Sh. 1918

ORNL-5360

ANALYTICAL CHEMISTRY DIVISION

MASTER

ANNUAL PROGRESS REPORT

Period Ending November 30, 1977

ORNL-5360
Distribution Category UC-4

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

For Period Ending November 30, 1977

W. D. Shults, Director

W. S. Lyon, Editor

Activities and Research Results Compilers
Brenda K. Shelton
Sharon J. Whitaker

Date Published: March 1978

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

The three-dimensional nature of the simultaneous multiwavelength liquid chromatography detection system described on pages 2 and 3 is illustrated by the series of spectra reproduced in the upper right-hand corner of the odd numbered pages of this report. To observe the absorbance vs wavelength vs time dependence of this separation, grasp the report between the thumb and index finger and then release each page in a smooth motion. The solutes are benzene, naphthalene, biphenyl, and pyrene.

Contents

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 1977 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 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 1977.
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 the laboratory; however, a significant fraction originates outside ORNL. Work from outside of an analytical service-assistance nature often involves the use of talent and or facilities in which the division is particularly strong or which are unusual or even unique. This effort accounted for approximately 50% of the budget during FY 1977.
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 is typically of a developmental nature or 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 measurements or 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 10% of the FY 1977 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 and accomplishments of the five divisional sections during the period December 1, 1976, through November 30, 1977. Some of these are highlighted in the following paragraphs.

Analytical Methodology (Chap. 1). Spectroscopy continues to be prominent in the Analytical Instrumentation Group activities. J. P. Young is the analytical member of a team that has been studying resonance ionization spectroscopy under G. S. Hurst's leadership in the Health and Safety Research Division. This technique was selected as one of the IR-100 award winners during 1977. "One-atom detection" was demonstrated with cesium in the presence of 10^{19} atoms of argon. Application to molecules has also been demonstrated by dissociating CsI molecules and then detecting the resulting cesium atoms. Resonance ionization spectroscopy is now being used in experiments that capitalize upon the uniqueness of the technique, for example, the study of one-atom events as in the proposed detection of single cesium fission fragments from californium-252. There is a natural bond between research in resonance ionization spectroscopy and the research done in the Transuranium Research Laboratory, and J. P. Young has continued to serve as liaison between the two research teams. The study of microgram quantities of the actinides—stability, reactivity, thermal properties—has continued, with microscopic-level spectrophotometry and x-ray diffraction as the prime tools. During this reporting period the chlorides, bromides, and iodides of both divalent californium and einsteinium were characterized for the first time. Higher oxidation states of californium and curium fluorides are under study.

Last year we reported initiation of work in laser-based optoacoustic spectrometry. Early emphasis has necessarily been placed on the instrumentation itself. The system is operative, though still evolving. R. W. Shaw is studying the system and its application to gases, thin layers of materials, and solids and liquids that have high optical density.

Work with a rapid-scan spectrometry system has continued, with emphasis on its use in the detection of liquid chromatographic effluents. Criteria and algorithms have been developed that allow one to acquire absorbance-wavelength-time information as chromatographic separation proceeds. The important feature here is that the computer continuously selects information for storage and processing, retaining only what is relevant. During this reporting period, we completed a study of high-powered microwave excitation sources as a potential element-selective detector for liquid chromatography; the technique lacks the desired sensitivity to be broadly useful. On the other hand, our "glow-discharge" approach continues to offer excellent sensitivity and selectivity as well as broad applicability as an element-selective detector for gas chromatography. Emphasis in this instance has been on improved background-correction techniques and on applications.

A new program was initiated this year in collaboration with the Instrumentation and Controls Division: the development of in-line monitoring instrumentation for the Advanced Fuels Recycle Program at ORNL. Our role is to conceptualize and demonstrate feasibility for the wide variety of monitors that are needed in a nuclear fuel processing facility; the I&CD role is to develop the needed software and hardware, once a given concept is selected. This is a challenging program in many respects and is especially interesting because of the diversity of measurements needs associated with the technology. Emphasis to date has been on monitors for free acid, uranium, and gadolinium.

The demand for the rather specialized measurements made in the Physicochemical Analysis Group has increased. The "fundamental parameters" approach to x-ray fluorescence analysis is now used on a wide variety of sample types. We acquired a new scanning electron microscope and have taken steps to add x-ray detection capabilities to it. Significant improvements in our electron spectrometer have been made with addition of a large sample chamber that allows isolation of sample pretreatment from sample examination. Construction of a new electrostatic spectrometer and an associated position-sensitive detector is under way.

One new program within the Physicochemical Analysis Group warrants special mention. In collaboration with the Environmental Sciences Division, we have begun to study the chemical changes that transpire in ponded fly ash. Samples have been acquired from a nearby coal-fired steam plant and are being investigated for trace element content and other characteristics that relate to "speciation." The program is designed to relate chemical change and fate with the age of ash that has been disposed of by a common practice, ponding. The determination of chemical "species" is a little-studied, extremely difficult undertaking but is important to understanding ecological and health effects. This program is sponsored by the Electric Power Research Institute.

Mass and Emission Spectrometry (Chap. 2). We mentioned construction and installation of a two-stage mass spectrometer for the International

Atomic Energy Agency (IAEA) in our last annual report. H. S. McKown has been on leave of absence, assigned to the IAEA Seibersdorf Laboratory near Vienna, Austria, to implement the use of this sophisticated instrumentation into IAEA programs. Additionally, R. L. Walker and C. A. Pritchard instructed personnel at the Seibersdorf Laboratory regarding our "resin-bead technique" and its use in safeguards analyses. We are continuing to develop applications of this technique because of its unique advantages. This year, methodology has been developed for determining traces of plutonium, uranium, and thorium in many matrices. We are now investigating the use of this method for the measurement of ^{99}Tc and ^{237}Np. Concurrently, we have initiated a project to develop a state-of-the-art *interface controller for the pulse-counting system* on the two-stage spectrometry instrumentation in this section.

Another significant new project has been initiated, which is hardware in nature. With the assistance and cooperation of personnel of the Y-12 Plant, we are conducting a feasibility study aimed at developing a spark-source mass spectrometry (SSMS) system that can be used for examination of highly radioactive (~100 R/hr of gamma radiation) materials. The ion source was modified such that it could be operated remotely in a Plexiglas mock-up hot cell located away from the instrument mainframe. Source components and samples are handled with a motorized remote manipulator and observed by television. The plan is to install SSMS instrumentation in our Radioactive Materials Analysis Laboratory, once the system design is completed and demonstrated. This instrumentation will provide powerful and unique methodology for *attacking many problems related to nuclear programs* at ORNL.

Studies of the use of inductively coupled plasma (ICP) excitation sources for emission spectrometry have continued, with emphasis on applications that benefit from the use of this approach. We have designed and constructed a new nebulizer and incorporated a dual monochromator into the system this year. These improvements have led to application of the technique to determine trace elements in organic liquids (e.g., fuel oils, crude oils) that are difficult to handle by other techniques. We were also able to use ICP for determining several trace elements (Ta, Ti, Sb, Nb, and Ru) in solutions that contained as much as 12 wt % of nickel. Another activity in emission spectrometry has been the gradual modernization of the electronics in our Paschen spectrometer system. This effort has been under way for the past 2 years and is now virtually complete.

W. H. Christie and others have continued to use and study the ion microprobe mass analyzer (IMMA) this year. Work with this unique instrument comprises "technique research," participation in specialized research projects with other ORNL personnel, and instrumentation development. Studies of the quantitation of IMMA measurements have shown that the sensitivity factor approach can provide virtually quantitative results when the matrix is well characterized and semi-quantitative results when average sensitivity factors are used. Comparative studies with other laboratories into quantitation of IMMA data continued. *In joint studies with other divisions at* ORNL, we have established the reason for decalibration of high-temperature thermocouples and recommended solutions to the problem, assisted with the study of tritium permeation into Incoloy-800, and participated in a study of laser vs thermal annealing of single-crystal silicon implanted with ^{11}B. Concurrently, we have begun to computerize the IMMA system to expedite both control and data acquisition.

Acquisition and installation of the ultrahigh-resolution AEI MS-50 and a companion DS-50 computer system were reported last year. We have put much effort into the development of methodology and computer software this year for maximum use of this state-of-the-art system. We are now able to use computer acquisition of data at resolutions as high as 40,000 and have used such resolution in collaborative work. The sensitivity at low masses has been greatly improved for gas *samples, and software has been written to allow* quantitative gas analyses, using a residual type calculation. The unique metastable scanning techniques have been of value in several problems and are being used in a basic study of alkylated phenol fragmentations.

We have developed equipment and techniques for air sampling, using Tenax absorption tubes with other (low-resolution) spectrometers. This approach has proved useful in several projects; we are investigating its application to personnel exposure monitoring. We have a continuing interest in the development and use of various "soft" ionization sources in organic mass spectrometry because these sources provide simplified spectra that have minimal fragmentation and maximal molecular ions. Emphasis has been on the field ionization technique this year. Considerable effort was put into improving the overall ionization efficiency of our low-resolution organic instrument to enhance its performance with field ionization sources, and a net gain of 200 to 400 × was achieved. Nickel and cobalt dendrites on tungsten have been prepared and used successfully as field ionization sources.

Analytical Services (Chap. 3). This section has continued to provide a broad spectrum of chemical measurements in support of numerous ORNL and extra-ORNL programs. During the reporting period, a small decrease in environmentally related work was experienced, while work related to reactor programs increased. Our work for the High Temperature Gas-Cooled Reactor Program has continued, with emphasis on the on-line monitoring of gaseous effluents from fuel fabrication operations, the experimental study of fission product behavior in components of the Peach Bottom Reactor and comparison with predicted behavior, the measurement of the percentage of defective fuel particles in samples with different types of particle coatings, and the determination of impurity sulfur in fuel rods. We also completed a study of analytical requirements for the Hot Engineering Test Facility, an inherent part of the HTGR Program, and participated in extensive planning for the needs of the Advanced Fuel Recycle Program. New work in this area has been initiated in several sections in the division. Because of the expanding effort in reactor programs, the Analytical Services Section has begun to upgrade the division's analytical hot-cell facilities.

The division's Data Management System was first reported in the last annual report. During this reporting period, the capabilities of the system have been expanded and the system has been implemented in two other laboratories. The system is now in use in the General Analysis Laboratory, the Radioactive Materials Analysis Laboratory and the Environmental Analysis Laboratory; progress has been made on plans to install the system in the Transuranium Laboratory and the Intermediate-Level Radiochemical Laboratory.

