiring gamma-ray spectrometry. Implementation of the division's data management system in the Radiochemical and Activation Analysis Group has been accomplished.

The principal technical activity in the section is sample analysis support for ORNL and UCC-ND programs. During this year there has been an appreciable expansion of the sample analysis load. Growth has been most pronounced in low-level radiochemical and neutron activation analysis. Overall, the sample analysis load for the section has approximately doubled over the year.

Developmental activities in the section are being pursued to improve existing analysis methodology, to offer new radioanalytical services, and to handle special problems. An effort was begun this year to develop techniques for analysis of  $^{99}\text{Tc}$  in environmental samples. Chemical separation techniques were devised for isolation of  $^{99}\text{Tc}$ , and low-level beta counting is currently being used for final measurements at the picocurie level. An improved method for neutron activation analysis of  $^{129}\text{I}$  in reactor fuel samples was developed and has been put into routine use. The improved method has resulted in more accurate and sensitive  $^{129}\text{I}$  analyses with an approximately 50% reduction in analysis costs. A developmental program on the application of gamma-ray spectrometry to environmental monitoring and surveillance has expanded. In collaborative studies with members of other divisions, the presence of radionuclides in

cores from the Clinch River, radioactive fallout from Chinese nuclear tests, and the possible presence of radionuclides in mammals and insects in the Oak Ridge area have been investigated. The quality assurance program of the section is being improved by updating manuals of routine analysis methods, establishing a routine quality control program for radioactive samples, and active participation in interlaboratory comparison studies.

## LOW-LEVEL RADIOCHEMICAL ANALYSIS

**Sample analysis program.** The Low-Level Radiochemical Analysis Group performs routine analyses in support of programs in several ORNL divisions. Over the past year, most of these programs have been expanded, resulting in a significant increase in the number of samples requiring low-level radiochemical analysis. Figure 5.1 shows the growth of our sample analysis program over the past 2 years. This growth

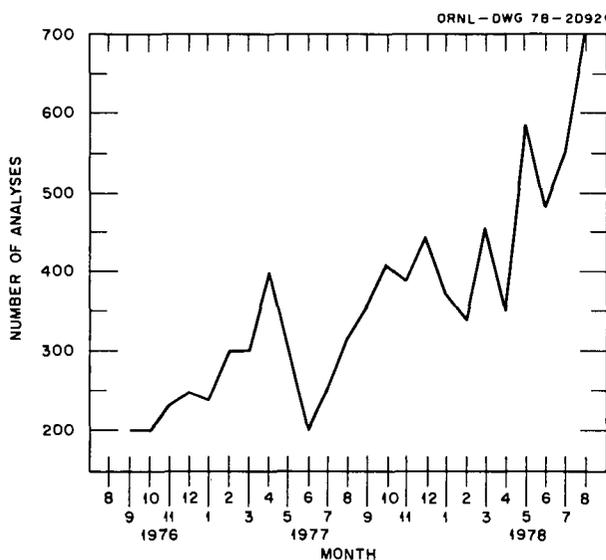


Fig. 5.1. Work load for low-level radiochemical analysis for past 2 years.

has required the addition of new laboratory facilities and personnel and acquisition of new instrumentation and laboratory equipment. Table 5.1 lists the number and types of analyses performed in our sample analysis program during the past year.

Several researchers in the Environmental Sciences Division are working on projects in the waste management program. During the study of one

Table 5.1. Number and types of low-level radiochemical analyses performed on various matrices

Radionuclide	Vegetation	Soils and sediments	Animal tissue	Solutions	Filters
$^{241}\text{Am}$	100	25	350	35	5
$^{244}\text{Cm}$	80	25	350	35	2
$^{131}\text{I}$				100	360
$^{210}\text{Pb}$				100	
$^{238}\text{Pu}$	100	312	415	130	10
$^{239}\text{Pu}$	100	312	415	130	15
$^{226}\text{Ra}$		20		132	
$^{90}\text{Sr}$	26	312	15	1067	14
$^{99}\text{Tc}$	25	15			
$^{228}\text{Th}$	10	25	6	20	12
$^{230}\text{Th}$	10	25	6	111	12
$^{232}\text{Th}$	10	25	6	20	12

drainage system,<sup>1</sup> samples taken downstream from the ORNL sewage treatment plant were found to contain higher-than-expected concentrations of  $^{90}\text{Sr}$ . On further investigation, the source of the  $^{90}\text{Sr}$  was determined to be the sewage treatment plant. To eliminate further releases, the Operations Division made changes in the operation of the plant and intensified monitoring of plant effluents. At another location, discharges from a waste pond were found to be contaminating White Oak Creek with  $^{90}\text{Sr}$ . This situation was corrected by improving the monitoring of the pond. We performed several hundred  $^{90}\text{Sr}$  analyses for this study and related operations.

We completed over 600 analyses on about 300 samples of sediments taken from core samples from the Clinch River as part of a study performed by the Environmental Sciences Division and the Industrial Safety and Applied Health Physics Division to inventory actinide elements in the Clinch River. Before the analyses were begun on the Clinch River samples, we made a study to evaluate the effectiveness of hot nitric acid leaching for extracting

1. A. M. Stueber, D. E. Edgar, A. F. McFadden, and T. G. Scott, *Preliminary Investigation of  $^{90}\text{Sr}$  in White Oak Creek Between Monitoring Stations 2 and 3, Oak Ridge National Laboratory*, ORNL/TM-6510 (December 1978).

radionuclides from sediments. Results of tests proved that the leaching was satisfactory for removal of nuclides of interest and that our method gave results of higher precision than a fusion technique used as a comparison in the study. All core samples were analyzed for  $^{90}\text{Sr}$  and  $^{238,239}\text{Pu}$ . Only a few selected samples were analyzed for  $^{241}\text{Am}$  and  $^{244}\text{Cm}$ . Generally,  $^{90}\text{Sr}$  was found to range from  $10^{-2}$  to  $10$   $\text{dis min}^{-1} \text{g}^{-1}$ . Concentrations of  $^{238,239}\text{Pu}$ ,  $^{241}\text{Am}$ , and  $^{244}\text{Cm}$  ranged from  $10^{-3}$  to about  $10$   $\text{dis min}^{-1} \text{ml}^{-1}$ . The highest concentrations of actinides and  $^{90}\text{Sr}$  were found in the vicinities of the 5-, 11-, and 14-mile markers on the river.

The Chemical Technology and Operations divisions conducted a short-term study to evaluate the operation of the ORNL waste treatment plant. Samples were taken from different stages of the plant on a daily basis for over a month and were submitted for determinations of gross beta activity,  $^{90}\text{Sr}$ , and gamma emitters. Results of analyses indicated inadequate removal of  $^{137}\text{Cs}$  from treated waste. On further investigation, the resin used in the system was determined to have a shorter lifetime than had been expected, and corrective actions were taken.

The Health and Safety Research Division submitted several groups of samples from sites in Middlesex, New Jersey, for determinations of  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  in water, sediment, and mixed-matrix samples. The levels of these radionuclides in the samples ranged from  $10^{-3}$  to  $10^2$   $\text{dis min}^{-1} \text{g}^{-1}$ .

Special samples were received for determinations of the isotopes of U, Np, Pu, and Tc. Preliminary examinations by alpha and gamma spectrometry permitted estimates of the nuclides to be made and showed the presence of thorium and curium. Mass spectrometry and neutron activation analyses produced results for most of the uranium isotopes except  $^{232}\text{U}$ , which was determined by radiochemical separation, alpha spectrometry, and mass ratio determination. Radiochemical separations and alpha-spectrometric measurements of neptunium and plutonium confirmed previous estimates with good agreement.

Unusual samples that required special attention were received from the Chemistry Division, with which we have two collaborative programs in progress. One group of samples, oil-well fluids, required screening for natural activities, particularly radon daughters. Screening was accomplished by neutron activation and by radiochemical and gamma-spectrometric methods. Samples from another program concerned with a search for

unusual alpha emitters in materials of natural origin required interpretation of very complex alpha spectra. (*T. G. Scott, A. R. Crook, S. A. Reynolds, N. A. Teasley, P. S. Gouge, C. C. Granger, J. W. Wade, J. M. Mahathy*)

**Environmental technetium-99 analysis.** The development of methodology for the analysis of low-level quantities of  $^{99}\text{Tc}$  in environmental soil and vegetation samples was initiated this year. Principal aspects of the work included an extensive literature search, development of a procedure for routine preparation of  $^{99\text{m}}\text{Tc}$  tracer, development of suitable sample preparation techniques, the testing of a large number of individual chemical steps, and investigation of several sample-mounting techniques for beta counting. A procedure was developed for the analysis of soil and vegetation.

In anticipation of the work, low-level background beta counters were checked for background, stability, and plateau characteristics, which we found to be within specifications. Arrangements were made for routine neutron irradiation of  $\text{MoO}_3$  at the ORR for preparation of the  $^{99\text{m}}\text{Tc}$  tracer used in this work. Solvent extraction into methyl ethyl ketone was found to be the best method for separation of the  $^{99\text{m}}\text{Tc}$  tracer from the  $^{99}\text{Mo}$  parent.

Sample preparation techniques were developed for soil and vegetation samples. Leaching under total reflux with  $8 M$  nitric acid gave good recoveries. Vegetation samples treated with ammonium hydroxide and then ashed showed  $<2\%$  loss of  $^{99\text{m}}\text{Tc}$  tracer activity. The ashed material was fused with Nicholson's flux and totally dissolved. Individual-chemical steps were tested, using real sample matrix material. The final analysis scheme chosen includes anion exchange, iron hydroxide scavenging, solvent extraction into methyl ethyl ketone, and coprecipitation of tetraphenyl arsonium pertechnetate with tetraphenyl arsonium perchlorate.

The procedure was tested using samples with suspected contamination, background level samples, and environmental samples with a known  $^{99}\text{Tc}$  content. Average results for analysis of an IAEA seaweed sample was within  $5\%$  of the standard value. One high-level sample was analyzed by neutron activation and measurement of  $^{100}\text{Tc}$ . The neutron activation analysis result was within  $2\%$  of the result obtained by beta counting. Typical recoveries of the method are between  $50$  and  $70\%$ . Samples are checked for radiochemical purity in a variety of ways, including beta-absorption measurements, alpha and gamma spectrometry, and decay counting.

Water samples have not yet been analyzed by this method but should pose no particular problem. Tissue samples do not ash well when wet with ammonium hydroxide; the sample preparation procedure must therefore be modified. (*A. R. Crook, T. G. Scott*)

**Waste management sample analysis.** The Waste Management Program initiated early this year is a multidivisional endeavor conducted by members of the Environmental Sciences, Operations, and Chemical Technology divisions. One principal objective of the program is to survey and monitor groundwaters and surface runoff for radioactive contamination from waste-burial areas and plant discharges at ORNL. Groundwater samples are taken from wells and trenches, and surface-water samples are taken from natural and man-made drainage systems for radiochemical analysis. All of the samples contain low to intermediate levels of activities. Several hundred samples from the Environmental Sciences Division have been analyzed so far in the program.

Water samples taken from wells and trenches generally contain higher concentrations of radionuclides than do surface-water samples. The activity of  $^{90}\text{Sr}$  ranges from  $10^{-2}$  to  $10^3$  dis  $\text{min}^{-1}$   $\text{ml}^{-1}$ , and  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  are at about the same range of activity level. Gross alpha activities from the various alpha emitters range from  $10^{-3}$  to  $10$  dis  $\text{min}^{-1}$   $\text{ml}^{-1}$ . Tritium activity is usually predominant and ranges from  $10$  to  $10^5$  dis  $\text{min}^{-1}$   $\text{ml}^{-1}$ . Concentrations of  $^{90}\text{Sr}$  are determined by radiochemical separations on large-volume samples and by low-background beta counting. Gamma emitters are assayed by Ge(Li) spectrometry using 900-ml samples in a Marinelli beaker and counting for 4 to 16 h. Gross alpha determinations are made by collection of alpha emitters on praseodymium fluoride and direct counting, using disposable phosphors. Tritium is determined by liquid scintillation counting.

The wide range of activities of the samples makes it necessary to screen certain groups before radiochemical separations are made; this screening is performed by liquid scintillation counting. The screening assay not only provides a means for direct determination of tritium but also gives an indication of the presence of high-energy beta activity and alpha activities in the samples. Samples found to contain high levels of beta emitters are routed to the Intermediate-Level Analysis Laboratory to avoid cross-contamination problems in the low-level analysis facilities.

The screening process was used to judiciously select 100 samples to send to a commercial laboratory

for analysis of  $^3\text{H}$ ,  $^{90}\text{Sr}$ , and gamma emitters. Eight controls and two blanks were submitted blindly along with the samples as a means of checking the quality of the analyses. Submitting work to commercial laboratories will be repeated as necessary to provide results on large collections of samples that cannot be assayed in ORNL facilities within a reasonable time. (*T. G. Scott, L. M. Jenkins, J. W. Wade, J. M. Mahathy*)

**Analysis of Clinch River core samples.** Core sampling of bottom sediments in the Clinch River from the outfall of White Oak Creek to the confluence of the Tennessee and Emory rivers was conducted during the summer of 1977. This sampling was performed to obtain information in a project entitled "Inventory of Transuranics and Fission Products in the Clinch River," a collaborative effort with the Environmental Sciences and Industrial Safety and Applied Health Physics divisions. Sampling effort resulted in the collection of several hundred cores up to 150 cm in length. Levels of gamma-emitting radionuclides in the cores were too low for measurement by automatic scanning methods of analysis. Consequently, it was decided to segment the cores at 2.5-, 7.6-, 12.7-, 18-, 23-, 30-, 41-, 51-, 61-, 76-, 91-, 102-, and 114-cm locations. Each of these segments from every core sample was then analyzed by high-resolution gamma-ray spectrometry to detect the presence of gamma-emitting radionuclides.

For those cores exhibiting only natural radioelements, top, middle, and bottom segments were selected for  $^{90}\text{Sr}$  and  $^{239}\text{Pu}$  determination by specific radiochemical separation. Cores containing fission- or activation-product nuclides were sampled at horizons exhibiting maximum gamma-ray activity.

Under the experimental conditions chosen for this work (70-g sample and 2000-s counting interval), it was possible to determine  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  at concentration levels as low as 0.2–0.5 pCi/g. Some sediments contained  $^{137}\text{Cs}$  concentrations as high as 600 pCi/g. The most active deposition sites occurred at a point about 9–10 km below the outfall of White Oak Creek.

The presence of  $^{241}\text{Am}$  was directly determined in several core segments, and a crude correlation was found between  $^{239}\text{Pu}$  and  $^{137}\text{Cs}$  content. A report describing this work is in preparation. (*J. S. Eldridge, T. W. Oakes,<sup>2</sup> L. D. Eyman<sup>3</sup>*)

2. Industrial Safety and Applied Health Physics Division.  
3. Environmental Sciences Division.

**New low-level radiochemistry facilities.** New facilities in Building 4500S are being set up for low-level radiochemical analysis. Two chemical laboratories and a counting facility are already in operation, and a third chemical laboratory is being renovated for occupancy. An 8-ft hood has been installed in one laboratory and is being used for general radiochemical separations. Another laboratory will serve as a sample-preparation area. Because of the large number of  $^{90}\text{Sr}$  analyses being requested, one laboratory is used almost exclusively for the radiochemical separation of strontium. A decided improvement in convenience and efficiency has already been realized by the centralization of our chemistry and measurements laboratories.