Each of the laboratories in this section must cope with a wide variety of analytical problems and special projects and characteristically participates in collaborative studies with members of other divisions. Of notable significance during this year was an extensive investigation of the amount of ^{14}C evolved when spent LWR fuel is dissolved. An all-glass apparatus for this study was designed, built, tested in mock-up, and then installed and used in the hot cells in the Radioactive Materials Analysis Laboratory. The ^{14}C content was found to be 1.95×10^4 dis sec^{-1} g^{-1} of fuel.

Another activity that warrants mention is our testing program for coatings (paints) used in the nuclear industry. G. Goldberg has set up and maintains capabilities whereby the three major tests can be performed: decontamination factor, radiation resistance, and simulated loss-of-coolant accident. During this reporting period, many steel-panel and concrete-block specimens were examined for 17 manufacturers and nuclear utility companies as part of this activity.

Bio-Organic Analysis (Chap. 4). The work of the Bio-Organic Analysis Section has continued to be 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 and interpret these studies. Some 12 projects are under way in the two major programmatic areas (1) health effects of tobacco smoke and (2) health and environmental effects of fossil-fuel technology.

Inhalation exposure is now being emphasized in programs that address the smoking-and-health question; that is, there has been some shift in our work away from assay of smokes and condensates toward development and evaluation of inhalation-exposure systems. Further work has been done this year with a standard exposure machine (the SEM-II). R. W. Holmberg and M. T. Kelley interfaced a Texas Instrument Company 5TI programmable controller to the SEM-II and programmed it to control machine operations in various modes. After evaluative studies, the system was demonstrated to the manufacturer and to the Council for Tobacco Research-USA, with the recommendation that the flexible new control system be installed on other SEM-IIs. In related work, we have designed a nebulizer for producing aerosols of controlled size from small samples, the aerosols to have known chemical and physical properties and known concentrations of specific hazardous compounds. These activities have led to increased collaboration with other laboratories that participate in inhalation bioassay programs for the National Cancer Institute. Section staff members periodically visit other laboratories and carry out experiments to ensure that the average smoke dose administered to test animals is well characterized.

Our study of the use of gel permeation chromatography on Sephadex LH-20 was first reported last year. That work has continued in support of fossil-energy programs. We have continued to fractionate and supply materials from coal- and shale-oil technologies to collaborators in the Biology and Environmental Sciences divisions and to characterize these materials. Of particular interest has been the characterization work that C.-h. Ho has done with the alkaline constituents, which are mutagenically active. W. H. Griest, H. Kubota, and many others in this section have emphasized methodology for the accurate and efficient determination of polynuclear aromatic hydrocarbons (PAH) because of the great interest attached to this class of compound in the fossil-energy programs. A new project has just begun whose objective is to develop rapid and semi-automated methodology for the PAHs.

One collaborative effort warrants special mention. A suite of shale-oil samples was obtained through the Laramie Energy Research Center and shipped to the Pittsburgh Energy Research Center for combustion under controlled conditions, and the resulting combustion-product samples were sent to ORNL for characterization and deposition in our sample repository. This interlaboratory activity should provide valuable data on the products of controlled combustion of synfuels and how they compare with the combustion products of other materials.

We have continued to study methods that define the fate of chemical insults after deposition in test animals. Studies to date have been smoke related, but the methodology has broad applicability. J. E. Caton completed a long-term study of the distribution of smoke-derived compounds in mice during this reporting period.

Nuclear and Radiochemical Analysis (Chap. 5). The Nuclear and Radiochemical Analysis Section was formed on July 1, 1977, by drawing appropriate staff and facilities from other sections and combining them into a single organizational unit. The section as currently structured comprises three groups: Low-Level Radiochemical Analysis, Intermediate-Level Radiochemical Analysis, and Neutron Activation Analysis. High-level radiochemistry (i.e., work requiring hot cells) and program support (e.g., the Transuranium Processing Facility) are not incorporated into the new section.

The Low-Level Radiochemical Analysis Group provides analytical development and sample analysis on materials containing pico- to nanocurie levels of radioactivity. Because of the increase in work load this year, three additional chemical laboratories and a counting room are being equipped for low-level analysis. New instrumentation has been acquired to provide increased alpha- and gamma-spectrometry capabilities, and equipment has been added for preparation of environmental samples for analysis. A portable spectrometer has been put into service for extra-laboratory identification and quantitation of gamma-emitting radionuclides. A developmental program has been initiated with the Industrial Safety and Applied Health Physics Division to devise new methodology for environmental monitoring and surveillance.

The Intermediate-Level Radiochemical Analysis Group performs development and sample analysis on materials containing micro- to millicurie levels of radioactivity. During the past year, the group has acquired and put into operation a new computer-multichannel analyzer system (Nuclear Data 6620). Addition of this system has resulted in significant improvements in analyses obtained by gamma-ray spectrometry. Also, initial steps have been taken to implement the division's data management system in the group. Full implementation is expected within the next few months and will result in more efficient and reliable processing of the large amounts of sample analysis data generated by the group.

The Neutron Activation Analysis (NAA) group provides analysis and development work for ORNL and UCC-ND programs and assists others in special projects that draw upon our expertise or use our special facilities. Approximately 7500 determinations were made this year. A new neutron detection system for uranium analysis (via delayed neutron counting) is being installed, which will result in greater sensitivity and improved efficiency. Efforts are under way to utilize fully our high flux irradiation facility at the HFIR reactor. Plans are also being made to automate counting measurements for multielement NAA.

Chapters 6 and 7 contain information that reflects on the division as a unit. Changes in the quality assurance and safety programs are presented in Chap. 6, along with a tabulation of analyses rendered. Publications, oral presentations, staff professional activities, educational programs, seminars, etc., are cited in Chap. 7. In general, the levels of these activities are comparable to those of the preceding year. Approximately 80 articles and reports have been published, and about 85 talks have been given during this reporting period. Educational programs, via faculty and student guests plus in-house training, have also continued at levels comparable to previous years.

1. Analytical Methodology

W. S. Lyon, Head

Having divested itself of the radiochemical and activation analysis activities, the Analytical Methodology Section is now composed of two research and development groups: Analytical Instrumentation and Physicochemical Analysis. A common thread joins these two endeavors, which can best be described by the prefix *multi*. The programs are multifaceted, multidisciplinary, and for the most part, concerned with techniques that are multielement or multicomponent in nature. Although a number of the projects are directed toward a basic understanding of some natural phenomenon and application of it through design and demonstration of an analytical instrument, other projects involve use or adaptation of existing instruments.

Work under Advanced Chemical Measurements Technology (a Basic Energy Sciences Program) encompasses both research at the actual frontier of science and development directed toward improving and expanding presently accepted analytical techniques. One-atom detection through the use of resonance ionization spectroscopy (RIS) is an example of the former; improvement of the helium glow discharge detector is representative of the latter. A number of multitechniques are being studied under Advanced Spectroscopic Methodology for Chemical Analysis (Basic Energy Sciences): software for the rapid-scan spectrometer (RSS) has been written and a simultaneous multiwavelength detector for liquid chromatography (LC) developed. The laser optoacoustic spectrometer (OAS) has been completed and some preliminary data obtained. The photoelectron spectroscopy program has moved ahead with construction of a new electrostatic spectrometer and upgrading of the magnetic one. The position-sensitive detector, vital for multielement determinations, is still under development. Software for the x-ray fluorescence equipment has enabled us to apply the technique to a variety of samples for multielement analysis. Other applied, programmatic research and development includes design and development of several in-line monitoring systems for the Advanced Fuel Recycle Program as well as assistance to a variety of researchers in a number of divisions working on a multiplicity of problems. For the latter we often use a combination of scanning electron and transmission microscopy, x-ray diffraction, x-ray fluorescence, and intuition. Intuition, per se, may not be mentioned in these pages, but it is the indispensable ingredient of applied research.

Finally, two new programs have begun: a speciation study of trace elements in ponded fly ash (EPRI) and a new concept in spectroscopy (seed money). The EPRI project is rather applied, the seed money one quite basic. Together they demonstrate the multifarious interests within the section.

BLANK PAGE

ANALYTICAL INSTRUMENTATION

H. H. Ross, Group Leader

Analytical Research

Array detector for multiwavelength spectroscopy. In 1976 a silicon Vidicon RSS was acquired and interfaced to a PDP-8/I computer. Since that time software for the operation of the RSS-computer system has been written, and the development of a simultaneous multiwavelength detector for liquid chromatography has been completed.

Because the RSS will be applied to a wide variety of analytical problems, each requiring on-line data processing, a new compiler, FOCRSS, was written. The philosophy embodied in FOCRSS is that data manipulation and operation of the RSS, as well as other peripherals, are accomplished via functions and commands at the algebraic programming language level. This compiler was adapted from FOCAL[1] (a conversational language written for the PDP-8 minicomputer) and is a disk-orientated program that not only stores spectral data on the disk but also permits the linking of program segments so that data-processing algorithms requiring extensive program coding can be accomplished. Fifteen functions are implemented in FOCRSS; six are mathematical functions, and nine are special functions related to acquisition and processing of spectral data.

FOCRSS contains 8 commands in addition to the 14 implemented in FOCAL. Three of these, the execute, disk, and cassette tape commands, are of particular importance because they facilitate program execution while reducing memory requirements and provide data storage-retrieval capability. The remaining commands control operation of input/output peripherals.

Several non-ORNL groups are investigating the capabilities of various rapid-scan spectrometers as multiwavelength liquid chromatography detectors.[2-5] Their approach has involved data acquisition during the chromatographic separation and later processing of the information. Our effort has focused on developing criteria and algorithms that provide real-time guidance for saving only that information necessary for successful interpretation of the chromatographic data. Five questions have been addressed: (1) Is a spectrum different from the background? (2) How many spectra are required to define an elution peak? (3) What value are spectra only at the chromatographic peaks? (4) Does this approach possess any quantitative capability? (5) Can complex samples—petroleum or coal-derived oils—be handled?