A low-level counting facility has been put into operation in Room G-49, Building 4500S. An existing ND-3300 multichannel analyzer system has been installed there to provide alpha and gamma spectrometry. The ND-3300 system was moved from another facility and has been expanded from a five- to an eight-input system by the addition of three new ND-570 ADCs and 2 ND-536 time-base units. Three  $7.6 \times 7.6$  cm NaI(Tl) detectors were moved with the system. An eight-port vacuum manifold was designed, fabricated, and placed in service with four surface-barrier detectors for alpha spectrometry. Two new  $15 \times 15$  cm well-type NaI(Tl) detectors are being calibrated and are expected to be operational shortly. The ND-3300 system is now providing over 400 accumulated hours per week of alpha- and gamma-ray spectrometry.

A Nuclear Data 6603 computer-based data-acquisition system was recently purchased for use with a Ge(Li) detector in the low-level counting facility. Initial calibration will be made with samples contained in Marinelli beakers. The system is of the multiuser type and is capable of job stream execution by each user. Data reduction consists mainly of peak analysis. Output devices are a 132-character line printer and an IBM-compatible magnetic tape unit. The magnetic tape unit will enable spectral data to be processed either on our ND-6620 or on the IBM 360 computer using the MONSTR program. The system is expected to be in operation in January 1979. (*T. G. Scott, J. F. Emery, M. E. Pruitt, K. A. Krasin*<sup>4</sup>)

**Quality assurance for low-level radiochemical analysis.** The quality assurance practices for low-level radiochemical analyses are designed to satisfy

varying demands of a number of programs. Control samples for technetium determination were prepared from an Amersham standard, and an IAEA seaweed standard was analyzed with satisfactory results. Control samples for other programs include a composite containing  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$ ; a water sample prepared by diluting a  $^{90}\text{Sr}$  standard from NBS; and others containing plutonium, americium, and uranium. Control analyses make up 5 to 10% of the work load whenever feasible. Participation continues in the intercomparison program conducted by the Environmental Measurements Laboratory for DOE. Local results generally agree with means of other participants within combined uncertainties.

The Ge(Li) gamma spectrometry system in Building 4500N is calibrated by use of NBS mixed radionuclide standards, and quality control samples are made from uranium ore standards from the New Brunswick Laboratory. In the counting facility in Building 4500S, performance of the multiinput alpha system is assured by weekly calibration with a standard source. Control samples consist of plates containing a mixture of three nuclides. In routine measurements of  $^{131}\text{I}$  in charcoal samples by gamma spectrometry, the NaI(Tl) equipment is tested by use of  $^{137}\text{Cs}$  sources and a pulser. Validity of measurement is assured by comparison of assays of selected samples on independently calibrated NaI(Tl) and Ge(Li) systems. In addition, certain samples are remeasured, and the results are found to compare well with the activities predicted from the  $^{131}\text{I}$  half-life. (*S. A. Reynolds, T. G. Scott, M. E. Pruitt, J. S. Eldridge*)

## RADIOCHEMICAL AND ACTIVATION ANALYSIS

**Sample analysis program.** The Radiochemical and Activation Analysis Group assists several divisions in providing radiochemical and activation analysis data for their various programs. During the past year, most of this assistance was given to the Chemical Technology Division, Operations Division, Industrial Safety and Applied Health Physics Division, Solid State Division, Environmental Sciences Division, and ORGDP. We continue to provide radiochemical services in support of decontamination studies of coated reactor-component specimens. During this period about 24,000 radiochemical analyses were made by the group. Procedures for determining tritium,  $^{14}\text{C}$ , and  $^{129}\text{I}$  have been improved in precision and accuracy by use of a new neutron

4. Great Lakes College Association student participant from Lawrence University, Appleton, Wis.

activation analysis method. A study of tritium and  $^{14}\text{C}$  in Peach Bottom graphite and charcoal traps is virtually complete. The Analytical Chemistry Division Sample Transaction System (STS) is now fully implemented for logging of samples and reporting of results to customers.

The demand for activation analysis has increased dramatically this year. About 12,000 samples were analyzed, providing about 23,000 elemental determinations. Uranium determinations for the National Uranium Resources Evaluation (NURE) Program comprise the largest group of routine analyses. About 9000 determinations of uranium in sediment samples were made for the NURE program by the delayed-neutron counting method. Multielement analyses on a variety of samples were also performed in large numbers during the year. About 10,000 elemental determinations were reported. Multielement samples consisted of coal, fly ash, resins, vegetable ashes, sediments, and MgO. Other materials analyzed consisted of flux monitors ( $\text{V-}^{238}\text{U}$ ,  $\text{V-}^{233}\text{U}$ ,  $\text{V-}^{235}\text{U}$ ,  $\text{V-}^{239}\text{Pu}$ ,  $\text{V-}^{237}\text{Np}$ , and the corresponding aluminum series).

A new  $\text{D}_2\text{O}$  tank installed in the Bulk Shielding Reactor was expected to be used for activation analyses requiring long irradiation times. This facility has proven inadequate in some respects; the new tank was designed for irradiation of large (15-cm-diam) silicon ingots in wet "holes" (normal water), but the presence of normal water created large neutron flux gradients in both vertical and horizontal directions in the dry tube. The use of this facility has been extremely limited because of the flux inhomogeneity. (*J. F. Emery, H. A. Parker, L. M. Jenkins, T. G. Harmon, L. R. Hall, K. J. Northcutt, S. H. Prestwood*)

**Increased capabilities for gamma-ray spectrometry.** More than one-half of the radiochemical analysis results reported by this group rely on gamma-ray spectrometric measurements. Consequently, increasing our capabilities in this area results in immediate improvement in efficiency and productivity.

The major gamma-ray spectrometry work load is met by the Nuclear Data 6620 analyzer system. Several pieces of instrumentation have been added to improve the performance of the system this year. An Elgar series 3000 B voltage regulator was installed to minimize the effects of line voltage variations on the computer's operation. The addition of 32K of 16-bit memory has increased the memory bank to 96K, enough to permit simultaneous data acquisition of four Ge(Li) detectors while performing data reduction or programming (FORTRAN and BASIC).

Two new Ge(Li) detectors, purchased from Ortec, Inc., have tripled our available detector time. The detectors have efficiencies of about 20% (relative to  $7.6 \times 7.6$  cm NaI) and resolutions of better than 2.0 keV (1.332-MeV  $^{60}\text{Co}$ ). Because of new equipment and the increased experience of the staff, we have usually met the goal of a two-week turnaround time for gamma spectrometric analysis. We have returned to the policy of performing duplicate analysis on all samples to reduce the possibility of undetected errors in chemical or counting procedures.

We have prepared numerous calibrations of special geometries for the analysis of environmental and waste management program samples. In addition, we have participated in the Environmental Monitoring Laboratory's (EML) quality assurance intercomparison study. Our gamma spectrometric data in the EML program have been consistently in good agreement with other reporting laboratories. (*L. M. Jenkins*)

**Data management.** The STS is a computerized data management system adopted by the Analytical Chemistry Division to replace manual sample accounting and reporting. Previously, we had used the BACKLOG feature exclusively to monitor our sample inventory and status. In the past year the second phase of converting to STS data management has been accomplished.

The group now reports most analytical data via computer readout and stores permanent copies of the data on microfiche. This service has been accomplished on a routine basis through the acquisition of a hard-wired hookup to ORNL's DEC System 10 computer, a Tektronix 4025 terminal, and Tektronix 4642 printer. The terminal gives us convenient and ready access to STS. The printer provides our customers with the option of submitting work requests via the computer from their own terminal, thereby saving time and paperwork while reducing the chances for error. In the coming year, we look forward to implementing the TIMKEEPING feature of the STS. We expect implementation will greatly facilitate the preparation of monthly charges and will be useful in preparing quarterly and annual progress reports. (*L. M. Jenkins, A. R. Crook*)

**Improved methods for analysis of  $^{129}\text{I}$ .** An improved method for the determination of  $^{129}\text{I}$  by activation analysis in fission product solutions was developed and has been in routine use for 6 months. In the new method,  $^{131}\text{I}$  is added prior to separation to correct for chemical yield. The  $^{129}\text{I}$  in the sample is extracted into  $\text{CCl}_4$ , stripped into water, and finally adsorbed on an anion exchange resin. The

resin column is a rabbit insert ( $\frac{3}{4} \times 1\frac{3}{4}$  cm) with several holes (0.4 mm diam) in the bottom to allow the solution to flow through under slight negative pressure. After adsorption of the  $^{129}\text{I}$ , the resin is air dried and the cap sealed prior to irradiation in the HFIR or ORR facility. The radioactivity measurements of  $^{130}\text{I}$  and  $^{131}\text{I}$  are made by gamma-ray spectrometry after a 16-h decay period.

Several anion exchange resins were evaluated for possible use in the modified procedure. Bio-Rad AG1X4 (100–200 mesh), nitrate form, proved to be best because the resin readily adsorbs iodide and is low in impurities that become radioactive during irradiation. Following irradiation, the only impurity observed in this resin after 16 h of decay is  $^{82}\text{Br}$ . Where greater sensitivity is required,  $^{82}\text{Br}$  can be removed by eluting the resin with 0.1 M  $\text{KNO}_3$  prior to the radioactivity measurements. A report describing this work is in preparation. (*L. C. Bate*)

**Technetium-99 analysis in reactor fuels reprocessing samples.** The determination of  $^{99}\text{Tc}$  in dissolved reactor fuel solutions is currently under investigation. Technetium is a high-yield fission product that can be volatilized under some conditions. Because of its nuclear decay characteristics,  $^{99}\text{Tc}$  is difficult to determine in highly radioactive matrices. Neutron activation analysis techniques are being examined as possible alternatives to direct counting methods. The method currently under investigation involves the neutron irradiation of  $^{99}\text{Tc}$  to produce 16-s  $^{100}\text{Tc}$ , which is determined by gamma spectrometry. Carrier-free chemical separation of  $^{99}\text{Tc}$  will be used for the isolation of the  $^{99}\text{Tc}$  from other fission products prior to neutron irradiation. Solvent extraction of the pertechnetate with cyclohexanone gives high extraction coefficients from basic media. Decontamination studies are currently in progress. Exploratory studies have shown that  $^{99}\text{Tc}$  as pertechnetate can be quantitatively adsorbed on anion exchange resins. (*L. C. Bate*)

**Measurement of fission gas release from HRB capsules.** The HFIR removable beryllium capsules contain fertile and fissile microspheres in graphite matrices. These fuel sticks are developmental HTGR fuel for irradiation tests. The capsule during irradiation has an inert gas flowing past it, and the gas stream is sampled to measure the released fission gas radioactivity in the gas ampoule. A computer program (AREA) is used to calculate the fission gas release rate, which is related to the number of broken fuel particles. The fission gases measured are  $^{85\text{m}}\text{Kr}$ ,  $^{87}\text{Kr}$ ,  $^{88}\text{Kr}$ ,  $^{131\text{m}}\text{Xe}$ ,  $^{133}\text{Xe}$ ,  $^{135\text{m}}\text{Xe}$ , and  $^{138}\text{Xe}$ . (*L. C. Bate*)

Anion resin separation of uranium from carbonate-methanol media. An anion exchange resin method of preconcentrating submicrogram quantities of uranium from large volumes of solution using  $(\text{NH}_4)_2\text{CO}_3$  and methanol has been developed and tested. An aqueous solution containing uranium is made 0.1 M in  $(\text{NH}_4)_2\text{CO}_3$  and 20% in methanol. Uranium is adsorbed on an anion resin column made from a rabbit insert ( $\frac{3}{4} \times 1\frac{3}{4}$  cm). After adsorption, the resin is air dried and placed in a rabbit for irradiation and subsequent measurement by neutron activation analysis. A paper describing this method is being prepared for publication. (*A. Haggag, L. C. Bate*)

Trace-element analysis of resin from wastewater processing plant. The ion exchange resin columns used to remove heavy metals from the wastewater processing plant at the High Flux Isotope Reactor often have diminished capacity. This effect can be caused by channeling of water through the resin during normal flow and/or regeneration. Samples of the resin from the plant were obtained at different places in the resin bed for trace-element analysis. The samples were dried and subjected to instrumental neutron activation analysis for trace-element concentration. The variation in the trace-element concentrations in the resin samples suggests that channeling exists in the resin bed. A detailed systematic sampling of the next loaded resin is being planned to determine the extent of the channeling. (*L. C. Bate*)

**Quality assurance for radiochemical and activation analysis.** Quality assurance (QA) efforts have continued on an expanded scale. The bench manual of radiochemical procedures has been reviewed and updated so that all procedures and certifications of analysts are now current. Laboratory practices were audited by a division QA team and found to be generally satisfactory.

A gamma-ray source containing lines from 81 to 1332 keV is used to test energy calibrations and efficiencies of gamma spectrometers each working day. The accumulated data demonstrate satisfactory performance. Mixed radionuclide standards from the National Bureau of Standards (NBS) are used for efficiency calibration, and, as each new one is received, it is used as a control sample. All analyses are performed in duplicate and the data tabulated, with the goal being to establish actual standard deviations of each method. The liquid scintillation beta counter is routinely calibrated with secondary

5. IAEA visitor from Atomic Energy Authority, Cairo, Egypt.

standards and frequently checked with  $^{14}\text{C}$  and  $^3\text{H}$  standards from NBS. Control samples for radiochemical analyses are being prepared from materials obtained from the reactor fuel program. These controls will be analyzed on a regular schedule to ensure the performance of radiochemical methods.

We have analyzed intercomparison samples furnished quarterly by the DOE Environmental Measurements Laboratory. Determinations included tritium and various gamma-emitting nuclides in water, soil, biological materials, and simulated air filters. Our results have generally been in good agreement with the means of values reported by other participants.

In our neutron activation analysis facilities, energy calibration checks of the gamma-spectrometry systems are made daily, and  $^{228}\text{Th}$  and  $^{60}\text{Co}$  sources are used to monitor absolute efficiencies. Two sets of point-source standards from Amersham have been measured recently, and NBS sources are checked from time to time. All values have been in good agreement with those of the suppliers. Uranium analysis by activation and delayed-neutron counting is a comparative method. National Bureau of Standards SRM 930 (uranium oxide) is used to prepare calibration samples. Uranium-silica standards were recently obtained from the DOE New Brunswick Laboratory for further calibrations. Fly ash and coal standards from NBS are used as controls; in addition, the NURE program includes

blind controls. Multielement analysis is accomplished by absolute neutron activation. Neutron fluxes are determined by Al-Mn and Al-Au monitors. Concentrations of elements are then calculated from known cross sections, irradiation times, and the measured fluxes. Reference materials such as NBS orchard leaves and Bowen's kale are used to verify the physical constants of the nuclides and to search for matrix effects. (*J. F. Emery, L. M. Jenkins, S. A. Reynolds*)

### SPECIAL PROJECTS

**Environmental surveillance.** Gamma-ray spectrometry is used in annual surveys of soil and vegetation radioactivity levels at perimeter and remote sampling stations in the East Tennessee area.<sup>6</sup> Radioactivity in air particulates is also determined in quarterly composited samples collected at the sampling locations. Specific radionuclide determinations during 1977 were greatly influenced by the collection time because environmental radioactivity levels were fluctuating as a result of Chinese nuclear testing.

Table 5.2 presents continuous air monitoring data for specific gamma-emitting radionuclides in air

6. J. S. Eldridge and T. W. Oakes, "Environmental Surveillance," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, pp. 69-70.

Table 5.2. Continuous air monitoring data for specific radionuclides in air (composite samples), 1977

Radionuclide	Perimeter stations					Remote stations				
	Quarter				Yearly average	Quarter				Yearly average
	1st	2nd	3rd	4th		1st	2nd	3rd	4th	
$^7\text{Be}$	127	140	121	101	122	132	170	127	99	132
$^{54}\text{Mn}$	ND <sup>a</sup>	0.22	0.27	0.16	≤0.22	~0.048	ND	ND	0.18	≤0.18
$^{57}\text{Co}$	0.10	ND	ND	ND	≤0.1	ND	ND	ND	ND	ND
$^{60}\text{Co}$	ND	~0.0054	0.11	ND	≤0.11	ND	0.018	ND	ND	≤0.018
$^{95}\text{Zr}$	8.3	35	19	6.5	17	12	42	20	7.8	21
$^{95}\text{Nb}$	15.0	70	35	23	36	23	84	38	25	43
$^{103}\text{Ru}$	9.3	19	16	4.8	12	11	22	18	5.5	14
$^{106}\text{Ru}$	2.3	14	18	10	11	2.7	20	14	11	12
$^{125}\text{Sb}$	0.16	1.4	1.8	0.87	1.1	0.42	1.7	2.1	1.0	1.3
$^{137}\text{Cs}$	0.42	2.1	2.2	1.8	1.6	0.42	2.2	2.2	1.7	1.6
$^{141}\text{Ce}$	7.7	11	17	4.5	10	13	12	20	4.7	12.4
$^{144}\text{Ce}$	3.8	30	30	18	21	5.4	36	30	18	22

<sup>a</sup>Not detectable.

particulates from quarterly composites during calendar year 1977. The concentration of each radionuclide is calculated at the midpoint of each quarter, that is, February 15, May 15, etc. World-wide fallout was detectable in samples from both networks at similar concentrations. The naturally occurring radionuclide  $^7\text{Be}$ , produced by cosmic-ray interactions with nitrogen and oxygen in the upper atmosphere, is seen to have the highest concentration in all samples.

Table 5.3 shows specific radionuclide concentrations in grass samples collected at the perimeter and remote sampling stations. Those results are expressed as picocuries per gram of oven-dried ( $100^\circ\text{C}$ ) sample. Samples are measured "as received" to prevent the loss of volatile radionuclides, and the dry weight is determined after the measurement. The grass sample from remote station 56 was collected

3 weeks after the final Chinese nuclear test of 1977. That sample contained the highest concentrations of short-lived fission products. It was found in a corollary study that analysis of  $^{131}\text{I}$  from forage grass is a convenient method of predicting the occurrence of elevated levels of that important radionuclide in dairy milk.

Table 5.4 presents results for specific radionuclides in soil samples from perimeter and remote stations for 1977. Those samples were taken at the exact sampling location from which the grass results from Table 5.3 were collected. The protective action of ground cover in preventing fallout from reaching the soil is evident by the absence of all fallout nuclides with the exception of  $^{137}\text{Cs}$  in the soil samples. The natural radioelements  $^{40}\text{K}$  and  $^{226}\text{Ra}$  were the only radioactive species measurable in these samples other than  $^{137}\text{Cs}$ .

Table 5.3. Specific radionuclides in grass samples from perimeter and remote monitoring stations, 1977

Units of pCi/g, dry weight.								
Sampling location	$^7\text{Be}$	$^{95}\text{Nb}$	$^{95}\text{Zr}$	$^{103}\text{Ru}$	$^{137}\text{Cs}$	$^{140}\text{La}$	$^{141}\text{Ce}$	$^{144}\text{Ce}$
<b>Perimeter stations</b>								
HP-23	17.1	9.5	4.4	2.8	0.44	8.9	8.1	6.9
HP-31	20.4	12.6	6.4	4.3	0.65	11.0	10.8	7.3
HP-32	19.8	11.3	5.2	3.4	0.75	10.1	9.3	7.1
HP-33	11.7	11.5	5.8	2.5	0.40	6.7	7.8	5.3
HP-34	141	32.1	11.1	5.0	1.3	ND <sup>a</sup>	17.2	22.2
HP-35	21.6	14.9	6.7	3.7	1.3	12.7	11.9	9.7
HP-36	14.5	9.5	4.8	2.6	0.51	6.7	7.9	5.6
HP-37	89.2	24.1	7.8	3.9	0.75	ND	12.3	16.6
HP-38	107	21.4	7.6	3.5	1.1	ND	11.0	19.9
HP-39	19.5	13.9	7.0	4.2	0.35	ND	10.2	7.7
Av	46.2	16.1	6.7	3.6	0.76	<9.4	10.7	10.8
<b>Remote stations</b>								
HP-51	17.2	9.9	3.3	2.8	0.30	ND	9.9	6.3
HP-52	17.4	13.1	6.4	4.3	ND	11.8	10.5	7.2
HP-53	11.1	6.8	4.1	2.2	0.24	ND	6.2	5.6
HP-54	10.5	4.3	3.0	1.6	ND	ND	4.1	4.3
HP-55	8.0	6.3	2.0	2.0	0.19	ND	6.3	3.7
HP-56	49.8	40.1	17.0	9.7	0.97	39.7	25.9	21.9
HP-57	8.0	3.2	1.6	0.8	0.29	ND	2.4	4.1
HP-58	8.5	2.3	1.7	0.6	0.58	ND	7.1	3.4
Av	16.3	10.8	4.9	3.0	<0.43	<25.8	9.1	7.1

<sup>a</sup>Not detectable.

Table 5.4. Specific radionuclides in soil samples from perimeter and remote monitoring stations, 1977

Sampling location	Units of pCi/g, dry		
	$^{40}\text{K}$	$^{137}\text{Cs}$	$^{226}\text{Ra}$
Perimeter stations			
HP-23	NA <sup>a</sup>	0.8	0.9
HP-31	12.0	1.5	1.0
HP-32	34.0	1.8	1.2
HP-33	13.2	3.0	1.8
HP-34	18.1	1.6	1.1
HP-35	6.4	1.8	1.7
HP-36	10.3	1.7	1.3
HP-37	11.9	1.3	1.1
HP-38	13.9	1.5	1.3
HP-39	18.1	1.8	1.2
Remote stations			
HP-51	9.6	2.1	1.5
HP-52	17.4	1.3	1.5
HP-53	NA	1.5	1.7
HP-54	24.6	1.3	1.0
HP-55	7.4	1.4	1.6
HP-56	5.8	1.7	1.2
HP-57	20.0	1.3	1.2
HP-58	19.6	1.4	1.4

<sup>a</sup>Not analyzed.

Data collected in these programs are used in an annual environmental monitoring report.<sup>7</sup> (J. S. Eldridge, T. W. Oakes<sup>2</sup>)

**Fallout monitoring.** Nuclear weapons testing by the People's Republic of China has continued to contribute radioactive fallout that is easily detectable in environmental samples. Our extensive sampling for the Chinese tests of 1976 and 1977<sup>8</sup> was reactivated in March of this year following a nuclear test of <20 kilotons on March 15, 1978.

Following the September 17, 1977, detonation, daily milk sampling was conducted in the East Tennessee area for a period of 3 weeks. The maximum level of  $^{131}\text{I}$  reached in area milk was 150

pCi/liter in samples collected 13 d after the test. Ten days after the test, rainwater at ORNL contained 90 pCi/liter of  $^{131}\text{I}$  and 130 pCi/liter of  $^{140}\text{Ba}$ - $^{140}\text{La}$ . On that same date, maximum values of  $3 \times 10^{-4}$  pCi/liter of  $^{239}\text{Np}$ ,  $5.7 \times 10^{-5}$  pCi/liter of  $^{131}\text{I}$ , and  $2.1 \times 10^{-7}$  pCi/liter of  $^{140}\text{Ba}$ - $^{140}\text{La}$  were also observed on an air filter.

The most recent Chinese explosion of March 15, 1978, resulted in activation of the Department of Energy and Environmental Protection Agency fallout networks. Our daily milk, air, and rainwater sampling commenced a few days after the test and continued for 5 weeks. The maximum concentration of  $^{131}\text{I}$  in a daily milk sample was 90 pCi/liter. A rainwater sample from one of the perimeter monitoring stations at ORNL contained  $^{131}\text{I}$  at a concentration of 230 pCi/liter; a grab sample of rainfall in Oak Ridge had an  $^{131}\text{I}$  concentration of 400 pCi/liter.

It should be noted that milk from one of the two dairy herds sampled daily always had substantially higher  $^{131}\text{I}$  concentrations. Grass was analyzed from both farms and found to have approximately the same content of  $^{131}\text{I}$  (5 to 10 pCi/g). Further investigation revealed that the herd with the higher values grazed on pasture as much as possible but that the herd with the lower values had substantial supplementary feeding of hay and grain. Feeding habits are therefore obviously important when assessing a possible health hazard. (J. S. Eldridge, T. W. Oakes,<sup>2</sup> K. E. Shank<sup>2</sup>)

**Low-level gamma-ray spectrometry development for environmental monitoring.** Biological sampling programs for environmental surveillance have mainly involved vegetation and fish sampling. Renewed interest in studying additional dose-to-man pathways has resulted in studies of other biological media. During the past year we have analyzed eight road-killed deer collected on or near the Oak Ridge reservation. These deer are part of a relatively large, uncontrolled population that inhabits the Oak Ridge area.

Samples of muscle were collected from each animal and freeze-dried for preservation. Analytical samples were prepared from the freeze-dried material by homogenization in a blender and compaction in a laboratory press. Radionuclide concentrations in deer muscle samples measured in this study are presented in Table 5.5, where values are presented in units of picocurie per gram on a "wet weight" basis. Future studies with deer will include direct measurement of muscle as well as liver homogenates by counting in Marinelli beakers without the freeze-drying step:

7. Union Carbide Corporation, Nuclear Division, *Environmental Monitoring Report—United States Department of Energy Oak Ridge Facilities—Calendar Year 1977*, DOE Rep. Y/UB-8, 1978.

8. J. S. Eldridge, T. W. Oakes, and J. E. Turner, "Monitoring of Radioactivity from Chinese Nuclear Device," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1977*, ORNL-5360, pp. 71-72.

Table 5.5. Radionuclide concentrations in deer muscle samples, 1977

Sample number	Location	On Oak Ridge reservation	Units of pCi/g, wet weight				
			$^{40}\text{K}$	$^{137}\text{Cs}$	$^{134}\text{Cs}$	$^{60}\text{Co}$	$^{65}\text{Zn}$
D-1	Chestnut Ridge Park	No	4.1	0.416	ND <sup>a</sup>	~0.03	~0.08
D-2	Norris Lake	No	3.8	0.136	ND	ND	ND
D-3	ORGDP Area	Yes	4.1	0.052	ND	ND	ND
D-4	White Oak Creek	Yes	4.5	$2.26 \times 10^3$	10.4	Trace	Trace
D-5	Burial Ground No. 5	Yes	4.2	6.73	ND	0.08	0.59
D-6	Junction of Highway 95 and Bear Creek Road	Yes	4.9	2.25	ND	ND	ND
D-7	One-half mile east of 7000 Area, ORNL	Yes	4.5	0.292	ND	ND	ND
D-8	Highway 95, one mile east of 95/58	Yes	4.5	0.537	ND	ND	ND

<sup>a</sup>Not detectable.

Preparations are under way for extending the biological sampling program to include in vivo determinations of radionuclide concentrations in small animals such as mice, rats, etc. We plan to use a sodium iodide detection system containing two  $13 \times 10$  cm detectors. This measurement scheme will entail the capture, tagging, counting, and release of the animals to their natural environment. The system will require the use of ALPHA-M, a least-squares gamma-ray spectral resolution code.

In a related pathway study, a wild bee colony in a "bee tree" near a surface radioactive burial site was sampled to determine the movement of radionuclides into the possible food substance honey. The honey sample contained only trace levels of radionuclides at or near the detection limit of 0.2–0.5 pCi/g. A water sample collected near the bee tree exhibited no detectable radionuclides other than natural radioelements. (Bees used large quantities of water in the hives.) (*J. S. Eldridge, W. C. Massey, T. W. Oakes*)

#### Radiochemical emergency preparedness program.

The computing gamma-ray spectrometer acquired for use in the emergency preparedness program at ORNL<sup>9</sup> has been used in two field exercises, in which its versatility and limitations were adequately demonstrated.

The first of these field applications of the portable spectrometer was a radiation survey at a contaminated facility located at the eastern boundary of Oak Ridge. A survey of inlets along the eastern shore of Melton Hill Lake (Oak Ridge city limits) was undertaken to determine the location of any residual radioactivity from earlier decontamination efforts. The inlets were reached by a boat launched from the Oak Ridge Marina about 800 m downstream. The portable spectrometer was carried in the open boat for onsite examination of sediments from the inlet bottoms. The ambient temperature at the time of the measurement was about  $-8^\circ\text{C}$ , and the relative humidity was very low. The spectrometer operated satisfactorily, but little information was obtained because of a lack of contained radioactivity. Subsequent visits to the area were made by land, and field surveys and sample collections were obtained at six locations. Gamma-ray spectral determinations showed that  $^{60}\text{Co}$  was the main contaminant with smaller quantities of  $^{137}\text{Cs}$ . Qualitative determinations performed in situ were valuable adjuncts to the quantitative determinations subsequently performed in the laboratory on samples collected in the field. Radioactivity levels in stream-sediment samples at the contaminated facility ranged from background levels to about 500 pCi/g of  $^{60}\text{Co}$ . A water sample from a stream traversing the property contained 200 pCi/liter  $^{60}\text{Co}$  and 1000 pCi/liter  $^{137}\text{Cs}$ .

The second field trial involved the identification of radioactivity in soil samples and materials uncovered at a local construction site during a routine health

9. J. S. Eldridge and M. E. Pruitt, "Emergency Sample Analysis," *Anal. Chem. Div. Annu. Prog. Rep.*, Nov. 30, 1977, ORNL-5360, pp. 70–71.

physics survey. The contaminated materials were suspected of being part of an early waste disposal operation at the location. Field spectrometry showed the contamination to be  $^{137}\text{Cs}$ . Subsequent field measurements helped establish the lack of contamination in core samples collected to determine the extent of spread of the radioactivity. Laboratory determinations of radioactivity in water and gravel samples from the site showed the presence of  $^{60}\text{Co}$  and  $^{134}\text{Cs}$  in addition to the primary  $^{137}\text{Cs}$  contaminant. The  $^{134}\text{Cs}$  was present at a concentration of about 0.6% of that of the  $^{137}\text{Cs}$ . The  $^{134}\text{Cs}$  content indicated that contamination was relatively recent, probably from a process drain in the area. This concept was found to be correct by means of simple dye tests and observation of the emergence of a plumber's "snake." (*J. S. Eldridge, T. W. Oakes*<sup>2</sup>)

**Geochemistry of achondritic meteorites: gamma-ray studies.** Equipment and techniques developed for the analysis of radioactivity in environmental samples are useful for the assay of radionuclide concentrations in a variety of geological samples. Gamma-ray analysis may be performed nondestructively on samples ranging from several grams to a few kilograms after appropriate calibration of the equipment. The gamma-ray method is excellent for determining average concentrations in large samples, thus eliminating inherent sampling inhomogeneities associated with some ion-microprobe and x-ray fluorescence techniques.

We are applying high-sensitivity, low-background, gamma-ray spectrometry to measurements of low levels of radioactivity in geological and environmental samples. A description of the gamma-ray spectrometer and the methods of calibration and data analysis have been published.<sup>10,11</sup> We are investigating a series of achondritic meteorites because of recent interest in petrogenetic models that suggest possible relations among the parent bodies of the several groups of these meteorites.

Nine meteorite samples have been analyzed in the current study, including duplicate specimens of the

widely studied Pasamonte and Stannern eucrites. The results show that the concentrations of potassium, thorium, and uranium are rather uniform for different stones from the same meteorite fall.