Criteria and or algorithms answering each of these questions have been developed and demonstrated. Distinguishing whether a spectrum is different from the background requires comparison of each resolution element in the spectral region of interest with the background and then ascertaining if a change in signal larger than that previously determined has occurred. This is accomplished via the use of an integration algorithm with twice the rms noise level that was selected as the decision criteria. Typically, a signal of more than 0.003 to 0.005 absorbance units is required to distinguish a spectrum from the background. The number of spectra required to define an elution band profile is determined by the band width and the accuracy desired in the reconstructed profile. Band width is determined by the number of theoretical plates (N) in the chromatographic column, the band retention time, and the distribution function describing the band shape. Assuming a Gaussian distribution for the band shape and imposing a maximum digitization error of 1%, it can be shown that the sampling interval (SI) is given by[6]

$$\mathrm{SI} \leqslant 0.2707 t \sqrt{N} ,$$

where t is the time elapsed since injection of the sample. However, numerous chromatographic bands deviate from the Gaussian distribution (i.e., exhibit nonzero third and fourth statistical moments), and detailed analyses of modified Gaussian functions are required to ascertain whether the above relationship is a generally applicable limiting expression. For

---

[1] Digital Equipment Corp., *Programming Languages*, vol. 2, Maynard, Mass., 1972, chap. 11.

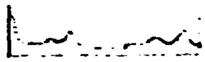
[2] M. S. Denton, T. P. DeAngelis, A. M. Yacynch, W. R. Heineman, and T. W. Gilbert, "Oscillating Mirror Rapid Scanning Ultraviolet-Visible Spectrometer as a Detector for Liquid Chromatography," *Anal. Chem.* **48**, 20 (1976).

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

[4] R. E. Dessy, W. D. Reynolds, W. G. Nunn, C. A. Titus, and G. F. Moler, "New Mini-computer Automated Linear Photodiode Array Spectrometer System for High-Resolution Liquid Chromatography," *J. Chromatogr.* **126**, 347 (1976).

[5] 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).

[6] P. C. Kelly and G. Horlick, "Practical Considerations for Digitizing Analog Signals," *Anal. Chem.* **45**, 518 (1973).



simple systems (e.g., fewer than 15 to 20 components and chromatographic resolution of approximately 1.0), spectra at the chromatographic peaks totally define the sample. Through use of a differentiation algorithm, these spectra are acquired without prior knowledge of the retention time or wavelength of maximum absorption. This capability is particularly useful in sample characterization studies. Because the RSS continuously records the spectrum of the column effluent, it provides data in the absorbance-wavelength-time domain as the separation proceeds. These data are required in the qualitative identification of the various sample components and in the selection of chromatographic resolution requirements and measurement wavelengths for quantitative analyses. The three-dimensional aspect of the RSS-LC detection is illustrated by the spectra obtained during the separation of a five-component polynuclear aromatic hydrocarbon mixture and reproduced in the upper right-hand corner of odd-numbered pages of this report. The time dependence of this separation can be viewed by grasping the report between the thumb and index finger and then releasing each page in a smooth motion. This three-dimension measurement capability allows one to extend quantitative liquid chromatography to samples in which the solutes of interest are not chromatographically resolved. This capability is demonstrated with the chromatogram shown in Fig. 1.1. The two solute bands are not resolved in the absorbance-time domain; however, they can be resolved and thus quantitated through analysis of the absorbance-wavelength data as a function of time. Typical quantitative results obtained with standard mixtures (resolution ≥ 1.25) revealed that peak-height measurements are slightly more precise than are peak-area measurements, with typical relative standard deviations of 3 and 5% respectively. Detection limits are poorer than the conventional single wavelength monitors, primarily because the RSS system operates in a single-beam mode. Two coal-derived oils, char-coal-energy development (COED) product oil and COED light hydrotreated oil, were briefly studied using a polyvinylpyrrolidine stationary phase and isopropanol as eluant. From a single chromatographic separation of each oil and chromatograms of known mixtures, a significant reduction in the polyaromatic hydrocarbon content above naphthalene occurs on hydrotreatment. The COED light hydrotreated oil contains primarily benzene and naphthalene chromophores, with anthracene and higher condensed ring chromophores of less than 0.04%.

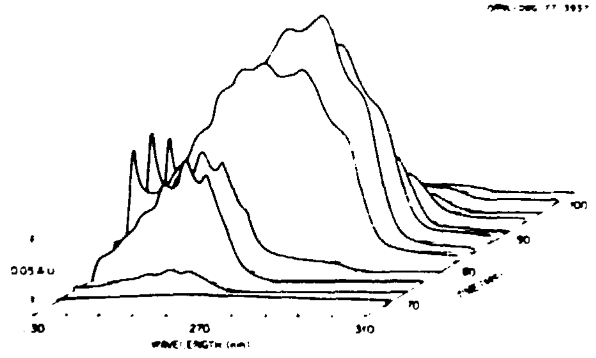


Fig. 1.1. **Three-dimensional representation of the chromatographic separation of benzene and naphthalene.** Column: 25 × 0.4 cm, packed with 10-μm silica particles containing permanently bonded octadecyl silane as stationary phase; eluant: 30 20 methanol-water, 2.9 ml min.

Development of a fluorescence detector is under way. Application of both detection modes to the characterization of selected fractions of coal-derived liquids will be undertaken. Subsequent research will be directed toward improving the response of array detector systems in the uv spectral region. (*L. N. Klatt*)

Optoacoustic spectroscopy. In 1976 a program was initiated to determine the analytical utility of laser optoacoustic spectroscopy (OAS). Last year's annual progress report[8] detailed the fundamental principles of OAS as well as the advantages of this technique over conventional spectrometry. That report described our initial experiments in which a breadboard-tuned amplifier was used for microphone signal treatment. Since that time the amplifier has been completed and is now in use for acquisition of optoacoustic spectra. The amplifier has two channels, each of which consists of three general components (1) a two-stage preamplifier, (2) an active filter, and (3) a precision rectifier. An analog divider combines the two channels to provide a ratio output for baseline normalization, a necessary operation due to the peaked character of the individual laser dye-tuning curves. Discrete tuned frequencies are panel-selectable from 5 to 30 Hz in 5-Hz increments. Voltage gain is variable

---

[7] G. Goldstein, "Separation of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography on Cross-linked Polyvinylpyrrolidine," *J. Chromatogr.* **129**, 61 (1976).

[8] R. W. [illegible], "Optoacoustic Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 3.

from 54 to 127 dB, and Q is adjustable from about 25 to 100. Flexibility was incorporated into this amplifier by modular design. The actual construction expense was reduced by development of a "general purpose" printed circuit board that will accommodate up to three operational amplifiers. By strategic placement of through-the-board contacts, a wide variety of circuits can be wired conveniently.

For pulsed OAS signals the performance of the tuned amplifier is slightly better than that of a commercial lock-in amplifier. The latter was designed for 50%-duty-factor sine waves and is not effective for the low-duty-factor pulsed optoacoustic signals (vide infra) measured here. Both signal treatment methods yield a signal-to-noise ratio (S:N) of approximately 100 for an optoacoustically determined R6G laser dye tuning curve, using an optically "black" sample and a 2-sec time constant. The observed S:N for weaker absorbers is somewhat less for both methods, as expected.

Some initial laser optoacoustic spectra of solids have been acquired and orally reported.[9] The samples analyzed include a dried human-blood smear and holmium oxide powder. The blood smear spectrum exhibits the well known α-β absorption band of hemoglobin in the 570- to 610-nm wavelength region (rhodamine 575 laser dye) and demonstrates the suitability of the OAS technique for opaque samples. The sensitivity of OAS was demonstrated by observing a weak f-f transition of holmium oxide at 538 nm. Although the extinction coefficient for that transition is only about 2, the absorbance of the pure powder sample was relatively easily detected.

To further improve sensitivity, two new matched sets of optoacoustic cells have been constructed. The first is basically the same cylindrical design reported last year but was constructed from quartz and has a smaller internal volume (~10 ml) for greater sensitivity. The second cell is actually a Helmholtz resonator. It features (1) an all-aluminum cell body (high thermal conductivity) for reduction of any cell-induced background level, (2) a reduced cell volume (1.3 ml) for high sensitivity, and (3) a small-bore acoustic coupling duct between the sample and microphone chambers for isolation.

The optoacoustic waveform (microphone voltage vs time) has been analyzed for pulsed optical inputs (1 μsec to 40 msec) derived from a chopped (variable-speed) CW source or from the dye laser.[10] The transient waveform was captured by averaging multiple input pulses with a signal-averaging instrument computer. For short light pulses, the frequency content of the optoacoustic waveform is divided between (1) a high-frequency component created by sample surface absorption, resulting in an instantaneous pressure pulse that oscillates back and forth in the cell cavity; and (2) a lower frequency component that exhibits both compression and rarefaction phases and results from time-delayed release of heat that is generated at and migrates from the sample interior. The balance of the high-to-low frequency components is strongly dependent on the nature of the sample. This balance can be shifted in favor of the low-frequency component through the use of the Helmholtz resonator cell that attenuates high-frequency oscillations acoustically.

At this point three experimental difficulties exist that prevent *routine* acquisiton of optoacoustic spectra. First, the ability to conveniently scan wide spectral ranges (several laser dyes) is necessary for molecular spectrometry. At present those scans require manual dye-solution changes, cavity mirror changes, and wavelength recalibrations. A portion of this problem has been solved by the design and construction of a digital "recorder driver." With the recorder driver in use, the recorder pen position (wavelength or x-axis) is locked to, and tracks the laser output frequency during scans. To scan wide ranges, however, manual laser adjustments are still required. These adjustments must be automated to facilitate scanning. The most important utility of laser OAS may, however, prove to be fixed-wavelength monitoring, which would eliminate the need for automation.

The second problem is noise and is a result of poor pulse-to-pulse amplitude stability of the laser output. This problem should be remedied by changing the signal-treatment scheme to gated

---

[9] R. W. Shaw, "Analytical Applications of Optoacoustic Spectroscopy," presented at the Anal. Chem. Div. Info. Mtg., Oak Ridge, Tenn., Mar. 31, 1977.

[10] R. W. Shaw, "Optoacoustic Spectroscopy with a Pulsed Dye Laser," Abstracts, 174th Amer. Chem. Soc. Natl. Mtg., Chicago, Ill., Aug. 28 Sept. 2, 1977, p. 53.

integration, with each pulse normalized individually. Time gating should also allow sample depth profiling.

Finally, the baseline normalization method (required to "flatten" the highly peaked dye-tuning curves) now in use is an analog division of the sample signal by an optoacoustic reference signal. The dynamic range of this analog division is only about 10. Other normalization methods such as digital division, log-subtraction-antilog "division," and self-normalizing cell designs, are currently being explored to improve this dynamic range.