Eucrites studied in this program (date of collection in parentheses) are: Pasamonte (1933), Stannern (1808), Nuevo Laredo (1950), Sioux County (1933), Juvinas (1821), and Haraiya (1878). In addition, the representative member of the nakhlite group of igneous meteorites, Nakhla (1911), has been studied. The range of concentrations of potassium, thorium, and uranium in these eucrites is about 280–620 ppm, 330–660 ppb, and 90–200 ppb, respectively. These values suggest somewhat more uniformity in primordial radioelement content than is usually assumed from trace-element data obtained by other methods having larger analytical errors.

We have received approval to study a unique achondrite from the Antarctic meteorite collection repository at the NASA Johnson Space Center. This meteorite is described as having a bulk composition intermediate between the chassignite and diogenite classes of achondrites. In addition, we have received the following samples for study: Chassigny (1815), Serra de Mage (1923), Jonzac (1818), Cachari (1916), and Bereba (1924). (*R. A. Muntean*,<sup>12</sup> *G. D. O'Kelley*,<sup>13</sup> *J. S. Eldridge*)

**Decay heat studies.** We have been involved with the Engineering Physics Division in a project to improve accuracy and precision in the measurement of the decay heat from radioactive fission products after reactor shutdown. The project was terminated after the completion of the measurements on  $^{241}\text{Pu}$ . Project goals of overall errors of less than 5% were realized for all nuclides studied ( $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Pu}$ ). (*J. F. Emery, K. J. Northcutt*)

**Calibration of neutron detection device.** An irradiation facility for the calibration of a high-sensitivity neutron measurement device required absolute flux mapping for both thermal and resonance neutrons. Because the neutron flux was expected to be low ( $\sim 10^4$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ ) pure monitors of manganese (0.25-mm) and gold (0.12-mm) foil were selected. Large concentrations of high cross-section materials attenuate the neutron flux in the facility. Because the attenuation depends on the neutron spectrum, the apparent thermal and resonance fluxes were computed by use of simultaneous equations.

10. J. S. Eldridge, G. D. O'Kelley, K. J. Northcutt, and E. Schonfeld, "Nondestructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-ray Spectrometer and a Novel Application of Least-Squares Fitting," *Nucl. Instrum. Methods* **112**, 319 (1973).

11. G. D. O'Kelley, J. S. Eldridge, E. Schonfeld, and P. R. Bell, "Primordial Radionuclide Abundances, Solar Proton and Cosmic-Ray Effects and Ages of Apollo 11 Lunar Samples by Nondestructive Gamma Ray Spectrometry," *Geochim. Cosmochim. Acta, Suppl.* **1**, 2, 1407 (1970).

12. Oak Ridge Associated Universities predoctoral fellow from The University of Tennessee, Knoxville.

13. Chemistry Division.

The initial values were then used to compute the total attenuation factor by successive approximations. The attenuation factor ranged from 0.48 to 0.69 for gold and 0.934 to 0.949 for manganese. The thermal

flux was found to range from  $0.75 \times 10^4$  to  $6.5 \times 10^4$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$  in the facility. (*J. F. Emery, K. J. Northcutt*)



## 6. Quality Assurance, Safety, and Tabulation of Analyses

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

### QUALITY ASSURANCE

The Quality Assurance (QA) Program has continued in much the same manner as in past years; however, programs are now being written to include quality assurance in our computer-based Sample Transaction System. As part of our formal QA program we have conducted quarterly internal QA audits by section. 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, the number of control determinations reported has increased 38%, and seven new control programs were initiated. In April a weighted average of the limits of error for the previous 15 quarters was calculated for each of the programs. This resulted in the lowering of the expected limits of error for eight of the programs.

### SAFETY

During the past year the Analytical Chemistry Division had seven first-aid cases and one recordable injury; all were cuts, burns, or falls. The division has continued to have unannounced safety and house-keeping inspections each quarter and to have safety

Table 6.1. Distribution by laboratory of control tests for October 1977–September 1978

Laboratory	Number of control results		Quality level <sup>a</sup> (%)	
	Total	Outside fixed limits	1977	1978
Environmental Analysis	808	32	98.65	96.04
Radioactive Materials	649	31	86.56	95.22
General Analytical	1371	74	93.58	94.60
Total	2828	137	93.13	95.16

<sup>a</sup>Control results within 2S limits.

meetings and films on a fairly regular basis. An outside facility for the storage of inflammable organic compounds was completed during the year. This facility will allow the groups in Building 4500S to maintain much smaller quantities of these compounds in the laboratories.

### 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 6.2. Distribution of control results (by method)  
for October 1977–September 1978**

Method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption spectrometry	Aluminum	1	16	
	Calcium	2	96	
	Chromium	1	28	
	Copper	2	14	
	Iron	1	91	
	Lithium	2	21	
	Magnesium	2	91	
	Nickel	1	29	
	Potassium	1	47	
	Sodium	1	50	
	Zinc	1	4	487
Colorimetry	Chloride	1	26	
	Iron	1	12	
	Molybdenum	1	27	
	Nitrate	1	17	
	Nitrogen	2	229	
	Phosphorus	1	98	
	Sulfate	2	154	
	Thorium	2	123	
	Uranium (NH <sub>4</sub> SCN)	2	110	
	Uranium (DBM)	1	66	
	Zirconium	2	50	912
Flame emission spectrometry	Potassium	1	43	
	Sodium	1	53	96
Fluorometry	Uranium	2	234	234
Gravimetry	Carbon (Leco)	1	106	
	Carbon (train)	1	33	
	Hydrogen (carbon train)	1	27	166
Infrared spectrometry	Carbon	1	85	85
Ion selective electrode	Ammonia	1	7	
	Fluoride	1	46	53
Volumetry	Acid	3	303	
	Nitrate	1	82	
	Sulfur	1	30	
	Thorium	4	118	
	Uranium	3	262	795
Total		53		2828

Table 6.3. Summary of analytical work

Organization	Number of results reported by						Total
	Mass Spectrometry Laboratory	General Analytical Laboratory	Environmental Analysis Laboratory	Radioactive Materials Analytical Laboratory	Physicochemical Laboratory	Nuclear and Radiochemical Analysis	
ORNL divisions							
Analytical Chemistry	1,102	600	4,337	86	275	2,223	8,623
Biology	36		8				44
Central Management <sup>a</sup>						46	46
Chemical Technology	25,229	22,542	3,266	42,266	1,306	11,617	106,226
Chemistry	3,437	1,880	47	348	899	1,252	7,863
Energy						7	7
Engineering		55					55
Engineering Physics	295	57		4	68	12	436
Engineering Technology	711	4,863			195	111	5,880
Environmental Sciences	235	625	27,766	5	916	10,657	40,204
Fusion Energy	29						29
Health	1,605						1,605
Health and Safety Research	148	15		2	43	2,854	3,062
Industrial Safety and Applied Health Physics		10	628	15		6,904	7,557
Instrumentation and Controls	282			69		32	383
Metals and Ceramics	13,329	4,277	165	642	751	168	19,332
Operations	1,144	1,684	693	6,047	15	8,321	17,904
Physics	148			12	35	7	202
Plant and Equipment	420	18				1	439
Quality Assurance and Inspection	14	8				37	59
Solid State	1,968	190	35	66	26	800	3,085
Others							
Protective Coating Testing				1,800			1,800
NURE <sup>b</sup>						6,101	6,101
K-25 and Y-12	1,314	309	3	7		1,020	2,653
Savannah River Laboratory		15					15
Miscellaneous	14,692	84	247	4	40	227	15,294
Total	66,138	37,232	37,195	51,373	4,569	52,397	448,904

<sup>a</sup>Not a division.

<sup>b</sup>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 and by making available facilities and supervision for student and faculty research and training programs.

### ADVISORY COMMITTEE

This year the division Advisory Committee was composed of:

- A. F. Findeis**, Program Director for Chemical Analysis, Division of Mathematical and Physical Sciences, National Science Foundation, Washington, D.C.,
- P. F. Kane**, Director of Materials Characterization Laboratory, Texas Instruments, Inc., P.O. Box 5936, MS 147, Dallas, Texas, and
- A. G. Sharkey**, Manager, Chemical and Instrumental Analysis Division, Technology Center, Department of Energy, 4800 Forbes Avenue, Pittsburgh, Pennsylvania.

### CONSULTANTS

- A. E. Cameron** advises the Mass and Emission Spectrometry Section of the division.
- M. T. Kelley** (Adjunct Research Participant) 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.

- Dr. S. R. Koirtyohann**, University of Missouri, Columbia,
- Dr. J. M. McKay**, Laramie Energy Research Center, Laramie, Wyoming,
- Dr. J. F. Holland**, Michigan State University, E. Lansing,
- Dr. H. L. Pardue**, Purdue University, Lafayette, Indiana,
- Dr. R. Barnes**, University of Massachusetts, Amherst,
- Dr. W. W. Harrison**, University of Virginia, Charlottesville,
- Dr. M. L. Lee**, Brigham Young University, Provo, Utah,
- Dr. J. D. Winefordner**, University of Florida, Gainesville,
- Dr. C. W. Sill**, Department of Energy, Idaho Falls, Idaho, and
- Dr. J. W. Kilty**, Federal Bureau of Investigation, Washington, D.C.

### PARTICIPATION IN ORNL IN-HOURS PROGRAM

The following divisional people completed courses during the 1977 fall term of the Continuing Education Program for Scientific and Technical Personnel:

- E-500. Survey of Microprocessors and Microcomputers:** L. K. Bertram and D. L. Donohue.
- M-100. Fortran I:** F. L. Ball, J. H. Cooper, E. H. McBay, and F. Y. Ohene-Aniapam.
- M-300. Fortran II:** F. L. Ball, W. R. Laing, and E. H. McBay.
- P-610. Laser Applications in Physical and Life Sciences:** C. Feldman, R. W. Shaw, and J. P. Young.
- S-210D. Grammar and Mechanics of Technical Writing:** D. N. Beals, R. Eby, L. Landau, and D. M. Watson.

Below are the courses completed during the winter 1978 term:

**M-100A. Fortran I:** L. K. Bertram and L. M. Jenkins.

**M-500B. Job Control Language I:** M. E. Pruitt.

**M-505. Job Control Language II:** M. E. Pruitt.

**M-600B. Practical Statistics:** C. S. MacDougall.

**P-400. Surface Physics:** J. M. Dale, H. W. Dunn, and E. Ricci.

**S-201E. Grammar and Mechanics of Technical Writing:** R. F. Apple, C.-h. Ho, C. R. Johnson, J. L. Marley, R. B. Quincy, and T. G. Scott.

**S-203B. Technical Writing Workshop:** J. L. Botts.

W. H. Christie and L. D. Hulett were instructors for **Surface Physics** during the winter 1978 term.

The following courses were completed during the spring and summer 1978 term:

**M-310. Introduction to the DEC System-10:** A. R. Crook.

**S-201F. Grammar and Mechanics of Technical Writing:** C. S. MacDougall.

**S-202E. Design and Structure of Technical Writing:** R. F. Apple, C. R. Johnson, and R. B. Quincy.

**S-400. Searching the Technical Literature:** J. E. Attrill, J. L. Botts, and C. Feldman.

**S-203C. Technical Writing Workshop:** F. L. Ball and C. R. Johnson.

Courses completed during the fall 1978 term were:

**C-250. Radiochemistry Revisited:** D. A. Bostick, R. D. Brooksbank, J. S. Eldridge, T. Harmon, L. M. Jenkins, K. A. Krasin, J. M. Mahathy, P. W. Pair, J. W. Wade, and W. B. Whitten.

**M-650. Computer Methods for Mathematical Computations:** A. R. Crook.

**S-203D. Technical Writing Workshop:** T. G. Scott.

J. S. Eldridge was an instructor for one session of **Radiochemistry Revisited**.

H. H. Ross attended the **Kepner-Tregoe Executive Problem Analysis and Decision Making Course** December 11-15, 1978.

#### WIGNER FELLOWSHIP

J. M. Ramsey was awarded a Wigner Fellowship by ORNL this year. He will come to ORNL early in 1979 after completion of doctoral work with Prof. G. M. Hieftje at Indiana University. Ramsey is the first Analytical Chemistry Division recipient of this award, which is given annually to a very limited number of outstanding young scientists at ORNL.

#### GREAT LAKES COLLEGES ASSOCIATION (GLCA) EDUCATION PROGRAM

This cooperative program is now in its ninth year. One student was assigned to the division during the fall 1978 semester: K. A. Krasin from Lawrence University, Appleton, Wisconsin, to work with M. E. Pruitt and J. R. Stokely in low-level gamma-ray spectrometry.

#### IAEA FELLOWSHIP PROGRAM

F. Ohene-Aniapam, IAEA Fellow, Chemistry Department, Ghana Atomic Energy Commission, Ghana, Africa, was assigned to the division from March to December 1977. He worked with J. R. Stokely in radiochemistry functions such as uranium and thorium assays, activation analysis, and general radiochemistry techniques and gained experience in low-level gamma counting of uranium and thorium.

A. H. Haggag, IAEA Fellow, Nuclear Chemistry Department, Atomic Energy Authority, Cairo, Egypt, was assigned to the division for 8 months beginning November 1977 but received an extension to his appointment in June and worked until October 1978. He was assigned to J. R. Stokely to work with radiochemistry functions, the determination of uranium and thorium by chemical techniques, activation analysis, and counting of uranium and thorium.

### ALIEN GUEST ASSIGNMENTS

Dr. Marie-France Gonnard is on sabbatical leave from Ecole Polytechnique, Paris, France, working with M. R. Guerin on gas chromatography for chemically characterizing the organic materials produced by and discharged from coal-based technologies. She is on a 1-year assignment to the division.

Mohammad R. Hosseini-Kupaie is on a guest assignment from Iran to receive on-the-job training in reactivity of fly ashes (bituminous and lignite) as a function of surface area and particle size distribution and to investigate the hydraulic nature, including porosity and degree of hydration, of lignite ashes. His assignment is for approximately 21 months beginning in August 1978.

Two people, Shigenori Irinouchi and Kazuo Kagami, from the Power Reactor and Nuclear Fuel Development Corporation, Tokyo, Japan, worked with J. A. Carter for about 6 weeks beginning October 30, 1978, on microsample preparation and analysis of irradiated dissolver solutions employing resin bead sampling and mass spectrometry, in support of the TASTEX program for safeguarding nuclear materials.

### ORAU GRADUATE PARTICIPATION PROGRAM

V. E. Norvell, University of Tennessee, has been working in the division since January 1977 with G. Mamanov and L. N. Klatt on his thesis research on the study of rapid scan spectrometry in analytical methodology.

### ORAU FACULTY RESEARCH PROGRAM

Dr. N. A. Goeckner, Western Illinois University, was appointed as a faculty research participant in August 1977 and worked through June 1978 with M. R. Guerin on a project involving the characterization of fossil fuel isolates related to environmental toxicology.

### SUMMER PROGRAM

During the summer, the division was host to representatives of several programs that have been developed to offer laboratory experience to college students and faculty members as well as to promising high school graduates. R. W. Holmberg served as "Dean" for these guests during their visit.

#### Summer Research Participants

Dr. Cheng Y. L. Ma, University of Mississippi, Oxford, worked with M. R. Guerin from May to September on chemical separation procedures and identification of components in synthetic fuels.

Dr. Thomas L. Theis, University of Notre Dame, South Bend, Indiana, worked for 6 weeks with L. D. Hulett to investigate the possibility that concentrations of certain metal ions in natural waters may be controlled by sorption processes on manganese oxide surfaces.