Because of the short duration of our laser pulses and the thermal transport properties of samples, pulsed-laser OAS will have its greatest impact for analysis of thin layers on surfaces, high optical density solids and liquids, and gases. When this technique is fully developed, it should prove to be a valuable tool in a variety of ORNL and Department of Energy (DOE) programs. Such programs include coal utilization (absorption spectroscopy of coal liquids and solids, coal liquefaction catalyst studies); environmental sciences [analysis of polynuclear aromatic hydrocarbon (PAH) materials on fly ash and skin]; biology (absorption spectroscopy of living plant and animal tissue); materials sciences (absorption spectroscopy of coatings on solids or of opaque bulk solids, absorptivity and heat transfer properties of solar energy materials); and chemistry (analysis of surfactants on minerals as related to tertiary oil-recovery methods). (*R. W. Shaw*)

Resonance ionization spectroscopy. The study of RIS has continued[11] in collaboration with G. S. Hurst's group in the Health and Safety Research Division. Several major accomplishments were achieved this year, which have led to, and will lead to, unique applications of RIS in the study of the physical sciences. We have reported the specific detection of single atoms by an RIS technique applied to cesium atoms contained in a proportional counter.[12,13] By this technique it is possible to specifically detect this single atom in the presence of many other atoms; in the demonstration, 10^{19} atoms of argon were present. The method as it currently exists will detect only atoms (neutral charge) and will detect them only if they are in the gas phase. We have also reported, however, the dissociation of CsI into neutrals followed by the RIS detection of cesium and have studied the reaction of this dissociated cesium with O_2.[14] Thus in the demonstrated cases, we can analytically determine atoms or molecules. We have not yet observed CsI at the single molecular level but have observed less than 100 molecules by RIS techniques applied to CsI in a proportional counter.

The reaction of cesium with O_2 was studied at the 10^4-atom level, with the CsI contained in a parallel plate counter.[14] For argon pressures (P_{Ar}) between 25 and 100 torr and oxygen pressure (P_{O_2}) between 0.001 and 0.3 torr, we found the reaction rate, β:

$$\beta = 3.9 \times 10^3 \; P_{Ar} \, (P_{O_2}) = 0.87 \pm 0.15 \; .$$

The above rate equation suggests that the reaction is three-body but that back reactions can be responsible for the nonunit power in P_{O_2}. The rate we found is about 10^2 times larger than a rate found for Cs-O_2-N_2 reactions in a flame.[15] The fact that our rate is faster at much lower temperatures might suggest that an intermediate CsO_2^* is formed which is thermally unstable with respect to the reactants. More studies are planned to evaluate these reactions and the usefulness of RIS as a kinetic tool.

A broad area of application of one-atom detection is in the realm of one-atom events. In cooperation with C. E. Bemis, Chemistry Division, we are investigating the formation of single cesium fission fragments from fissioning ^{252}Cf. Based on statistical data obtained to date, we have detected single cesium atoms coming from ^{252}Cf. The data suggest, moreover, that not all *cesium fission fragments are neutral at thermalization*. We are currently determining the extent

---

[11] J. P. Young, "Resonance Ionization Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 2.

[12] G. S. Hurst, M. H. Nayfeh, and J. P. Young, "A Demonstration of One Atom Detection," *Appl. Phys. Lett.* **30**, 229 (1977).

[13] G. S. Hurst, M. H. Nayfeh, and J. P. Young, "One Atom Detection Using Resonance Ionization Spectroscopy," *Phys. Rev.* A15, 2283(1977).

[14] L. W. Grossman, G. S. Hurst, S. D. Kramer, M. G. Payne, and J. P. Young, "A Sensitive, Absolute, and Time Resolved Method for the Study of Reactive Atoms," *Chem. Phys. Lett.* (in press).

[15] R. Carabetta and W. E. Kaskan, "The Oxidation of Sodium, Potassium, and Cesium in Flames," *J. Phys. Chem.* **72**, 2483 (1968).

of neutral formation and are also determining parameters that might influence this process. These studies will form the background for many future detection schemes for synthesized atoms.

In theory, if one can detect single atoms by the RIS technique, it is also possible to detect very few, even one, photon absorptions. In practice, one can study absorption line shape and line broadening far away from line center. We have studied collisional line broadening of the 7 *P* state of cesium as a function of pressure. The results for line broadening at 760 torr of argon have been reported[16] and show that absorption persists even as far as 70 Å toward lower energies from 4593 Å. (*J. P. Young*)

Spectrophotometric studies at the Transuranium Research Laboratory. In cooperation with J. R. Peterson and R. L. Fellows, University of Tennessee at Knoxville, and R. G. Haire, Chemistry Division, spectrophotometric studies of transuranium compounds have been continued.[17] Such studies aid in the characterization and identification of various transuranium compounds and determine the extent of reaction of such compounds with added reactants. Such information, coupled where possible with x-ray powder-diffraction studies, is used to determine stabilities, reactivities, and relative thermodynamic information for these man-made elements. In all of these studies, which involve the chemical synthesis of 1- to 10-μg amounts of compounds, spectrophotometry offers a sensitive and useful way to investigate products, reaction rates, possible side reactions, etc., as spectral information from individual crystals; or crystal parts can be obtained by the use of our microscope-spectrophotometer. This individual spectral analysis coupled with x-ray diffraction studies of the total quantity (few μg) of sample offers a powerful tool for studying reactions of the transuranium element ions.

A rather routine change in our experimental apparatus[18] resulted in major advances in our ability to synthesize divalent californium and einsteinium halides. The change involved altering the design of our quartz reaction capillary so that the volume of excess H_2 gas reductant available in the system was increased several orders of magnitude. We prepared $CfCl_2$,[19] $EsCl_2$, $EsBr_2$, and EsI_2 this year. This is the first time that any of these compounds have been prepared in pure form in the solid state. The first-named compound, $CfCl_2$, is particularly interesting. Based on predictions of Nugent et al.,[20] it should be possible to reduce $CfCl_3$ with H_2, but many workers have tried unsuccessfully. The $CfCl_2$ that we prepared was characterized by spectrophotometric and x-ray diffraction methods. Because of the extreme radioactivity of einsteinium, the identification of its dihalides was made by spectrophotometric studies. In related studies, we cooperated with personnel of Lawrence Livermore Laboratory[21] in the spectrophotometric characterization of both CfI_3 and CfI_2 and carried out spectral studies and further x-ray studies of $CfBr_2$ and some mixed trivalent lanthanide-divalent actinide halides, for example, Cf(II)-Gd(III) chlorides of the type M_5Cl_{11} or M_6Cl_{13}.

We are also using our general microtechniques to study oxidation states of transuranium ions above three. We have spectrophotometric and x-ray diffraction data on CmF_4 and CfF_4. We are currently following the stability of these tetravalent fluorides by spectrophotometry as a function of time. Out of these studies will come a better understanding of the chemical reactivity of the 5-*f* electrons and possibly some information on solid-state chemical stability in radiation fields.

We are continuing to amass information on mother-daughter-granddaughter relationships in the solid state. Some data were discussed previously,[17] and more have been obtained. In the series

$$^{253}\mathrm{Es}\xrightarrow[20\ d]{\alpha}{}^{249}\mathrm{Bk}\xrightarrow[350\ d]{\beta}{}^{249}\mathrm{Cf}$$

---

[16] M. H. Nayfeh, G. S. Hurst, M. G. Payne, and J. P. Young, "Collisional Line Broadening Using Laser Excitation and Ionization," *Phys. Rev. Lett.* **39**, 604 (1977).

[17] J. P. Young, "Spectrophotometric Studies at the Transuranium Research Laboratory," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 13.

[18] J. P. Young, R. G. Haire, R. L. Fellows, and J. R. Peterson, "Spectrophotometric Studies of Transcurium Element Halides and Oxyhalides in the Solid State," *J. Radioanal. Chem.* (*in press*).

[19] J. R. Peterson, R. L. Fellows, J. P. Young, and R. G. Haire, "Stabilization of Californium (II) in the Solid State: Californium Dichloride, $^{249}CfCl_2$," *Radiochem. Radioanal. Lett.* (in press).

[20] L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryan, "Electron-transfer and *f-d* Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (II-III) Oxidation Potential for Each Member of the Lanthanide and Actinide Series," *J. Phys. Chem.* **77**, 1528 (1973).

[21] J. F. Wild, E. K. Hulet, R. W. Lougheed, W. N. Hayes, J. R. Peterson, R. L. Fellows, and J. P. Young, "Studies of Californium (II) and (III) Iodides," *J. Inorg. Nucl. Chem.* (in press).

we have seen that such compounds as EsI_3 or $EsBr_3$ ultimately yield spectrally identifiable CfI_3 or $CfBr_3$. We have strong indications that the sensitivity of Bk *f-f* absorption peaks are much weaker than those of daughter californium. We have made spectral studies of EsX_2 with respect to time (in days) to determine what transpires as Es(II) transmutes to apparently unstable Bk(II). Our first results indicate that local order breaks down and no discernable spectrum of berkelium is seen; work on this aspect of radioactive decay is continuing. (*J. P. Young*)

Element-specific detector for gas chromatography. The helium glow discharge detector (GDD) described previously[22] has been improved in two ways (1) Swagelok components are used to hold the electrodes, eliminating the need for preparing glass electrode assemblies, and (2) alignment of the electrodes is provided automatically by constrictions in the arms of the chamber.

We have begun an investigation into methods of improving GDD sensitivity by increasing the fraction of the glow radiation that reaches the photomultiplier tube. When a short focal-length vertical-axis cylindrical lens was used to project an image of the discharge on the slit of the monochromator and a spherical or horizontal-axis lens at this slit was used to project an image of the discharge on the entrance aperture of the monochromator,[23] the signal detected was 2.[illegible] times as intense as it was with the previous arrangement.[22] To broaden the range of modes of illumination available, a *new discharge chamber* was *designed in* which the foresection containing the observation window, gas inlet, and discharge gap is 25 mm in diam. This permits use of a wide (e.g., 15-mm) discharge gap. A set of spherical and cylindrical lenses has been ordered to explore all modes of illumination applicable to this system. For the mode eventually selected as best for use with the existing (fixed) GDD and monochromator, the detector-to-slit distance should be adjustable. To make this possible, the monochromator and its optical bench were mounted on a movable base. To insure accurate alignment of the external illumination system with the internal optics of the monochromator, a jig was designed and built to locate the point of intersection of the monochromator's optic axis with the entrance and exit slits.

A new gas chromatograph–glow detector–monochromator background correction and detection system is being built, with a full-aperture uv beam-splitting mirror (heretofore unavailable) to replace the cut mirror used previously. This will make the action of the background corrector independent of spatial nonuniformity of the line-to-background ratio in the light source. A mathematical analysis of the operation of the background corrector shows that it will always be able to cancel a false chromatographic peak (i.e., a peak produced by a compound not containing the element sought), provided that the shape of the spectral band that produced the peak remains constant as the impurity passes through the discharge.