#### ORAU Summer Undergraduate Research Trainees

The division was host to four undergraduate research trainees:

Z. K. Barnes, Western Kentucky University, worked with J. E. Caton on low resolution separation of complex organic mixtures for biological testing.

M. C. Burrell, Bloomsburg State College, Harrisburg, Pennsylvania, worked with D. A. Lee on the determination of kinetic parameters for the thermal decomposition of urania-gels by mass spectrometry.

E. M. Holland, Murray State University, Gilbertsville, Kentucky, worked with W. R. Laing on the determination of niobium in sediment samples.

T. M. Mamantov, Georgia Institute of Technology, Atlanta, worked with B. R. Clark on the isolation of mutagenic components of the basic fraction of tobacco smoke condensation.

### 22D ANNUAL ORNL CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

This year's conference was held at the Riverside Motor Lodge in Gatlinburg, Tennessee, October 10-12, 1978. Attendance was about 230 with 11 exhibitors. Five topics were covered during 3 full days: Ion Chromatography (one session), Thorium (two sessions), Environmental and Effluent Monitoring (three sessions), Analytical Problems in New Energy Systems (one session), and Lasers in Analytical Methodology (one session).

L. J. Brady was Arrangements Chairman, W. S. Lyon was Technical Program Chairman, and A. L. Harrod was Treasurer and Exhibits Coordinator. Other committee members included W. H. Christie, L. T. Corbin, J. S. Eldridge, W. R. Laing, R. R. Rickard, R. W. Shaw, and W. D. Shults.

### ADDITIONAL PROFESSIONAL ACTIVITIES

Members of the division continue to serve on professional, civic, and educational boards and committees. These activities are listed below as part of the division's overall outreach.

#### 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

#### 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  
 Member: ORNL Management and Supervisory Development Program Advisory  
 Committee  
 ORNL Personnel Development Chemistry Course

#### CATON, J. E.

Consultant: National Cancer Institute  
 Lecturer: ORAU Traveling Lecture Program  
 Instructor: ORNL Personnel Development Chemistry Course

#### CHRISTIE, W. H.

Lecturer: ORAU Traveling Lecture Program  
 Secretary: Subcommittee E-42:06, SIMS, Committee E-42 on Surface Analysis,  
 ASTM  
 Chairman: Analytical Chemistry Division Seminar Committee

#### CLARK, B. R.

Member: Analytical Chemistry Division Seminar Committee

**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.**

Member: Committee E-42, Surface Analysis, ASTM

**DYER, F. F.**

Lecturer: ORAU Traveling Lecture Program

**ELDRIDGE, J. S.**

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

**FELDMAN, C.**

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

**GUERIN, M. R.**

Consultant: National Cancer Institute  
 Session Chairman: ORNL Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, Gatlinburg, Tennessee, September 25-28, 1978  
 DOE Contractor Meeting-Workshop on the Status of DOE Programs Involving Development and Use of Short-Term Bioassays for Identifying Toxic Agents in Complex Mixtures and Prospects for Standardization, Boca Raton, Florida, November 11-15, 1978

- Cochairman: LASL and American Petroleum Institute Meeting on the Health and Environmental Effects of Oil Shale Development, Los Alamos Scientific Laboratory, Albuquerque, New Mexico, August 2-3, 1978  
Committee E-19, Chromatography, Meeting, Atlanta, Georgia, October 22-25, 1978, ASTM
- Cochairman and Panel Member: DOE/EPA/DHEW Chemistry Panel Workshop on the Health and Environmental Effects of Coal Gasification and Liquefaction Technologies, Leesburg, Virginia, August 20-25, 1978
- Invited Participant: EPA Symposium on the Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Virginia, February 21-23, 1978  
EPRI Source Assessment Meeting, Palo Alto, California, September 6-7, 1978  
American Health Foundation Site Review of Naylor Dana Institute, Valhalla, New York, April 27, 1978
- HIGGINS, C. E.**  
Coordinator: Analytical Chemistry Division Affirmative Action Program
- HOLMBERG, R. W.**  
Coordinator: Analytical Chemistry Division University Relations  
Analytical Chemistry Division Metrics Conversion
- HORTON, A. D.**  
Member: Committee E-19, Chromatography, ASTM  
Subcommittee E-19:07, Indexing of Chromatographic Methods, ASTM
- HULETT, L. D.**  
Member: Committee E-42, Surface Analysis, ASTM  
Lecturer: ORAU Traveling Lecture Program
- JENKINS, R. A.**  
Consultant: National Cancer Institute  
Enviro Control, Inc.  
Invited Participant: Site Review for the Department of Health and Welfare, University of Guelph, Guelph, Ontario, Canada
- KLATT, L. N.**  
Member: Program Advisory Committee, Division of Analytical Chemistry, ACS  
Associate Editor: *Chemical Instrumentation*  
Chairman: Analytical Group of East Tennessee Section, ACS
- LAING, W. R.**  
Chairman: Subcommittee C-26:05, Test Methods, Nuclear Fuel Cycle, ASTM  
Coordinator: Analytical Chemistry Division B.S./M.S. Recruiting  
Division Representative: ORNL Coal Technology Program Steering Committee  
UCCND Environmental Control 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
- Regional Editor: *Journal of Radioanalytical Chemistry*  
 Associate Editor: *Radiochemical and Radioanalytical Letters*  
 Technical Program Chairman: 22nd ORNL Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tennessee, October 1978  
 Session Chairman: Nuclear Activation Techniques in the Life Sciences, IAEA, Vienna, Austria, May 1978  
 Program Chairman: Isotopes and Radiation Division, ANS

**PRUITT, M. E.**

- Instructor: (Part-time) Roane State Community College, Harriman, Tennessee

**REYNOLDS, S. A.**

- Member: Committee D-19, Water, ASTM  
 Committee E-10, Nuclear Technology and Applications, ASTM Environmental Sciences Division, ANS  
 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

**RICCI, E.**

- Secretary: Isotope and Radiation Division, ANS  
 Chairman: Planning Committee, Isotopes and Radiation Division, ANS

**ROSS, H. H.**

- Member: ORNL Graduate Student Selection Panel  
 ORNL Technology Utilization Committee  
 Editorial Advisory Board, *Journal of Radioanalytical Chemistry*  
 Education Committee, ORNL Credit Union

**SHAW, R. W.**

- Co-instructor: "Laser Applications in Physical and Life Sciences" (ORNL Continuing Education Program, fall 1977)

**SHULTS, W. D.**

Member:

UCCND Technical Services Committee  
UCC Analytical Specialist Group  
ORNL In-Hours Continuing Education Committee  
Fellowship Committee, Analytical Chemistry Division, ACS  
Committee on Environmental Analytical Methodology, ACS  
DBER Site Review Team, Ames, Iowa  
Editorial Board, *Analytical Chemistry*

**SMITH, D. H.**

Coordinator:

Analytical Chemistry Division Ph.D. Recruiting

**WIKE, J. S.**

Secretary-Treasurer:

Analytical Group, East Tennessee Section, ACS

**YOUNG, J. P.**

Invited Speaker:

Symposium on "New Applications of Lasers to Chemistry" 176th Meeting, ASC, Anaheim, California, March 12-17, 1978

Invited Participant:

DBER Physical and Technological Programs Contractors' Workshop on Advanced Laser Technology for Pollutant Measurements, ORNL, Oak Ridge, Tennessee, February 9-10, 1978  
Department of Technical Utilization/ Commercialization, Workshop on One Atom Detection, ORNL, Oak Ridge, Tennessee, June 27-28, 1978

## 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 nonnuclear — 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

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Carter, J. A.	Carter, J. A.; Donohue, D. L.; Franklin, J. C.; Walker, R. L. "Trace Impurities in Coal and Fly Ash by Isotope Dilution Mass Spectrometry"	<i>Analytical Methods for Coal and Coal Products</i> , C. J. Karr, ed., Academic Press, New York, 1978, chap. 13, p. 403
	Carter, J. A.; Franklin, J. C.; Donohue, D. L. "Multielement Isotope Dilution Techniques for Trace Analysis"	<i>High Performance Mass Spectrometry, Chemical Applications</i> , M. L. Gross, ed., ACS Symposium Series No. 70, American Chemical Society, Washington, D.C., 1978, p. 299
Clark, B. R.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Chemical Class Fractionation of Fossil-Derived Materials for Biological Testing"	<i>Analytical Chemistry of Liquid Fuel Sources; Tar Sands, Oil Shale, Coal, and Petroleum</i> , P. C. Uden, S. Siggia, and H. B. Jensen, eds., Advances in Chemistry Series 170, American Chemical Society, Washington, D.C., 1978, p. 282
Donohue, D. L.	Carter, J. A.; Donohue, D. L.; Franklin, J. C.; Walker, R. L. "Trace Impurities in Coal and Fly Ash by Isotope Dilution Mass Spectrometry"	<i>Analytical Methods for Coal and Coal Products</i> , C. J. Karr, ed., Academic Press, New York, 1978, chap. 13, p. 403
	Carter, J. A.; Franklin, J. C.; Donohue, D. L. "Multielement Isotope Dilution Techniques for Trace Analysis"	<i>High Performance Mass Spectrometry, Chemical Applications</i> , M. L. Gross, ed., ACS Symposium Series No. 70, American Chemical Society, Washington, D.C., 1978, p. 299
Franklin, J. C.	Carter, J. A.; Donohue, D. L.; Franklin, J. C.; Walker, R. L. "Trace Impurities in Coal and Fly Ash by Isotope Dilution Mass Spectrometry"	<i>Analytical Methods for Coal and Coal Products</i> , C. J. Karr, ed., Academic Press, New York, 1978, chap. 13, p. 403

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Guerin, M. R.	Guerin, M. R. "Energy Sources of Polycyclic Aromatic Hydrocarbons"	<i>Polycyclic Hydrocarbons and Cancer: Chemistry, Molecular Biology and Environment</i> , P. O. P. Ts'o and H. V. Gelboin, eds., Academic Press, New York, 1978, vol. 1, p. 3
Ho, C.-h.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Chemical Class Fractionation of Fossil-Derived Materials for Biological Testing"	<i>Analytical Chemistry of Liquid Fuel Sources; Tar Sands, Oil Shale, Coal, and Petroleum</i> , P. C. Uden, S. Siggia, and H. B. Jensen, eds., Advances in Chemistry Series 170, American Chemical Society, Washington, D.C., 1978, p. 282
Jones, A. R.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Chemical Class Fractionation of Fossil-Derived Materials for Biological Testing"	<i>Analytical Chemistry of Liquid Fuel Sources; Tar Sands, Oil Shale, Coal, and Petroleum</i> , P. C. Uden, S. Siggia, and H. B. Jensen, eds., Advances in Chemistry Series 170, American Chemical Society, Washington, D.C., 1978, p. 282
Krause, M. O.*	Krause, M. O.;* Ricci, E.; Sparks, C. J.;* Nestor, C. N.* "Calculation of X-Ray Fluorescence Cross Sections for <i>K</i> and <i>L</i> Shells"	<i>Advances in X-Ray Analysis</i> , C. S. Barrett and D. E. Leyden, eds., Plenum Press, New York, 1978, vol. 21, p. 119
Lindberg, S. E.*	Turner, R. R.;* Lindberg, S. E.;* Talbott, C. K. "Dynamics of Trace Element Export from a Deciduous Watershed, Walker Branch, Tennessee"	<i>Watershed Research in Eastern North America: A Workshop to Compare Results</i> , D. L. Correll, ed., Smithsonian Institution, Edgewater, Md., 1978, vol. 1, pp. 661-79
Natusch, D. F. S.	Natusch, D. F. S.;* Tomkins, B. A. "Theoretical Consideration of the Adsorption of Polynuclear Aromatic Hydrocarbon Vapor onto Fly Ash in a Coal-Fired Power Plant"	<i>Carcinogenesis, Volume 3: Polynuclear Aromatic Hydrocarbons</i> , Raven Press, New York, 1978, p. 145
Nestor, C. N.*	Krause, M. O.;* Ricci, E.; Sparks, C. J.;* Nestor, C. N.* "Calculation of X-Ray Fluorescence Cross Sections for <i>K</i> and <i>L</i> Shells"	<i>Advances in X-Ray Analysis</i> , C. S. Barrett and D. E. Leyden, eds., Plenum Press, New York, 1978, vol. 21, p. 119
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Tomkins, B. A.	Natusch, D. F. S.;* Tomkins, B. A. "Theoretical Consideration of the Adsorption of Polynuclear Aromatic Hydrocarbon Vapor onto Fly Ash in a Coal-Fired Power Plant"	<i>Carcinogenesis, Volume 3: Polynuclear Aromatic Hydrocarbons</i> , Raven Press, New York, 1978, p. 145
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Ball, F. L.	Taylor, F. G.;* Parr, P. D.;* Ball, F. L. "Interception and Retention of Simulated Cooling Tower Drift by Vegetation"	<i>Proc. Cooling Tower Environment, A Symposium on Environmental Effects of Cooling Tower Emissions</i> , University of Maryland, College Park, Md., May 2-4, 1978, Water Resources Research Center, University of Maryland, College Park, 1978, p. 1-39
Botts, J. L.	Botts, J. L.; Wichner, R. P.* "Fuel Particle Failure Fraction in Peach Bottom HTGR Fuel Elements"	<i>Proc. Am. Nucl. Soc. Meeting, San Diego, Calif., June 18, 1978; Trans. Am. Nucl. Soc.</i> <b>28</b> , 689 (1978)
Carter, J. A.	Carter, J. A.; Donohue, D. L., "An Electro-Optical Detector for Spark Source Mass Spectrometry"	<i>Proc. 26th Annu. Conf. Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978</i> , American Society for Mass Spectrometry, St. Louis, Mo., 1978, p. 383
	Carter, J. A.; Walker, R. L. "Preparation and Isotopic Analysis of U and Pu for Safeguards"	<i>Proc. 21st Conf. Anal. Chem. in Energy Technology, Gatlinburg, Tenn., Oct. 4-6, 1977</i> , Science Press, Princeton, N.J., 1978, p. 84
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	Christie, W. H.; Eby, R. E.; Kollie, T. G.* "Investigation of Pt <sup>+</sup> Secondary Ion Yield Enhancement Observed in Platinum and Platinum-Rhodium Alloys"	<i>Proc. 26th Annu. Conf. Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978</i> , American Society for Mass Spectrometry, St. Louis, Mo., 1978, p. 369

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	Guerin, M. R.; Clark, B. R.; Ho, C.-h.; Epler, J. L.;* Rao, T. K.* "Short-Term Bioassay of Complex Organic Mixtures: Part I. Chemistry"	<i>Proc. Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Va., Feb. 21-23, 1978</i> , EPA-600-9-78-027, Environmental Protection Agency, Washington, D.C., (September 1978), p. 247
	Epler, J. L.;* Clark, B. R.; Ho, C.-h.; Guerin, M. R.; Rao, T. K.* "Short-Term Bioassay of Complex Organic Mixtures: Part II. Mutagenicity Testing"	<i>Proc. Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Va., Feb. 21-23, 1978</i> , EPA-600-9-78-027, Environmental Protection Agency, Washington, D.C., (September 1978), p. 269
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Dale, J. M.	Hulett, L. D.; Dunn, H. W.; Dale, J. M.; Emery, J. F.; Lyon, W. S.; Murty, P. S.* "The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron, X-ray and Nuclear Physics Methods"	<i>Measurement, Detection, and Control of Environmental Pollutants</i> , IAEA SM 206/1, International Atomic Energy Agency, Vienna, Austria, 1977
Donohue, D. L.	Carter, J. A.; Donohue, D. L. "An Electro-Optical Detector for Spark Source Mass Spectrometry"	<i>Proc. 26th Annu. Conf. Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978</i> , American Society for Mass Spectrometry, St. Louis, Mo., 1978, p. 383
Dunn, H. W.	Hulett, L. D.; Dunn, H. W.; Dale, J. M.; Emery, J. F.; Lyon, W. S., Murty, P. S.* "The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron, X-ray and Nuclear Physics Methods"	<i>Measurement, Detection, and Control of Environmental Pollutants</i> , IAEA SM 206/1, International Atomic Energy Agency, Vienna, Austria, 1977

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Dyer, F. F.	Dyer, F. F. "ANGEL: A Conversational Program for Nuclear Fuel Element Scanning by Ge(Li) Gamma Spectroscopy"	<i>Proc. ANS Conference on Computers in Activation Analysis and Gamma-Ray Spectroscopy, Mayaguez, Puerto Rico, Apr. 30-May 4, 1978</i> , vol. 28, suppl. 1, American Nuclear Society, LaGrange Park, Ill., 1978, p. 66
Eby, R. E.	Christie, W. H.; Eby, R. E.; Kollie, T. G.* "Investigation of Pt <sup>+</sup> Secondary Ion Yield Enhancement Observed in Platinum and Platinum-Rhodium Alloys"	<i>Proc. 26th Annu. Conf. Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978</i> , American Society for Mass Spectrometry, St. Louis, Mo., 1978, p. 369
Eldridge, J. S.	Oakes, T. W.*; Shank, K. E.*; Eldridge, J. S. "Quality Assurance Applied to an Environmental Surveillance Program"	<i>Proc. 4th Joint Conf. Sensing of Environmental Pollutants, New Orleans, La., Nov. 6-11, 1977</i> , American Chemical Society, Washington, D.C., 1978, Paper No. 64, p. 226
Emery, J. F.	Hulett, L. D.; Dunn, H. W.; Dale, J. M.; Emery, J. F.; Lyon, W. S.; Murty, P. S.* "The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron, X-ray and Nuclear Physics Methods"	<i>Measurement, Detection, and Control of Environmental Pollutants</i> , IAEA SM 206/1, International Atomic Energy Agency, Vienna, Austria, 1977
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	Guerin, M. R.; Clark, B. R.; Ho, C.-h.; Epler, J. L.*; Rao, T. K.* "Short-Term Bioassay of Complex Organic Mixtures: Part I. Chemistry"	<i>Proc. Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Va., Feb. 21-23, 1978</i> , EPA-600-9-78-027, Environmental Protection Agency, Washington, D.C., (September 1978), p. 247
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Guerin, M. R.	Guerin, M. R.; Epler, J. L.;* Griest, W. H.; Clark, B. R.; Rao, T. K.* "Polycyclic Aromatic Hydrocarbons from Fossil Fuel Conversion Processes"	<i>Proc. 2d Int. Symposium on Polynuclear Aromatic Hydrocarbons, Carcinogenesis: Polynuclear Aromatic Hydrocarbons</i> , P. W. Jones and R. I. Freudenthal, eds., Raven Press, New York, 1978, p. 21
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Ho, C.-h.	Guerin, M. R.; Ho, C.-h.; Clark, B. R.; Epler, J. L.;* Rao, T. K.* "Separation of Mutagenic Components in Synthetic Crude"	<i>Proc. 175th Am. Chem. Soc. Nat. Meeting, Anaheim, Calif., Mar. 12-17, 1978</i> , ACS Division of Environmental Chemistry Preprint 18, No. 1, American Chemical Society, Washington, D.C., 1978, p. 34
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Layton, F. L.	Layton, F. L. <i>Laboratory Procedures for the Analysis of HTGR Fuels and Materials</i>	GCR-78/12 (June 1978)
	Layton, F. L. <i>Evaluation of Techniques for Detecting Defective Silicon Carbide Coatings</i>	ORNL/NFW-78/5 (October 1978)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Lee, D. A.	Lee, D. A.; Stinton, D. P.* <i>Evaluation of Urania Gel Pyrolysis by Mass Spectrometry</i>	ORNL/TM-6538 (October 1978)
Lewis, E. B.*	Ross, R. H.*; Yeatts, Jr., L. B.; Lewis, E. B.*; Dailey, G. A.*; Harnden, D. S.*; Michelson, D. C.*; Frogge, L. M.* <i>Environmental and Health Aspects of Selected Organohalide Compounds: An Information Overview</i>	ORNL/EIS-105 (1978)
Longest, A. W.*	Pruitt, M. E.; Longest, A. W.* <i>In-Line Tritium Monitoring in the GCFR Vented Irradiation Capsule GB-10</i>	ORNL/TM-6387 (August 1978)
Love, T. A.*	Dickens, J. K.*; Emery, J. F.; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.*; Weaver, H.* <i>Fission-Product Energy Release for Times Following Thermal-Neutron Fission of Pu-239 Between 2 and 14,000 Seconds</i>	ORNL/NUREG-34 (April 1978)
	Dickens, J. K.*; Love, T. A.*; McConnell, J. W.*; Emery, J. P.; Northcutt, K. J.; Peelle, R. W.*; Weaver, H.* <i>Delayed Beta- and Gamma-Ray Production Due to Thermal-Neutron Fission of U-235 Spectral Distributions for Times After Fission Between 2 and 14,000 Seconds; Tabular and Graphical Data</i>	ORNL/NUREG-39 (August 1978)
	Dickens, J. K.*; Emery, J. F.; Freestone, R. M.*; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for April-June 1977</i>	ORNL/NUREG/TM-156 (November 1977)
	Dickens, J. K.*; Emery, J. F.; Freestone, R. M.*; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for July-September 1977</i>	ORNL/NUREG/TM-174 January 1978)
	Dickens, J. K.*; Emery, J. F.; Freestone, R. M.*; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for October-December 1977</i>	ORNL/NUREG/TM-191 (May 1978)
	Dickens, J. K.*; Emery, J. F.; Freestone, R. M.*; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.* <i>Final Progress Report Fission Product Beta and Gamma Energy Release Progress Report for January-May 1978</i>	ORNL/NUREG/TM-223 (August 1978)
Lyon, W. S.	Lyon, W. S. <i>Analytical Chemistry Division Research and Development Summary for December 1977; Analytical Methodology Section</i>	ORNL/CF-77/506 (1978)
	Lyon, W. S. <i>Analytical Chemistry Division Research and Development Summary for April 1978; Analytical Methodology Section</i>	ORNL/CF-78/182 (1978)
	Lyon, W. S. <i>Report of Foreign Travel</i>	ORNL/FTR-388 (1978)
	Lyon, W. S. <i>Analytical Chemistry Division Research and Development Summary for August 1978; Analytical Methodology Section</i>	ORNL/CF-78/291 (September 1978)
	Lyon, W. S. <i>Analytical Chemistry Division Research and Development Summary for December 1978; Analytical Methodology Section</i>	ORNL/CF-79/15 (January 1979)
MacDougall, C. S.	MacDougall, C. S. <i>Literature Survey of Assay Methods for Thorium</i>	ORNL/CF-78/93 (1978)
	MacDougall, C. S. <i>Determination of Mono butylphosphoric Acid and Dibutylphosphoric Acid in Tributyl Phosphate-Dodecane Extracting Solutions</i>	ORNL/TM-6268 (1978)
	MacDougall, C. S. <i>Evaluation of the Mettler Automatic Titrator</i>	ORNL/CF-78/156 (1978)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Manning, D. L.	Manning, D. L. <i>Gas Chromatographic Study of Organophosphorus Compounds Using Dexsil 300 as a Stationary Phase and Hydrogen Flame Ionization Detector</i>	ORNL/TM-6423 (1978)
	Manning, D. L. <i>Separation of Nitrate-Nitrite and Nitrate-Azide Mixtures by Liquid Chromatography</i>	ORNL/TM-6335 (1978)
Martin, W. J.*	Dyer, F. F.; Wichner, R. P.;* Martin, W. J.;* Fairchild, L. L.* <i>Distribution of Fission Products in Peach Bottom HTGR Fuel Element F03-01</i>	ORNL/TM-5996 (May 1978)
McConnell, J. W.*	Dickens, J. K.;* Emery, J. F.; Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.;* Weaver, H.* <i>Fission-Product Energy Release for Times Following Thermal-Neutron Fission of Pu-239 Between 2 and 14,000 Seconds</i>	ORNL/NUREG-34 (April 1978)
	Dickens, J. K.;* Love, T. A.;* McConnell, J. W.;* Emery, J. F.; Northcutt, K. J.; Peelle, R. W.;* Weaver, H.* <i>Delayed Beta- and Gamma-Ray Production Due to Thermal-Neutron Fission of U-235 Spectral Distributions for Times After Fission Between 2 and 14,000 Seconds; Tabular and Graphical Data</i>	ORNL/NUREG-39 (August 1978)
	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for April-June 1977</i>	ORNL/NUREG/TM-156 (November 1977)
	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for July-September 1977</i>	ORNL/NUREG/TM-174 (January 1978)
	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for October-December 1977</i>	ORNL/NUREG/TM-191 (May 1978)
	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Final Progress Report Fission Product Beta and Gamma Energy Release Progress Report for January-May 1978</i>	ORNL/NUREG/TM-223 (August 1978)
Michelson, D. C.*	Ross, R. H.;* Yeatts, Jr., L. B.; Lewis, E. B.;* Dailey, G. A.;* Harnden, D. S.;* Michelson, D. C.;* Frogge, L. M.* <i>Environmental and Health Aspects of Selected Organohalide Compounds: An Information Overview</i>	ORNL/EIS-105 (1978)
Musick, W. R.	Carter, J. A.; Franklin, J. C.; Donohue, D. L.; Landau, L.; Musick, W. R. <i>High Radiation Level Spark Source Mass Spectrometry; Instrumental and Laboratory Feasibility Study</i>	ORNL/TM-6203 (1978)
Nestor, Jr., C. W.*	Krause, M. O.;* Nestor, Jr., C. W.;* Sparks, Jr., C. J.;* Ricci, E. <i>X-Ray Fluorescence Cross Sections for K and L X-Rays of the Elements</i>	ORNL-5399 (June 1978)
Northcutt, K. J.	Dickens, J. K.;* Emery, J. F.; Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.;* Weaver, H.* <i>Fission-Product Energy Release for Times Following Thermal-Neutron Fission of Pu-239 Between 2 and 14,000 Seconds</i>	ORNL/NUREG-34 (April 1978)
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	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for July-September 1977</i>	ORNL/NUREG/TM-174 (January 1978)
	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Fission Product Beta and Gamma Energy Release Quarterly Progress Report for October-December 1977</i>	ORNL/NUREG/TM-191 (May 1978)
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Peelle, R. W.*	Dickens, J. K.;* Emery, J. F.; Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.;* Weaver, H.* <i>Fission-Product Energy Release for Times Following Thermal-Neutron Fission of Pu-239 Between 2 and 14,000 Seconds</i>	ORNL/NUREG-34 (April 1978)
	Dickens, J. K.;* Love, T. A.;* McConnell, J. W.;* Emery, J. F.; Northcutt, K. J.; Peelle, R. W.;* Weaver, H.* <i>Delayed Beta- and Gamma-Ray Production Due to Thermal-Neutron Fission of U-235 Spectral Distributions for Times After Fission Between 2 and 14,000 Seconds; Tabular and Graphical Data</i>	ORNL/NUREG-39 (August 1978)
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	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peelle, R. W.* <i>Final Progress Report Fission Product Beta and Gamma Energy Release Progress Report for January-May 1978</i>	ORNL/NUREG/TM-223 (August 1978)
Pruitt, M. E.	Pruitt, M. E.; Longest, A. W.* <i>In-Line Tritium Monitoring in the GCFR Vented Irradiation Capsule GB-10</i>	ORNL/TM-6387 (August 1978)
Quincy, R. B.	Griest, W. H.; Quincy, R. B.; Guerin, M. R. <i>Selected Constituents in the Smoke of Domestic Low Tar Cigarettes</i>	ORNL/TM-6144 (1978)
Raridon, R. J.*	Botts, J. L.; Raridon, R. J.;* Costanzo, D. A. <i>Density, Acidity, and Conductivity Measurements of Uranyl Nitrate/Nitric Acid Solutions</i>	ORNL/TM-6491 (October 1978)
Ricci, E.	Krause, M. O.;* Nestor, Jr., C. W.;* Sparks, Jr., C. J.;* Ricci, E. <i>X-Ray Fluorescence Cross Sections for K and L X-Rays of the Elements</i>	ORNL-5399 (June 1978)
Ross, R. H.*	Ross, R. H.;* Yeatts, Jr., L. B.; Lewis, E. B.;* Dailey, G. A.;* Harnden, D. S.;* Michelson, D. C.;* Frogge, L. M.* <i>Environmental and Health Aspects of Selected Organohalide Compounds: An Information Overview</i>	ORNL/EIS-105 (1978)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Smith, D. H.	Smith, D. H. <i>Report of Foreign Travel to Vienna, Austria</i>	ORNL/FTR-343 (1978)
	Carter, J. A.; Smith, D. H. <i>Report of Foreign Travel</i>	ORNL/FTR-401 (1978)
	Smith, D. H. <i>Mass and Emission Spectrometry in the Analytical Chemistry Division of Oak Ridge National Laboratory</i>	ORNL/TM-6485 (November 1978)
	Carter, J. A.; Smith, D. H.; Walker, R. L. <i>Summary Report of TASTEX Task J: Resin Bead Mass Spectrometry for Safeguards</i>	ORNL/TM-6612 (October 1978)
	Smith, D. H.; Walker, R. L.; Bertram, L. K.; Carter, J. A. <i>Single-Stage Mass Spectrometric Analyses of Resin Bead Samples (Progress Report for: Division of Safeguards and Security)</i>	ORNL/TM-6563 (October 1978)
Sparks, Jr., C. J.*	Krause, M. O.*; Nestor, Jr., C. W.*; Sparks, Jr., C. J.*; Ricci, E. <i>X-Ray Fluorescence Cross Sections for K and L X-Rays of the Elements</i>	ORNL-5399 (June 1978)
Stinton, D. P.*	Lee, D. A.; Stinton, D. P.* <i>Evaluation of Urania Gel Pyrolysis by Mass Spectrometry</i>	ORNL/TM-6538 (October 1978)
Stokely, J. R.	Stokely, J. R. <i>Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section (March 1978)</i>	ORNL/CF-78/169 (1978)
	Stokely, J. R. <i>Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section</i>	ORNL/CF-78/267 (August 1978)
Strain, J. E.	Strain, J. E. <i>The Fluorophotometric Determination of Uranium: An Automated Sintering Furnace and Factors Affecting Precisions</i>	ORNL/TM-6431 (1978)
	Strain, J. E. <i>An In-Line Neutron Poison Monitor</i>	ORNL/TM-6432 (1978)
Walker, R. L.	Carter, J. A.; Smith, D. H.; Walker, R. L. <i>Summary Report of TASTEX Task J: Resin Bead Mass Spectrometry for Safeguards</i>	ORNL/TM-6612 (October 1978)
	Smith, D. H.; Walker, R. L.; Bertram, L. K.; Carter, J. A. <i>Single-Stage Mass Spectrometric Analyses of Resin Bead Samples (Progress Report for: Division of Safeguards and Security)</i>	ORNL/TM-6563 (October 1978)
Weaver, H.*	Dickens, J. K.*; Emery, J. F.; Love, T. A.*; McConnell, J. W.*; Northcutt, K. J.; Peelle, R. W.*; Weaver, H.* <i>Fission-Product Energy Release for Times Following Thermal-Neutron Fission of Pu-239 Between 2 and 14,000 Seconds</i>	ORNL/NUREG-34 (April 1978)
	Dickens, J. K.*; Love, T. A.*; McConnell, J. W.*; Emery, J. F.; Northcutt, K. J.; Peelle, R. W.*; Weaver, H.* <i>Delayed Beta- and Gamma-Ray Production Due to Thermal-Neutron Fission of U-235 Spectral Distributions for Times After Fission Between 2 and 14,000 Seconds; Tabular and Graphical Data</i>	ORNL/NUREG-39 (August 1978)
Wichner, R. P.*	Dyer, F. F.; Wichner, R. P.*; Martin, W. J.*; Fairchild, L. L.* <i>Distribution of Fission Products in Peach Bottom HTGR Fuel Element F03-01</i>	ORNL/TM-5996 (May 1978)
Yeatts, Jr., L. B.	Ross, R. H.*; Yeatts, Jr., L. B.; Lewis, E. B.*; Dailey, G. A.*; Harnden, D. S.*; Michelson, D. C.*; Frogge, L. M.* <i>Environmental and Health Aspects of Selected Organohalide Compounds: An Information Overview</i>	ORNL/EIS-105 (1978)