Figure 1.2 shows the results of chromatographic analysis of a silylized mixture of three hydrocarbons

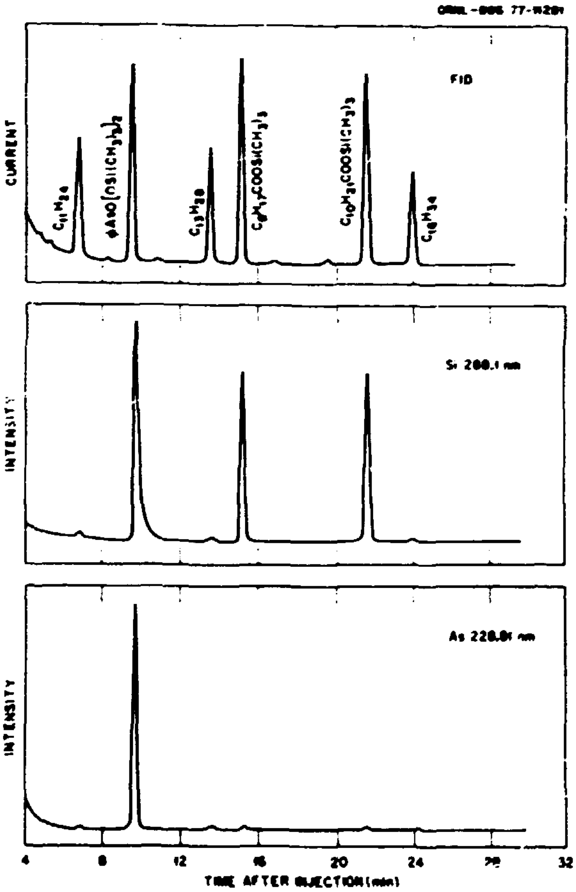


Fig. 1.2. Gas chromatograms of a silylated mixture of aliphatic acids, phenylarsonic acid, and hydrocarbons. Top curve: Flame ionization detector (FID). Center and bottom curves: glow discharge detector (GDD), with monochromator set as indicated.

---

[22] C. Feldman, D. A. Batistoni, and R. A. Jenkins, "Helium Arc Detector for Gas Chromatography," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp. 4–6.

[23] C. Feldman, "Standard Recommended Practice for Photographic Photometry in Spectrochemical Analysis" *1976 Annual Book of ASTM Standards*, part 42, Amer. Soc. Testing and Materials, Philadelphia, Pa., 1976.

($C_{11}H_{24}$, $C_{13}H_{28}$ and $C_{16}H_{34}$), two aliphatic acids ($C_8H_{17}COOH$ and $C_{10}H_{21}COOH$) and phenylarsonic acid. In each experiment, the effluent stream was split between the flame ionization detector (FID) and the GDD, with the monochromator monitoring a specific spectral line. As expected, the FID detected all components of the mixture. With the monochromator set at $\lambda_{Si} = 288.1$ nm, the GDD detected only the silylized compounds; when set at $\lambda_{As} = 228.81$ nm, it detected only the phenylarsonic acid. No background correction was applied in these cases; fortunately, the compounds not containing the element sought produced only minor false positive peaks at the wavelengths monitored.

Figure 1.3 shows a case in which false chromatographic peaks were a serious problem in the detection of phosphorus-bearing compounds in a mixture. Figure 1.3*B*, a spectral scan of the helium carrier gas, shows that the phosphorus doublet is located on the slope of an intense band. Figure 1.3*A* shows chromatograms of a mixture containing 2.3-ng atoms of phosphorus as tributyl phosphate (TBP) and 35.8-ng atoms of C as $C_{17}H_{36}$ (in addition to the C in the TBP). The upper curve, as before, shows that the FID detected both substances. The center curve was made by the GDD monitoring $\lambda_p = 213.62$ nm, without background correction. In this case, a strong but false "phosphorus" signal was given when the hydrocarbon $C_{17}H_{36}$ passed through the GDD. When a background correction was applied by subtracting a constant fraction of the background reference intensity at $\lambda_r = 214.6$ nm from the $\lambda_p = 213.62$ nm signal (lower curve), only the TBP was detected. The background corrector has thus greatly improved the specificity of the GDD in this case.

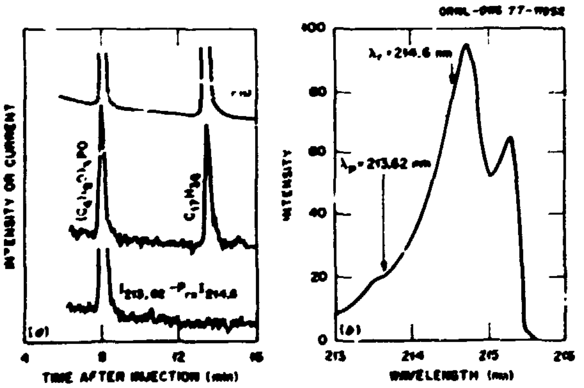


Fig. 1.3. Background correction for phosphorus detection. *A*: Gas chromatogram of mixture of tributyl phosphate and heptadecane. Top curve: FID trace. Center and bottom curves: GDD trace using phosphorus 213.6-nm radiation, without and with background correction respectively. *B*: Wavelength scan of spectral region used.

A paper describing the GDD and background corrector has been accepted for publication.[24] (*C. Feldman*)

Determination of arsenic and the methylarsines. One of the most persistent difficulties encountered in the arsine accumulation-glow discharge procedure for determining traces of arsenic[25] has been finding a suitable desiccant for the gas stream to prevent plugging of the liquid nitrogen (LN_2) trap by water vapor. The customary desiccants [$CaCl_2$, $CaSO_4 \cdot \frac{1}{2}H_2O$, $Mg(ClO_4)_2$, silica gel] adsorbed and/or reacted with AsH_3 in an unpredictable way; concentrated H_2SO_4 added new vapors to the gas stream. Since most of the water to be removed was in the form of a liquid aerosol, it was decided to direct the gas stream as a rapid jet against the surface of a pool of 85% H_3PO_4. This has had the desired effect: it prevents plugging of the LN_2 trap without contaminating the gas stream. The efficiency with which $NaBH_4$ solution converts arsenate or arsenite to AsH_3 decreases with the pH of the solution, although at any pH, arsenite is reduced more efficiently than arsenate. Since $NaBH_4$ is a strong alkali, the higher the buffering capacity of the solution (i.e., the slower the increase in pH as $NaBH_4$ is added), the greater the yield of AsH_3 and the greater the ratio of the yield from arsenite to that from arsenate. Discrimination between arsenite and arsenate is quantitative in phosphate buffer at pH 6.5; no AsH_3 is produced from arsenate at this pH. In mixtures of arsenite, arsenate, methylarsonic acid, and cacodylic acid in various buffers from pH 1.8 to 4, the amount of AsH_3, CH_3AsH_2, or $(CH_3)_2AsH$ produced depends only on the amount of the respective compound present; at lower pH values, the alkyl arsines are split, giving additional AsH_3. The dynamic range of the log AsH_3 peak height vs log concentration curve was followed from 1 to 10,000 ng of arsenic. It is linear (slope 1.14) from 1 to 50 ng and bends upward and is linear

---

24. C. Feldman and D. A. Batistoni, "Spectroscopic Element Detector for Gas Chromatography," *Anal. Chem.* **49** (submitted for publication).

25. C. Feldman, D. A. Batistoni, and R. A. Jenkins, "Helium Arc Detector for Gas Chromatography," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp. 4–6.

(slope 1.39) from 80 to 10,000 ng. These slope values are not affected by helium flowrate, arsenic valence, choice of desiccant, or parameters of the detection system. An attempt was made to augment the sensitivity of the detection system at short wavelengths ($\lambda < 200$ nm) by introducing fluorescent screens of sodium salicylate (1.70 to 5.15 mg cm^{-2}) immediately in front of the 1P28 photomultiplier. This caused a substantial improvement in photomultiplier response for arsenic of 189.04, 197.26, and 200.34 nm; but substantial reflection losses at the available grating and mirror (in addition to transmission losses at lenses and windows) destroyed any possible advantage of working at these wavelengths. These tests will be repeated with a uv-blazed grating.

The chemical yield of arsine in the acidified arsenate-NaBH$_4$ reaction was tested by using the LN$_2$-trap-accumulation helium-glow-discharge method. A known (nominal) amount of AsH$_3$ was produced from a standard arsenate solution by using the NaBH$_4$ reaction, accumulated in an LN$_2$ trap, and determined as usual.[26] In a separate experiment, the same nominal quantity of AsH$_3$ was introduced directly into the LN$_2$ trap in the form of a calibrated mixture of 11 ppm of AsH$_3$ in helium. The peak heights obtained were the same to within 1%, indicating that the yield of AsH$_3$ in the arsenate-NaBH$_4$ reaction was essentially quantitative. (*C. Feldman*)

In-Line Sensor Development for the Advanced Fuel Recycle Program

Introduction. The Analytical Chemistry Division has joined with the Instrumentation and Controls Division in the development of chemical measurement systems for fuel recycle process analysis. Our primary responsibilities are to:

1. help identify required chemical measurements for proper process control,
2. recommend off-the-shelf commercial instrumentation when available,
3. suggest modifications of commercial devices to perform specific analyses when possible,
4. aid in testing and calibration of chemical (or physical) measurement systems, and
5. investigate the development of new and unique methods of analyses for problems where no conventional system is known to exist.

We have studied the overall processing system with the objective of making a preliminary assessment of required analyses for each processing subsystem. These projected analyses were further identified as being relatively routine, moderately difficult (small R&D effort needed), and quite difficult (significant R&D required). Individual problems are approached on a projected "need" schedule by drawing together members of the Analytical Chemistry Division with the required expertise on an ad hoc basis. Our plan is to develop one or more possible solutions to a given problem, establish realistic R&D priorities, and propose a work plan for consideration. After acceptance of a final work outline, manpower will be committed to carry out the experimental work.

Using the above approach, we have developed three initial "activity plans" for engineering research studies; these have been submitted and approved, and the associated R&D programs are in progress.

Free acid concentration. Current fuel recycle technology favors a chemical processing strategy that requires the measurement and adjustment of free nitric acid concentration throughout the processing system. Proper acid concentration is necessary for efficient dissolution of the fuel and is vital for stabilizing the dissolved cationic species and for setting the optimum conditions in the extraction stages. Two particularly important problems occur whenever acid concentrations become too low (1) changes of cation oxidation state which may be accompanied by polymer formation and (2) possible hydrolysis and precipitation of fuel material. Conversely, high-acid concentrations adversely affect the dynamics of the extraction processes.