## ORAL PRESENTATIONS

As in previous years, staff members have presented papers 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

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Ball, F. L.	Ball, F. L.; Gude, W. D.;* Weinberger, A. J. "Optical and Electron Microscopy Studies of the Retention of Asbestos Fibers in Rat Lung"	22d Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 10-12, 1978
Bell, J. T.*	Bell, J. T.;* Redman, J. D.;* Bittner, H. F.;* Christie, W. H. "Tritium Permeation Through Incoloy 800 Oxidized In Situ by Water Vapor"	Fusion Technology Meeting, Los Alamos, N.M., May 10, 1978
Buchanan, M. V.	Buchanan, M. V. "Positional and Geometric Characterization of Olefinic Double Bonds Using Fluorine Magnetic Resonance Spectrometry"	Chemistry Department, University of Tennessee, Knoxville, Nov. 21, 1978
Canada, D. C.	Canada, D. C. "Ion Structure Analyses: Using the MS-50 Combined Scan Mode"	KRATOS Users' Meeting, St. Louis, Mo., Apr. 26-27, 1978
Carter, J. A.	Carter, J. A.; Walker, R. L. "Contributions of Mass Spectrometry to Nuclear Safeguards"	Seminar on Contributions of Mass Spectrometry to Nuclear Safeguards, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada, Apr. 14, 1978
	Carter, J. A.; Walker, R. L. "Application of Resin Bead and Mass Spectrometry for the Determination of Nanogram Amounts of Plutonium and Uranium Isotopes"	12th Middle Atlantic Regional Meeting of the American Chemical Society, Hunt Valley, Md., Apr. 4-6, 1978
Christie, W. H.	Christie, W. H.; White, C. W.;* Pronko, P. P.;* Appleton, B. R.;* Wilson, S. R.;* Young, R. T.;* Wang, J. C.;* Wood, R. F.;* Magee, C. W.* "Dopant Profile Changes Induced by Pulsed Laser Annealing of Ion Implanted Silicon"	International Conference on Ion Beam Modification of Materials, Budapest, Hungary, Sept. 4-8, 1978
	Christie, W. H.; Narayan, J.;* Young, R. T.;* Wood, R. F.* " <i>p-n</i> Junction Formation by Laser-Induced Diffusion"	Workshop on Laser Effects in Ion Implanted Semiconductors, Cantania, Italy, Aug. 31-Sept. 2, 1978
	Christie, W. H.; Wang, J. C.;* Wood, R. F.;* White, C. W.;* Appleton, B. R.;* Pronko, P. P.;* Wilson, S. R.* "Dopant Profile Changes Induced by Laser Irradiation of Silicon - Comparison of Theory and Experiment"	Symposium sponsored by the Materials Research Society on Laser-Solid Interactions and Laser Processing, Boston, Mass., Nov. 28-Dec. 1, 1978
	Christie, W. H. "Indexed Sensitivity Factors as a Technique for Quantifying SIMS Data"	Post-Seminar Symposium, Japan Microbeam Society, Shigaku-kaikan, Tokyo, Japan, Oct. 30, 1978
	Christie, W. H.; Young, R. T.;* White, C. W.;* Narayan, J.* "Characterization of Boron-Implanted, Laser Annealed Silicon"	153d Meeting of the Electrochemical Society, Seattle, Wash., May 21-26, 1978
	Christie, W. H.; White, C. W.;* Wang, J. C.;* Young, R. T.;* Eby, R. E.; Clark, G. J.* "Redistribution of Ion-Implanted Boron Induced by Pulsed Laser Annealing"	153d Meeting of the Electrochemical Society, Seattle, Wash., May 21-26, 1978

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
	Christie, W. H.; Kollie, T. G.;* Eby, R. E. "Investigation of Pt <sup>+</sup> Secondary Ion Yield Enhancement Observed in Platinum and Platinum-Rhodium Alloys"	26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978
	Christie, W. H.; White, C. W.* "The Effect of Laser Annealing on the Redistribution of Boron in Ion Implanted and Boron Deposited Silicon"	U.S.-Japan Seminar on Fundamentals and Applications of SIMS, Takarazuka, Japan, Oct. 26-27, 1978
	Christie, W. H. "The Use of Indexed Sensitivity Factors in the Analysis of Nickel and Iron Based Alloys: A Study of the Decalibration of Sheathed Chromel/Alumel Thermocouples"	U.S.-Japan Seminar on Fundamentals and Applications of SIMS, Takarazuka, Japan, Oct. 26-27, 1978
Clark, B. R.	Clark, B. R.; Goeckner, N. A.;* Rubin, I. B. "Organic Chemical Characterization of a Crude Shale Oil"	Confab 78: Government, Industry, and Academic Technical Conference on Fossil Fuel Chemistry and Energy, Saratoga, Wyo., July 25-28, 1978
	Clark, B. R.; Horton, A. D.; Higgins, C. E.; Guerin, M. R.; McBay, E. H.; Ekman, J.;* Bienstock, D.;* White, C. M.;* McCann, C. R.;* Mathur, M. P.;* Schweighart, F. K.;* Sharkey, A. G.;* Poulson, R. E.* "The Nature of Stack Emissions from the Experimental-Scale Combustion of Crude Oil"	Symposium on Potential Health and Environmental Effects of Fossil Fuel Technologies, Gatlinburg, Tenn., Sept. 25-28, 1978
Coffin, D. L.*	Coffin, D. L.;* Guerin, M. R.; Griest, W. H. "The Interagency Program in Health Effects of Synthetic Fossil Fuels Technologies: Operation of a Materials Repository"	Symposium on Potential Health and Environmental Effects of Fossil Fuel Technologies, Gatlinburg, Tenn., Sept. 25-28, 1978
Corbin, L. T.	Corbin, L. T. "Analytical Methods and Laboratories for Safeguards and Accountability Present and Future"	American Nuclear Society Topical Meeting on Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Material, Williamsburg, Va., May 15-17, 1978
Cowser, K. E.*	Cowser, K. E.;* Guerin, M. R.; Klein, J. A.* "Monitoring and Testing Program for a Low-BTU Gasifier"	DOE Environmental Control Symposium, Washington, D.C., Nov. 28-30, 1978
Dale, J. M.	Dale, J. M.; Hulett, L. D. "High Temperature Effects on Co-Mo-Alumina Catalysts"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 28-30, 1978
Donohue, D. L.	Donohue, D. L.; Carter, J. A. "An Electro-Optical Detector for Spark Source Mass Spectrometry"	26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28-June 2, 1978
Dunn, H. W.	Dunn, H. W. "X-Ray Diffraction Sample Holder for Radioactive Samples or Samples that React with Air or Light"	American Nuclear Society Topical Meeting on Analytical Methods for Safeguards and Accountability Measurements of Special Nuclear Material, Williamsburg, Va., May 15-17, 1978

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Dyer, F. F.	Dyer, F. F. "ANGEL: A Conversational Program for Nuclear Element Scanning by Ge(Li) Spectroscopy"	American Nuclear Society Topical Conference on Computers in Activation Analysis and Gamma Ray Spectroscopy, Mayaguez, Puerto Rico, Apr. 30-May 4, 1978
	Dyer, F. F. "The Use of Neutron Activation Analysis Criminalistics - A Look at the Past and a Peek at the Future"	ORAU Traveling Lecture Series, Western Maryland College, Westminster, Md., Feb. 13, 1978
Eldridge, J. S.	Eldridge, J. S.; Oakes, T. W. * "Gamma-Ray Spectral Determinations with a Portable Analyzer"	11th Midyear Symposium, Health Physics Society, San Diego, Calif., Jan. 15-19, 1978
Ellis, Y. A. *	Ellis, Y. A.;* Emery, J. F. "Levels in U-233 Observed in Pu-237 Alpha Decay"	American Physical Society Meeting, Washington, D.C., Apr. 24-27, 1978
Ensor, D. D. *	Ensor, D. D.;* Young, J. P.; Peterson, J. R.;* Haire, R. G.* "Spectrophotometric Study of Berkelium and Einsteinium Fluorides in the Solid State"	30th ACS Southeastern Regional Meeting, Savannah, Ga., Nov. 8-10, 1978
Epler, J. L. *	Epler, J. L.;* Young, J. A.;* Rao, T. K.;* Guerin, M. R.; Ho, C.-h.; Clark, B. R. "Isolation and Identification of Mutagenic Components from Synthetic Fuels"	9th Annual Meeting of Environmental Mutagen Society, San Francisco, Calif., Mar. 9-13, 1978
	Epler, J. L.;* Clark, B. R.; Ho, C.-h.; Guerin, M. R.; Rao, T. K.* "Short-Term Bioassay of Complex Organic Mixtures: Part II. Mutagenicity Testing"	Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Va., Feb. 21-23, 1978
Feldman, C.	Feldman, C. "Improvements in the Arsine Accumulation-Helium Glow Detector Procedure for Determining Traces of Arsenic"	1st Symposium on Environmental Analytical Chemistry, Brigham Young University, Provo, Utah, June 21-23, 1978
	Feldman, C.; Batistoni, D. A. * "Spectroscopic Element Detector for Gas Chromatography"	American Chemical Society Meeting, Anaheim, Calif., Mar. 12-18, 1978
Franklin, J. C.	Franklin, J. C. "Spark Source Mass Spectrometry at ORNL"	Seminar at Rocky Flats, Colo., July 20-21, 1978
Goldberg, G.	Goldberg, G. "Testing of Coatings for the Nuclear Industry"	1st International Conference on Durability of Building Materials and Components, Ontario, Canada, Aug. 21, 1978
Griest, W. H.	Griest, W. H. "Multicomponent Polycyclic Aromatic Hydrocarbon Analysis of Inland Water and Sediment"	International Symposium on Analysis of Hydrocarbons and Halogenated Hydrocarbons, McMaster University, Ontario, Canada, May 23-25, 1978
	Griest, W. H.; Kubota, H.; Eatherly, W. P. * "Characterization of PAH-Containing Fugitive Emissions from a Laboratory Scale Graphite Production Operation"	Light Metals Session of Meeting of American Institute of Mining, Metallurgical, and Petroleum Engineers, Denver, Colo., Feb. 26-Mar. 2, 1978
	Griest, W. H.; Guerin, M. R.; Clark, B. R.; Ho, C.-h.; Rubin, J. B.; Jones, A. R. "Relative Chemical Composition of Selected Synthetic Crudes"	Symposium on Assessing the Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries, Upton, N.Y., Nov. 6, 1978

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Guerin, M. R.	Guerin, M. R.; Clark, B. R.; Ho, C.-h.; Epler, J. L.;* Rao, T. K.* "Short-Term Bioassay of Complex Organic Mixtures: Part I. Chemistry"	Symposium on Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, Va., Feb. 21-23, 1978
	Guerin, M. R.; Ho, C.-h.; Clark, B. R.; Epler, J. L.;* Rao, T. K.* "Separation of Mutagenic Components in Synthetic Crudes"	American Chemical Society, Division of Environmental Chemistry, Anaheim, Calif., Mar. 12-18, 1978
	Guerin, M. R. "Bioassay Chemistry of Complex Mixtures"	USDOE/DBER Contractor Meeting-Workshop on Review and Development of Biotesting Programs for Energy Utilization, Boca Raton, Fla., Nov. 11-15, 1978
	Guerin, M. R.; Horton, A. D.; Maskarinec, M. P. "Separation of Tobacco Volatiles by GC and LC"	7th Annual Meeting on the Practice of Chromatography presented by Committee E-19 of the ASTM, Atlanta, Ga., Oct. 22-25, 1978
Herbes, S. E.*	Herbes, S. E.;* Southworth, G. R.;* Griest, W. H. "Field Site Evaluation of Aquatic Transport of Polycyclic Aromatic Hydrocarbons"	Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, Gatlinburg, Tenn., Sept. 25-28, 1978
Hobart, D. E.*	Hobart, D. E.;* Young, J. P.; Peterson, J. R.* "Spectroelectrochemical Investigations of Some Lanthanides and Actinides"	30th ACS Southeastern Regional Meeting, Savannah, Ga., Nov. 8-10, 1978
Hulett, L. D.	Hulett, L. D.; Turner, R. R.; Dale, J. M.; Weinberger, A. J.; Dunn, H. W.; Feldman, C.; Thomson, J. O.* Ricci, E. "Some Studies of Chemical Species in Fly Ash"	Symposium on Advances in Particle Sampling and Measurement, Research Triangle Park, N.C., May 15-17, 1978
	Hulett, L. D.; Dunn, H. W. "Quantitative Analysis by X-Ray Fluorescence Using First Principles for Matrix Correction"	ORAU Traveling Lecture Series, Oklahoma State University, Stillwater, Okla., Feb. 9, 1978
	Hulett, L. D. "Surface Analysis by Electron Spectroscopy and Electron Microscopy Methods"	ORAU Traveling Lecture Series, University of North Carolina, Wilmington, Feb. 17, 1978
	Hulett, L. D.; Dale, J. M.; Dunn, H. W.; Ricci, E.; Weinberger, A. J.; Feldman, C.; Thomson, J. O.* "Some Suggestions for the Analysis and Study of Fly Ash Surfaces"	EPRI Workshop in Fly Ash, Palo Alto, Calif., May 23-26, 1978
	Hulett, L. D.; Weinberger, A. J.; Turner, R. R.;* Dale, J. M.; Dunn, H. W.; Feldman, C.; Thomson, J. O.* "The Chemical Speciation of Fly Ash"	22d Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 10-12, 1978
Hurst, G. S.*	Hurst, G. S.;* Young, J. P.; Kramer, S. D.* Bemis, C. E.* "Detection of Single Atoms in Particle Tracks"	6th Symposium on Microdosimetry, Brussels, Belgium, May 22-26, 1978
Jenkins, R. A.	Jenkins, R. A.; Guerin, M. R. "Monitoring of the NCI Cigarette Smoke Inhalation Bioassays"	NCI Smoking and Health Consultants Workshop, Bethesda, Md., May 24, 1978
	Jenkins, R. A.; Gill, B. E. "Procedures for the Determination of Nitric Oxide and Nitrogen Dioxide in Cigarette Smoke by Chemiluminescent Analysis"	32d Tobacco Chemists' Research Conference, Montreal, Canada, Oct. 31-Nov. 1, 1978