A method for the determination of free-acid concentration in *pure* acid streams appears to be essentially completed (by density). Alternate methods, however, will be required for dissolved-fuel solutions because of the complexities introduced by the high-solute concentration (and other materials) in these solutions.

The determination of free acid by a condensation of the vapor phase over the digestor tank is especially attractive because it permits a relatively low-level sample to be extracted from the intensely radioactive dissolver solution. Proof-of-principle experiments have been completed, which show that a sample can be distilled at 65°C from a nitric acid solution

---

[26] C. Feldman, "Determination of Arsenic," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5109, p. 6.

(2 to 8 *M*) and condensed to yield a sample whose conductivity is proportional to the acid concentration of the dissolver solution. Data are now being collected to elucidate the relationship of the measured conductivity to temperature of distillation, total ionic strength of the nitric acid containing dissolved salts, and the evolutions of volatile gases or fission products (NO_2, NO, Xe, etc.).

Measurement of uranium. The continuous in-line analysis of dissolved uranium and plutonium is important for the determination of dissolver operation efficiency and for the adjustment of the feed solutions out of the digester tank system. One of the complicating factors in such measurements is that plutonium species can assume a variety of oxidation states and polymeric forms in solution. Parameters affecting specific plutonium compositions include acid concentration, plutonium concentration, time since dissolution, and other ions that might be present. A practical monitoring system will be required to detect and measure all significant uranium and plutonium ionic forms that exist in the dissolution stream. Other measurement difficulties are the presence of large chemical amounts of fission product material, and the intense radiation field. The molecular absorption characteristics of uranium and plutonium in solution appears to be a reasonable approach to making the required measurements.

The spectrum of uranium is currently being studied in the visible region (500 to 340 nm). Major absorption peaks of interest occur at 426, 416, 403, and 359 nm. The absorption at these wavelengths was found to be dependent on both the uranium and nitric acid concentrations. If nitric acid concentration is held constant, the absorption (0.1 cm pathlength) is proportional to uranium concentration over the 0- to 200-g/liter range. The relative sensitivity is greatest using the 416-nm line and consecutively decreases at 426, 403, and 359 nm. The absorption is linearly dependent on nitric acid concentration over the 2- to 5-*M* range if the uranium concentration does not exceed 100 g/liter. The dependence deviates negatively above 4.5 *M* HNO_3 for higher uranium concentrations. The 426-nm absorption line is most affected by nitric acid concentration, followed by the 403- and 416-nm lines. Both free acid and nitrate ion concentration contribute to the increased absorbance at these three wavelengths at a given uranium concentration. Absorption at the 359-nm line is only slightly affected by nitrate ion concentration and not at all by the presence of free acid.

The proposed uranium monitoring scheme will be based on measurement of the sample absorption at two of the three major wavelengths. Nitric acid–nitrate and uranium concentration could be determined simultaneously from these measurements. Analysis of uranium samples containing varying concentrations of nitric acid and sodium nitrate indicates that data obtained from the 416- and 426-nm lines give the most accurate and reproducible determination of uranium concentration. Calculation of uranium concentration based on data obtained from the 403-nm line in combination with either of the other two wavelengths results in a uranium value that is overestimated by at least 5%.

Bhargava et al.[27] describe the spectral characteristics of possible ionic species present in the dissolution stream. The predominant spectral interferences occur at wavelengths shorter than 380 nm. Therefore, uranium analysis in the dissolution stream would not be possible by using the 359-nm line. However, uranium determination based on a single wavelength might be possible in the final product stream. Interfering elements will not be present in quantities that would interfere, and the analysis would be simplified because it is not dependent on free acid concentration.

A preliminary investigation was also made to determine the feasibility of uranium analysis based on fluorescence. Uranium determination in dissolution streams does not seem possible by using fluorescence because fluorescent intensity will be affected by self-absorption at the high uranium concentrations present. Nitric acid in the 2- to 5-*M* HNO_3 range was found to quench the fluorescence, and other interfering species present in the solution might also act as quenchers. Fluorometric analysis might be used to test the efficiency of uranium extraction in streams that contain less than 10^{-2} *M* of uranium and are free from major contaminating species.

Gadolinium measurement. To meet the safeguards requirement of a critically safe dissolver, it is necessary to incorporate a soluble neutron poison in the dissolver acid. It is also necessary to control and monitor the presence of this high cross-section material to assure safety and prevent waste.

---

[27] V. K. Bhargava, E. S. Chandrasekharan, R. H. Iyer, V. K. Rao, M. V. Ramaniah, and N. Srinivasan, "In-line Analytical Methods for Fuel Reprocessing Streams, Part I. Direct Calorimetry for Uranium and Free Acid," B.A.R.C.-510 Bombay, India (1970).

The use of neutron absorption techniques to measure continuously the effective neutron absorption cross section of the acid solution has been demonstrated to be accurate, sensitive, and reliable. Existing data indicate that a monitor can be constructed using a 2-Ci ^{241}Am-Be neutron source that will produce a direct readout of the gadolinium concentration every 15 sec with a 2-σ relative standard deviation of less than 5%. We are accumulating the equipment needed for this project so that the experimental phase can be started. (*J. E. Strain, D. A. Bostick, H. H. Ross*)

Special Projects

Analysis of water-soluble sulfate in atmospheric filter samples. A continued effort has been under way to develop and evaluate new analytical methodology for the determination of water-soluble sulfate concentration present in atmospheric filter samples. A gas chromatographic (GC) technique was previously developed at this laboratory for the determination of milligram quantities of oxyanions contained in aqueous samples.[28] The procedure is based on the formation of trimethylsilyl (TMS) derivatives of the anions, followed by GC separation and detection. The procedure is being reviewed and modified for the analysis of microgram levels of sulfate in environmental samples.

Several parameters, including water content, organic solvent, reaction time and reaction temperature, have been studied to optimize the chemical reaction conditions for this concentration level. It was found that the aqueous sulfate sample must be evaporated to dryness prior to silylizing the sample. If more than 10 μl of water is present in the reaction mixture, a precipitate will form and no TMS sulfate will be produced. Smaller amounts of water result in less than maximum yield of the derivative.

The reaction yield is also affected by the organic solvent present in the mixture. The percent yield and the production of side products were compared by using the silylizing agent, *bis*(trimethylsilyl)trifluoracetamide (BSTFA), alone or in combination with dimethylformamide, acetonitrile, pyridine, or methylene chloride as the solvent. An organic solvent was required in addition to BSTFA to form the TMS sulfate. The greater the solvent-to-BSTFA ratio, the more quantitative the yield and the faster the reaction progresses. Presently, a ratio of 2.5:1 is used. Methylene chloride was found to be the solvent of choice because it produced the greatest TMS-sulfate yield in the absence of secondary products.

The reaction temperature has a dramatic effect on the percent yield of TMS sulfate. No sulfate derivative was formed if the temperature was below 25°C. Fifty percent of the maximum yield was obtained at 45°C, and the maximum was obtained above 55°C. A 60°C-reaction temperature is used for preparing sulfate samples. At reaction temperatures above 60°C, solvent loss caused by volatility becomes a problem. In the presence of BSTFA and methylene chloride, sulfate samples require an overnight reaction time at 60°C to obtain the optimum yield.

In addition to chemical reaction conditions, the gas chromatographic conditions were also optimized for ppm quantities of TMS sulfate. The derivatized oxyanions were separated previously, using a 5% SE-30 coating on Chromosorb G(HP).[29] The analysis of sulfate was found to be extremely irreproducible because of irreversible adsorption of TMS sulfate on the column. The detection limit of the analysis was 2 μg of sulfate.

Several columns have been prepared recently to determine the GC parameters that contribute to the loss of TMS sulfate. The performance of columns that differed either in the solid support used or in the percentage of loading of the liquid phase (SE-30) was compared according to the amount of tailing of the TMS-sulfate peak, the detection limit, and the linearity of the calibration curve. The detection limit is primarily defined by the percentage of loading of the SE-30 stationary phase on a given solid support. Less TMS sulfate is adsorbed or decomposed if the amount of SE-30 is reduced. The amount of tailing is also minimized if the percentage of loading is reduced to <1%.

The linearity of the curve is affected most by the reactivity of the solid support. The most nearly linear TMS-sulfate calibration curve was obtained on Chromosorb 750, whereas that on Chromosorb W(HP) was somewhat less linear. The procedure was not linear on gas Chrom Q.

Under optimum conditions, detection limit of 0.2 μg of sulfate can be achieved by using 1% SE-30 on Chromosorb 750. The detection limit must be reduced by at least a factor of 10 before the GC analysis is suitable for environmental samples.

---

[28] W. C. Butts, "Gas Chromatography of Trimethylsilyl Derivatives of Common Anions," *Anal. Lett.* 3, 29-34 (1970).

[29] D. R. Matthews, *The Gas Chromatographic Determination of Trace Anions in Aqueous Media*, Ph.D. thesis, University of Tennessee at Knoxville, 1972.

Future work should include the investigation of a column prepared with a few-tenths percent of SE-30 on silylized glass beads and the use of other liquid phases on Chromosorb 750. (*D. A. Bostick*)

Spectroelectrochemistry in low-temperature melts. Molten chloroaluminates ($AlCl_3$–NaCl mixtures) are of considerable importance to the development of high-energy molten salt batteries[30–34] and may be useful in catalytic coal conversion technology.[35] In these melts, the chemistry of sulfur, which is of particular importance in the sodium-sulfur (IV) system, is complex. A full understanding of this system requires the application of both electrochemical and spectroscopic techniques. We are currently developing spectroelectrochemical methodology for studies of solutes in molten chloroaluminates. The principal goal of this research is to characterize the positive oxidation states of sulfur produced electrochemically and to ascertain the mechanism for the oxidation of sulfur in chloroaluminates. A secondary application will be the characterization of metal-metal bonded entities involving Group IV-VI elements.

The technique developed for this research involves the use of optically transparent electrodes, OTE. In this technique, the radiant energy entering the spectrometer passes through a grid-type electrode, the potential of which is controlled by a potentiostat. Spectra of species produced at the OTE are recorded with a rapid-scan spectrometer to allow study of short-lived intermediates. Vitreous carbon, tungsten, and platinum OTEs are being investigated Based on results obtained in aqueous media,[36] the vitreous carbon OTE appears to be particularly promising because of its inertness and large surface area. Preliminary studies in molten chloroaluminate media are concerned with the acquisition of spectra for the various positive oxidation states of sulfur present under equilibrium conditions. Investigations of reaction pathways and characterization of short-lived intermediates are being pursued. (*L. N. Klatt, V. E. Norvell, G. Mamantov*)

Miscellaneous activities. Approximately 40 samples were analyzed for oxygen content, using 14-MeV neutron activation analysis. Almost all of the samples were reactive materials such as lithium metal, lithium aluminum alloys, FES, etc.

A cooperative program with Argonne National Laboratory to determine the solubility of Li_2O in lithium was completed and the results reported at the June 1977 meeting of the American Nuclear Society. An open literature publication covering the program is now in preparation. (*J. E. Strain*)

Fluorometric uranium determination. The use of MgO ceramic dishes to replace currently used platinum dishes was investigated. Because of the one-use–throw-away nature of the dishes and their uniformity, it is hoped that their use will save money and time as well as improve the precision of the analysis. Preliminary tests indicate that there is no quenching of the emitted fluorescence and no decrease in sensitivity. Statistical evaluation will be done as time is available. (*J. E. Strain*)

Microwave-excited plasmas for in-line monitoring. This program to apply high-powered microwave plasmas (2.45 GH_z = GH_z 2.5 kW) to multielement analysis in liquid streams was discontinued during the year. The decision to abandon this research was based on the poor sensitivity realized ($\geq$ 10 μg ml) and the serious interference caused by common ion effects. A summary report of the work is in preparation. (*J. E. Strain*)

PHYSICOCHEMICAL ANALYSIS

L. D. Hulett, Task Leader

Scanning and Transmission Electron Microscopy

The division has acquired a second scanning electron microscope, an ISI Super-3, manufactured by Akashi-Seisakusho, Ltd., Tokyo, and marketed by International Scientific Instruments. The microscope has a guaranteed resolution of 70 Å and a magnification range of 30 to 200,000 diameters. A computer-based Si(Li) x-ray spectrometer is on order

---

[30] J. Werth, *Sodium-Chloride Battery Development Program for Load Leveling*, ESB Technology Center, EPRI EM-230, Interim Report, Jan. 1, 1975–Dec. 31, 1975, Yardley, Pa.

[31] C. L. Hussey, J. K. Erbacher, and L. A. King, *High Energy Density Pelletized Aluminum Chloride Thermal Batteries*, F. J. Seiler Research Laboratory Technical Report 78-0003, Colorado Springs, Colo., January 1976.

[32] G. Mamantov, R. Marassi, and J. Q. Chambers, "Cathode Systems for Aluminum Molten Chloroaluminate Batteries," Extended abstract No. 8, Meeting of the Electrochemical Society, New York City, October 1974.

[33] G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer, and E. J. Frazer, "Sulfur (IV) Cathode in Molten Chloroaluminates," Abstract No. 89, Meeting of the Electrochemical Society, Atlanta, Ga., October 1977.

[34] G. Mamantov and R. Marassi, "A Cathode for Molten Salt Batteries," U.S. Patent Application SN 734,836 allowed July 19, 1977.

[35] G. C. Demitras and E. L. Muetterties, "Metal Clusters in Catalysis – A New Fischer-Tropsch Synthesis," *J. Am. Chem. Soc.* **99**, 2796 (1977).

[36] V. E. Norvell and G. Mamantov, "Optically Transparent Vitreous Carbon Electrode," *Anal. Chem.* **49**, 1470 (1977).

for attachment to the instrument, which will provide the capability for on-line quantitative elemental analysis by use of the x-ray fluorescence induced by the electron beam of the microscope.

Most of the operation time of the new ISI has been devoted to morphological studies of precipitates and scales formed in a dynamic geothermal system, in support of research by personnel in the Chemistry Division. The deposits are silica with traces of NaCl in most cases. In addition to Si, we have detected Fe, Ca, and Ti in some of the deposits. The usual "opal" structure was observed in most instances. In a recent experiment, a hard material was scraped from the system which differed in appearance from many of the other scales. In this sample, produced from a brine containing 4 *M* NaCl and 0.05 *M* Na_2CO_3, some of the particles appeared to be flat platelets 45 × 65 microns. When examined at 40,000 diameters, some of the platelets showed opal structures, whereas others did not. The two structures did not appear to differ chemically; only silicon lines were obtained by electron-induced x-ray analysis. Scales scraped from other regions of the system showed structural differences that appeared to be related to the presence of calcium and titanium.

Most of our transmission electron microscopy studies have been related to the LMFBR hypothetical accident studies that are directed by G. W. Parker, Chemical Technology Division. We have examined many samples of UO_2 and U_3O_8 from a capacitor discharge vaporization system, collected by means of thermal precipitation, plateout, and fallout. The samples were collected on 300- or 400-mesh copper specimen grids (3 mm in diam) that had been coated with a thin film of Formwar (200 to 300 Å) and an evaporated carbon layer (100 to 200 Å thick) and were then examined in the transmission microscope. The sizes of the resulting particles were dependent on the amount of power used, that is, the more power used, the smaller the particles.

Other miscellaneous problems include the examination of various crystal compounds in connection with synthetic nuclear waste studies and a study of changes in the epicuticular waxes on pine needles and bean, poplar, and willow leaves as a result of treatment with water at various acid concentrations. This project is a cooperative effort with D. Shriner of the Environmental Sciences Division. (*F. L. Ball, H. W. Dunn, L. D. Hulett*)

X-Ray Methods

X-ray diffraction. The Comparative Animal Research Laboratory (CARL) is attempting to determine the amount of soil eaten by cattle and the pattern of its distribution in their digestive tracts. Quartz was chosen as a tracer because it is present in soil and is nonreactive with the digestive juices of the cattle. Complete records were kept by CARL of the diets and defecation rates of the animals. After a period of time, the animals were sacrificed, and fecal samples from their digestive tracts were removed, dried, and ground. Samples from the feed, the feces, and the sections of the digestive system were then submitted to our x-ray diffraction laboratory for quartz determinations. NBS standard orchard leaves have about the same consistency as the dried samples from the cattle; we therefore spiked the orchard leaves with varying amounts of quartz and a fixed amount of Al_2O_3 for use as an internal standard. A working curve was made from the data taken from these standard samples by plotting the ratio of the net x-ray line intensity of the strongest line of quartz to the net x-ray line intensity of the strongest line of Al_2O_3 against the known concentration of quartz. A known weight of sample (0.20 g) was spiked with a fixed weight of Al_2O_3 (0.05 g), and the two were homogenized by grinding. The net x-ray intensities of quartz and Al_2O_3 were measured. From these data the concentration of quartz was determined for each sample. Samples from nine steers were analyzed.

Our heavy sample load has left little time for instrument construction this past year, but we have continued efforts to develop a low-background diffractometer. X-ray diffraction measures the intensity of a selected x-ray beam (CuKα, for example) that has been Bragg-diffracted from crystalline material. The sensitivity of this measurement depends on the intensity of the background, which may be due to bremsstrahlung from the x-ray source or from fluorescence generated in the sample. We are attempting to reduce background conditions by monochromating the diffraction beam before and after it is scattered by the sample; pyrolytic graphite crystals are used as monochromators. Preliminary measurements indicate some improvement, but some of our hardware has presented synchronization problems. We are currently installing a stepping motor that will drive both the goniometer and the recorder chart simultaneously. (*H. W. Dunn, R. L. Sherman*)

X-ray fluorescence analysis. It has been known for many years that x-ray fluorescence is a quick, easy, and sensitive method of analyzing for heavy elements, but the nonlinear relationship between fluorescence intensities and element concentrations has made quantitation difficult. Self-absorption and interelement-enhancement effects of the matrix have been dealt with by empirical standardization, but this is time consuming. As indicated in the 1976 progress report,[37] a new method of applying matrix corrections has been developed, which uses fundamental constants. For some alloys, Co-Mo supported catalysts, and certain other matrices, the need for empirical standardization has been completely eliminated. This past year we have applied the correction procedure extensively to stainless steels and many other alloys. Over 300 samples, averaging six elements each, have been analyzed.

This correction program was written for samples having as many as 12 elements, using our Tracor Northern apparatus with an 8K PDP-11. In light of our success, we decided to write a general program to cover the entire periodic table. It was necessary to use a larger computer, IBM 360/95, to store all of the necessary cross sections, and we were beginning to have mild success. We discovered at the Denver x-ray conference in August 1977, however, that J. W. Criss of the Naval Research Laboratory had "scooped" us. Criss and associates have made available through a commercial company a huge program that purports to do all the things that we had contemplated. We are therefore currently in the process of testing the Criss program. (*L. D. Hulett*)

Photoelectron Spectroscopy Instrumentation

During the past year we continued efforts toward upgrading the performance of the magnetic spectrometer as well as construction of a new electrostatic spectrometer. Further progress on the position-sensitive detector (PSD) now depends upon completion of the electrostatic instrument so that it may be used for testing the PSD.

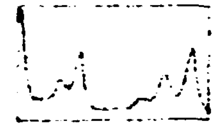
The new source chamber has been installed on the magnetic instrument. The new design allows the spectrometer chamber and source chamber to be evacuated separately. It is now possible to open the source chamber to atmospheric pressure without closing down either pumping system. This operation is a great improvement over the previous arrangement that required raising the entire large volume of the spectrometer to atmospheric pressure when it became necessary to remove the x-ray source for maintenance. It is also now possible to remove the x-ray source without dismantling the entire source chamber, as previously required, which affords a large savings in time and reduces exasperation. The removal and reinstallation of the x-ray source can be carried out in a few hours, an operation which formerly made the instrument inoperable for a week. The source chamber can be evacuated to 3×10^{-8} torr, two orders of magnitude better than the old system. A cold trap is yet to be installed for added pumping efficiency. For samples with minimal outgassing, spectra may be taken approximately 1 hr after loading; formerly this required overnight pumping. We are still using the old sample loading device that is prone to occassional leaks; we plan, however, to design an improved loading system.