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Klatt, L. N.	Klatt, L. N. "Simultaneous Multi-Component Detection in Liquid Chromatography"	American Chemical Society Analytical Summer Symposium, Boulder, Colo., June 26-28, 1978
	Klatt, L. N. "Simultaneous Multi-Wavelength Detection in Liquid Chromatography"	Seminar at the Measurement Research Branch, NIOSH, Cincinnati, Ohio, Dec. 1, 1977
Kramer, S. D.*	Kramer, S. D.;* Young, J. P.; Bemis, C. E.;* Hurst, G. S.* "Selective, Laser One-Atom Detection of Neutral Prompt Fission Fragments"	10th International Quantum Electronics Conference, Atlanta, Ga., May 29-June 1, 1978
Lyon, W. S.	Lyon, W. S.; Carter, J. A.; Emery, J. F.; Rickard, R. R.; Lindberg, S. E.;* Van Hook, R. I.;* Raridon, R. J.* "Analytical Determination and Statistical Relationships of Forty-One Elements in Coal from Three Coal-Fired Steam Plants"	International Symposium on Nuclear Activation Techniques in the Life Sciences, Vienna, Austria, May 22-26, 1978
	Lyon, W. S. "Trace Metal Releases"	Invited lecture, ORAU Professional Training Programs, Oak Ridge, Tenn., Aug. 3, 1978
MacDougall, C. S.	MacDougall, C. S. "Potentiometric Determination of Thorium"	22d Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 10-12, 1978
Mamantov, G.	Mamantov, G.; Norvell, V. E.;* Klatt, L. N. "Spectroelectrochemistry in Melts: Applications to Molten Chloraluminates"	Fall Meeting of the Electrochemical Society, Pittsburgh, Pa., Oct. 15-19, 1978
Maskarinec, M. P.	Maskarinec, M. P.; Caton, J. E.; Guerin, M. B. "Characterization of Physiological Fluids; Dosimetry and Impact"	NCI Smoking and Health Consultants Workshop, Bethesda, Md., May 24, 1978
	Maskarinec, M. P.; Harvey, R. W.; Caton, J. E. "Rapid, Quantitative Determination of Nicotine by High-Pressure Liquid Chromatography"	32d Tobacco Chemists' Research Conference, Montreal, Quebec, Canada, Oct. 31-Nov. 1, 1978
Mueller, T. R.	Mueller, T. R. "An Electronics Bug with a Calomel Hat"	Symposium in Honor of Professor Ralph N. Adams, University of Kansas, Lawrence, June 16-17, 1978
Pearlstein, R. M.*	Pearlstein, R. M.;* Whitten, W. B.; Olson, J. M.* "Absorption Spectra of Green Bacterial Reaction Center Complexes at 5°K"	American Physical Society, Washington, D.C., Mar. 27-29, 1978
Peterson, J. R.*	Peterson, J. R.;* Young, J. P.; Ensor, D. D.;* Fellows, R. L.;* Haire, R. G.* "Preparation, Characterization, and Decay of Einsteinium(II) in the Solid State"	3d International Conference on the Electronic Structure of the Actinides, Grenoble, France, Aug. 30-Sept. 1, 1978
Rao, T. K.*	Rao, T. K.;* Schmidt-Collerus, J. J.;* Leffler, L.;* Guerin, M. R. "Biological Monitoring of Oil Shale Products and Effluents Using Short-Term Genetic Analyses"	Oil Shale Sampling, Analyses, and Quality Assurance Symposium, Denver, Colo., Nov. 6-10, 1978
Shaw, R. W.	Shaw, R. W. "Opto-Acoustic Spectroscopy with a Pulsed Dye Laser"	Seminar, Department of Chemistry, University of Tennessee, Knoxville, Feb. 7, 1978
	Shaw, R. W. "Opto-Acoustic Spectroscopy with a Pulsed Dye Laser"	Seminar, TRL/ORNL, Oak Ridge, Tenn., May 2, 1978
Sparks, Jr., C. J.*	Sparks, Jr., C. J., Raman, S.; Ricci, E.; Krause, M. O.; Gentry, R. V. "X-ray Fluorescence with Synchrotron Radiation,"	5th Conference on the Use of Small Accelerators in Research, Teaching and Industrial Applications, Denton, Tex., Nov. 6-8, 1978, invited paper.

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Taylor, F. G.*	Taylor, F. G.;* Parr, P. D.;* Ball, F. L. "Interception and Retention of Simulated Cooling Tower Drift by Vegetation"	Cooling Tower Environment 1978, University of Maryland, College Park, May 2-4, 1978
Tomkins, B. A.	Tomkins, B. A.; Griest, W. H.; Epler, J. L.;* Rao, T. K.* "Characterization of Multialkylated Polycyclic Aromatic Hydrocarbons in Energy-Related Materials"	3d International Symposium on Polynuclear Aromatic Hydro- carbons, Columbus, Ohio, Oct. 25-27, 1978
Walker, R. L.	Walker, R. L.; Smith, D. H. "Thorium Analysis by the Isotope-Dilution-Resin Bead Method"	22d Annual Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 10-12, 1978
	Walker, R. L. "Mass Spectrometry of Th, U, and Pu in Environmental Matrices"	Analytical Chemistry Division, Information Meeting, Mar. 29-30, 1978
White, C. W.*	White, C. W.;* Christie, W. H.; Eby, R. E.; Wang, J. C.;* Young, R. T.;* Clark, G. J.* "Redistribution of Ion Implanted Boron Induced by Pulsed Laser Annealing"	Topical Conference on Characteri- zation Techniques for Semi- conductor Materials and Devices, Seattle, Wash., May 21-26, 1978
	White, C. W.;* Christie, W. H.; Pronko, P. P.;* Appleton, B. R.;* Wilson, S. R.;* Wang, J. C.;* Wood, R. F.* "Changes in Dopant Profiles by Pulsed Laser Annealing of Ion Implanted Silicon"	Laser Annealing Workshop, Catania, Italy, Aug. 31, 1978
	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"	International Conference on Ion Beam Modification of Materials, Budapest, Hungary, Sept. 4-8, 1978
Young, J. P.	Young, J. P.; Bemis, C. E.;* Kramer, S. D.;* Allman, S. L.;* Hurst, G. S.* "Recent Applications of Resonance Ionization Spectroscopy to the Study of Single Atoms"	175th National American Chemical Society Meeting Symposium on New Applications of Lasers to Chemistry, Anaheim, Calif., Mar. 12-18, 1978
	Young, J. P. "Analytical Applications of Resonance Ionization Spectroscopy"	DBER Advanced Laser Technology Workshop, ORNL, Oak Ridge, Tenn., Feb. 9, 1978
	Young, J. P. "Analytical Applications of Resonance Ionization Spectroscopy"	Workshop on One Atom Detection, ORNL, Oak Ridge, Tenn., June 27-28, 1978
	Young, J. P.; Hurst, G. S.;* Kramer, S. D.;* Bemis, C. E.;* Payne, M. G.* "Analytical Applications of Resonance Ionization Spectroscopy at the Few or Single Atom Level"	22d Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 10-12, 1978
	Young, J. P.; Haire, R. G.;* Fellows, R. L.;* Peterson, J. R.* "Chemical Consequences of the Delay of Some $^{253}\text{Es}$ and $^{249}\text{Bk}$ Halides"	175th National American Chemical Society Meeting, Anaheim, Calif., Mar. 12-17, 1978

## Analytical Chemistry Division Seminars at ORNL

SPEAKER(s)	TITLE	DATE
Koirtyohann, S. R. University of Missouri Columbia	"Spatial Structure of the ICP Discharge and Its Effects on Analytical Utility"	Dec. 15, 1977
McKay, John M. Laramie Energy Research Center Laramie, Wyo.	"Infrared Spectrometry in the Characterization of Petroleum Heavy Ends and Coal Liquids"	Jan. 17, 1978
Holland, J. F. Michigan State University E. Lansing	"Relative Fluorescence Efficiency Studies Using Natural Fluorescing Biological Systems"	Feb. 16, 1978
Pardue, H. L. Purdue University Lafayette, Ind.	"Evaluation of Energy Detectors for Analytical Applications"	Mar. 14, 1978
Oakes, T. W. ORNL	"Environmental Surveillance: Why, Where, and When?"	Apr. 20, 1978
Barnes, Ramon University of Massachusetts Amherst	"Recent Developments in Inductively Coupled Plasma Emission Spectroscopy"	May 22, 1978
Harrison, W. W. University of Virginia Charlottesville	"The Hollow Cathode Discharge as an Analytical Ion Source"	June 13, 1978
Lee, Milton L. Brigham Young University Provo, Utah	"Capillary Column Gas-Chromatographic Mass Spectrometry of Polycyclic Aromatic Hydrocarbons in Complex Mixtures"	July 24, 1978
Winefordner, J. D. University of Florida Gainesville	"Analytical Spectrometric Methods of Trace Analysis; The Past, Present and Future"	Sept. 19, 1978
Sill, C. W. Department of Energy Idaho Falls, Idaho	"Radioactive Disequilibria in Uranium Ores and Dusts"	Oct. 17, 1978
Kilty, J. W. Federal Bureau of Investigation Washington, D.C.	"Applications of Analytical Methods in the Examination of Physical Evidence"	Nov. 9, 1978

## ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodical														Total			
	<i>Anal. Chem.</i>	ASTM Methods	<i>At. Energ. Rev.</i>	<i>Biotechnol. Bioeng.</i>	<i>Chem. Instrum.</i>	<i>Environ. Sci. Technol.</i>	<i>J. Agric. Food Chem.</i>	<i>J. Electron Spectros.</i>	<i>J. Environ. Qual.</i>	<i>J. Phys. Chem. Solids</i>	<i>J. Radioanal. Chem.</i>	<i>Nucl. Technol.</i>	ORNL Reports	Proceedings		Proposals	<i>Talanta</i>	<i>Tob. Sci.</i>
Cooper, J.	1																	1
Eldridge, J. S.		1																1
Emery, J. F.		3																3
Feldman, C.		6													1			7
Guerin, M. R.																	1	1
Holmberg, R. W.						1												1
Hulett, L. D.	1						4								2			7
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Lyon, W. S.	6	1	1			3	1				2	1			7			22
Manning, D. A.		2																2
Mueller, T. R.		2			2													4
Reynolds, S. A.	1	5						1			1		2					10
Ross, H. H.										1								1
Shaw, R. W.												1			1			2
Shults, W. D.										1					2			3
Smith, D. H.	1																	1
Whitten, W.				1					1									2
Young, J. P.															2			2
Total	25	7	1	1	2	4	1	4	1	1	4	2	3	2	18	1	1	78

**DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY  
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	Funding (in thousands)	Person-years
<b>DOE PROGRAMS</b>		
Basic Energy Sciences	850	14.0
Biomedical and Environmental Research	733	12.0
Reactor Research and Development	152	2.0
Advance Fuel Recycle Program	300	4.0
Safeguards and Security	135	2.0
Miscellaneous	10	
Total DOE Programs	<u>2,180</u>	<u>34.0</u>
<b>WORK FOR OTHERS—FEDERAL AGENCIES</b>		
National Cancer Institute	420	7.5
Environmental Protection Agency	307	5.0
SRO-LWR (Savannah River)	60	1.0
SAMSO-Mass Spect	60	1.0
Miscellaneous	60	1.0
Total work for others—federal agencies	<u>907</u>	<u>15.5</u>
<b>WORK FOR OTHERS—NONFEDERAL AGENCIES</b>		
Council for Tobacco Research <sup>a</sup>	381	7.5
International Atomic Energy Agency	48	1.0
Electric Power Research Institute	232	4.0
Protective coatings companies	150	2.5
Miscellaneous	50	1.0
Total work for others—nonfederal agencies	<u>861</u>	<u>16.0</u>
ORNL DIVISIONS—SUPPORT	4,585 <sup>b</sup>	83.0
OTHERS	655 <sup>b</sup>	12.0
<b>TOTAL FINANCIAL PLANS</b>	<u>9,188</u>	<u>160.5</u>

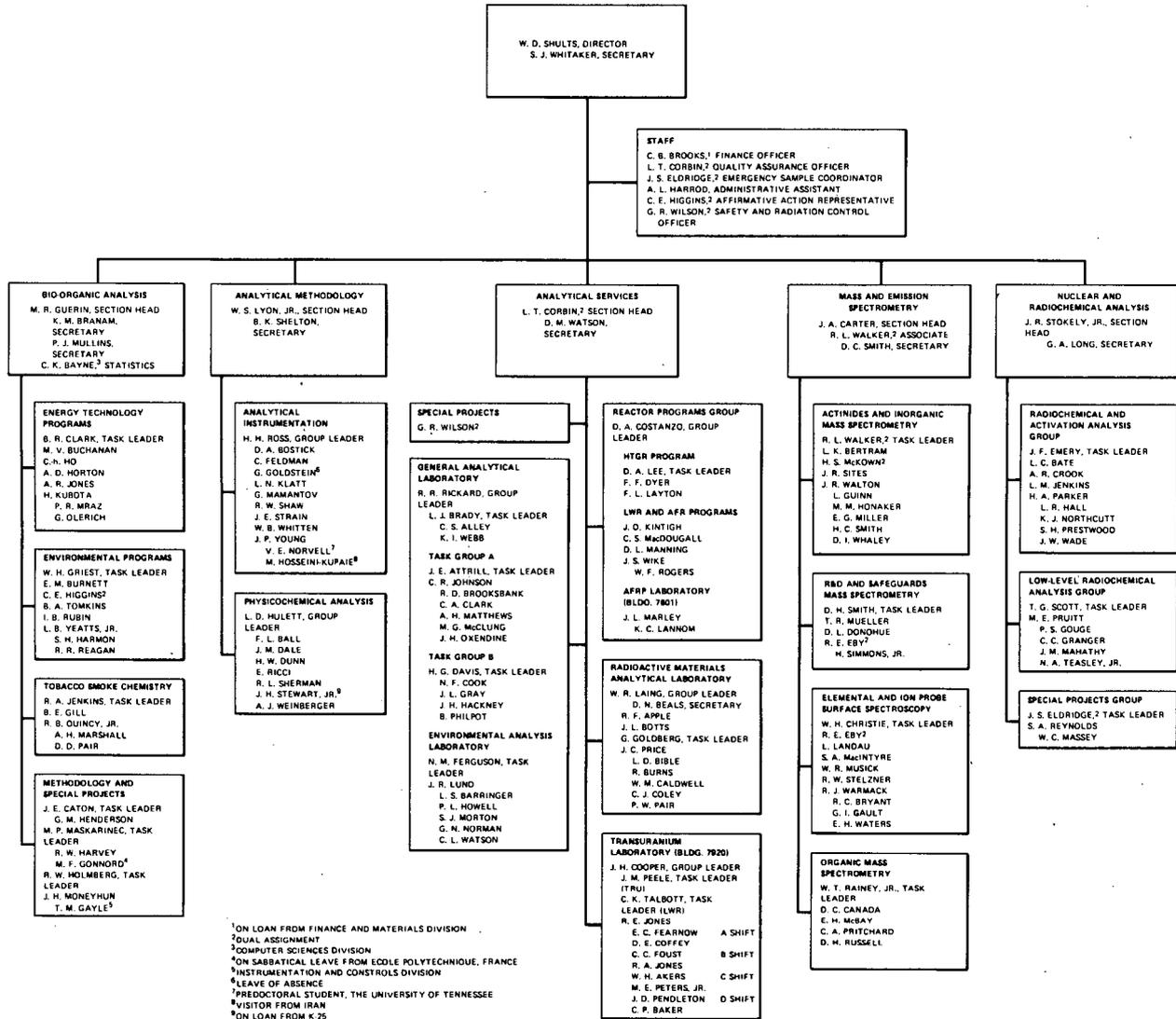
<sup>a</sup>Contract overlaps fiscal years; dollars reflected.

<sup>b</sup>Reflects Laboratory General and Administrative/General Plant Services.



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