The new x-ray source caused a lengthy delay in getting the magnetic instrument back into operation. The original design used a press fit between the metal anode material and a copper cooling tube. The anode metal-to-copper interface was not adequate to transfer the heat produced by 160 W of x-ray power, and aluminum anode materials melted when power was applied. Attempts at clamping the anode metal to the cooling tube were also unsatisfactory. Arcing was a problem, and tungsten deposition from the filament onto the anode metal caused drastic reductions in x-ray intensity. The present design incorporates an aluminum-zinc braze between the aluminum anode material and the copper cooling tube. The filament has been relocated, and a baffle has been positioned between the filament and the anode to shield the anode from the tungsten evaporation. The electrons from the filament pass around the baffle and strike the anode because of the focusing action of the potential field. This new design has been operated at a power of 450 W, with negligible arcing. The baffle appears to be keeping the anode free of tungsten, because a freshly evaporated gold film gives a signal of about 10,000 counts/sec for the Au $4f_{7/2}$ peak and is not diminished with time. Also, no gold photoelectron peaks are present that correspond to tungsten $M\alpha$ x-ray excitation. We are still pursuing the development of a method for bonding magnesium to copper which will allow the use of a dual anode x-ray source of aluminum and magnesium. Such a source would provide greater versatility for eliminating Auger electron interference from electron energy regions where photoelectron energy peaks are to be measured.

An intermittent bug still exists somewhere in the power supply for the spectrometer coils, which causes apparent electron energy shifts by as much as 4 eV. The shift might occur between data-taking periods or in the middle of a spectrum. This situation is intolerable and must be corrected.

---

[37] L. D. Hulett and H. W. Dunn, "X-ray Fluorescence (XRF) Instrumentation and Quantitative Analysis," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp. 14-15.



Recent progress on the electrostatic instrument and the PSD has suffered to some extent because of the need to make the magnetic instrument operational. However, fabrication of the major components of the electrostatic instrument and the PSD attachments are complete, and have been assembled for leak testing. Accomplishments with the magnetic instrument are encouraging, and it is felt that more time will be available presently for the electrostatic instrument and PSD.

To make intelligent decisions in the design of the PSD, it was necessary to have a precise knowledge of the theory of electron trajectories of the spherical-plate electrostatic spectrometer. We made our own derivation of the focusing of charge particles by a spherical condenser and found what appears to be an oversimplification in the theory as originally derived in the literature. Particle theory reveals that an electron of specific energy moving in the electric field of a spherical condenser will retain a constant angular momentum per unit mass for a particular path, but this constant term is not equal for all paths. Implementation of the theory by numerical computer calculations allows us to evaluate electron angular dispersions, electron energy dispersions, plate voltage settings, and source slit and baffle requirements, all of which affect the focal properties of the system. We confirmed that all angularly dispersed electrons whose kinetic energy matches the spectrometer voltage setting will focus on a line that is colinear with the source and the center of curvature of the spherical plates. However, for electrons with higher and lower kinetic energies, we predict that the position of the focal line depends upon the value of the plate sector angle and is colinear with the source and center of curvature only in the case of a 180° sector angle. (*J. M. Dale, L. D. Hulett*)

Problem Solving

The five techniques [scanning electron microscopy energy dispersive x-ray fluorescence (SEM-EDX), x-ray fluorescence (XRF), transmission electron microscopy (TEM), x-ray diffraction (XRD), and electron spectroscopy for chemical analysis (ESCA)] at the immediate command of all members of this group often allow us to function as problem solvers for researchers in other divisions. Each year we are given several extended problems that require a coordinated study, using two or more methods. The most common problem is the question, "What compounds are in my sample?" The usual gambit for this is first to perform an elemental analysis by XRF, SEM-EDX, or ESCA and then to determine crystal structures by x-ray or electron diffraction. Procedures of this type usually provide unambiguous compound identification. Last year[38] we described our work with Co-Mo-supported catalysts. We have continued and expanded this work in 1977, but many other intriguing problems have also come our way.

We were requested to determine the type of a kidney stone. The SEM showed that it consisted of very large crystals containing calcium as a cation in combination with an anion having only first-row elements. X-ray diffraction of the stone revealed calcium oxalate. The SEM also showed a thin layer of very small crystallites, 1 μm or smaller, containing calcium and phosphorus, which we interpret as calcium phosphate. Another problem involved the passivation of concrete. John Moore and Gene Devaney, Chemical Technology Division, discovered that concrete corrodes much more slowly in sea water than in fresh water; optical microscopy revealed a rather coherent layer on the outside surfaces, which apparently was acting as a barrier to dissolution. SEM and x-ray diffraction showed the layer to be MgOH. Apparently, the magnesium ions of the sea water are plating out or exchanging with calcium to form a protective coating. (*L. D. Hulett, R. L. Sherman*)

NEW PROJECTS

Geothermal brines. Several new projects were begun this year. One short-term project involved a round-robin analysis of water from two different geothermal wells in California. The objective of the project was to ascertain which analytical techniques could be used satisfactorily for such samples and to prepare a manual of standard methods. The round-robin samples were sent to about 15 different laboratories. Samples were analyzed at ORNL by a variety of techniques including activation analysis, isotope dilution spark source mass spectrometry, x-ray fluorescence, and atomic absorption for elemental constituents. Radiochemical analyses were performed for natural radioactivities, and gamma spectrometry was used. Determinations using standard methods of water analysis were also made. The first samples were received in July and the second in August. The data are being correlated at Battelle Northwest Laboratories, whence a final report will emerge. (*W. S. Lyon et al.*)

---

[38] L. D. Hulett, J. M. Dale and J. Tarter, "Characterization of Cobalt-Molybdate Catalysts," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp. 16.

Speciation study of elements in fly ash. A proposal to EPRI on this subject was funded beginning in August 1977. The objective of the work is to determine the chemical form of ponded fly ash removed from Bull Run Steam Plant fly ash collectors. This is a joint program between Analytical Chemistry and Environmental Sciences divisions. Responsibility for sampling has been assumed by Ralph Turner of the Environmental Sciences Division, and the first several months of the project have been spent in reviewing the literature, making test samplings, and doing some preliminary washing studies and magnetic separations. The project is most challenging; little, if any, previous work has been reported on speciation of fly ash. (*W. S. Lyon, L. D. Hulett, Ralph Turner, Environmental Sciences Division*)

Seed money proposal. In late November 1977 a seed money proposal authored by H. H. Ross was approved by ORNL management. The funding, which is for one man-year, is for a study of a new concept in spectroscopy. (*H. H. Ross*)

2. Mass and Emission Spectrometry

J. A. Carter, Section Head
R. L. Walker, Associate

The Mass and Emission Spectrometry Section operates a variety of expensive spectrometers, sophisticated and sensitive, to measure chemical and physical characteristics of inorganic and organic constituents. Concomitant with research and development (R&D) programs devoted to improving the state of the art in several areas of spectrometry are support activities, from which came spinoffs in the form of developed methodology that provides ORNL, IAEA, DOE and others with techniques for solving practical real-life problems. In areas of spark source, gas, organic, and actinide mass spectrometry, techniques developed just a few years ago are now being used with visible impacts on programs such as international safeguards, space applications, environmental assessment, and nuclear fuel cycle research and development. This present climate stimulates and encourages the researcher to direct his attention to new R&D projects that will perhaps be applicable to other existing and exciting analytical problems.

During the past year, the unique sensitivity and depth-profiling capability of the ion microprobe mass analyzer (IMMA) has been effectively applied to a number of important research programs. One such effort was the study of the effect of laser annealing on the distribution of ion-implanted ^{11}B in single-crystal silicon, which may have important impacts on solar devices. In yet another effort, an important contribution was made to the field of thermometry. In joint studies with the Instrumentation and Controls Division, IMMA measurements elucidated chemical and physical properties of thermocouples which explained the decalibration phenomena. Recommendations thus established guidelines for improving high-temperature thermocouples.

Development studies are continuing, using NBS glass and iron standards to access IMMA's quantitative capability. From the reproducibility of the sensitivity factor (SF) method, we have established that IMMA analysis becomes quantitative with a known matrix. For cost effectiveness and to aid in the IMMA programs, a dedicated computer system will soon be installed.

Developments in actinide methodology have continued this past year. A sensitive, reliable method has been established for the determination of trace amounts of Pu, U, and Th in a variety of matrices. Also, feasibility studies have been conducted for the possible isotope dilution measurement of ^{99}Tc and ^{237}Np at low levels.

Two significant hardware improvements are under development. These are (1) an interface controller system to upgrade the pulse counting system on the two-stage mass spectrometer and (2) a channel electron multiplier array (CEMA), which will be used as an electronic ion detection system for spark source mass spectrometry (SSMS).

We have spent much time in the development of methodology and computer software for maximum utilization of the Associated Electrical Industries (AEI) MS50 DS50 system. We are able to use computer acquisition of data at resolutions of up to 40,000 and have used such resolutions in collaborative work. The sensitivity at low masses has been greatly improved for gas samples, and software has been written to allow quantitative gas analyses by using a residual type calculation. The unique metastable scanning techniques have been of value in several problems and are being used now in a basic study of alkylated phenol fragmentations. We have developed equipment and techniques for air sampling, using Tenax adsorption tubes with low-resolution spectrometers, and are investigating application of these techniques to personnel-exposure monitoring. We have also been able to obtain field ionization spectra with the ORNL spectrometer, using metal dendrite emitters, and are continuing this development. Organic mass spectrometry support was given to other divisions when needed, especially in Occupational Safety and Health Administration (OSHA)-related problems at all Oak Ridge plants. The Du Pont 490B system at the X-10 site has been devoted almost entirely to support of the Bio-Organic Analysis Section.

Developments in spark source mass spectrometry (SSMS), inductively coupled plasma (ICP), optical emission spectrometry, and isotopic mass spectrometry have continued in support of many ORNL programs. For example, a project is under way to construct an SSMS instrument capable of analyzing radioactive samples with γ-activation of up to 100 R/hr. A feasibility study has been conducted in which a spark source instrument was modified and operated remotely with nonradioactive samples. Additional development work has been done with the ICP spectrometer on the analysis of organic liquids and nickel solutions. We have designed an improved nebulizer and purchased a double monochromator for the instrument. We are using a combination of optical emission, ICP, and spark source for the analysis of fly ashes and other difficult samples. The combined data are used to detect interferences, sample loss, and other error sources.

Support analyses have been performed for 17 ORNL divisions as well as K-25, Y-12, NASA, the U.S. Air Force, Argonne National Laboratory, EPA, and TVA. Light Water Reactor fuel solutions and leachates have been analyzed for uranium and plutonium by isotope dilution mass spectrometry (IDMS) and for impurities by SSMS and optical emission (OE). In the gas analysis laboratory, we have continued the analysis of enriched ^{133}Xe and ^{85}Kr as well as the routine high-purity gas analyses. The static gas mass spectrometer has successfully analyzed small (10^{-11}-liter) samples from electronic tubes.

MASS SPECTROMETRY RESEARCH AND DEVELOPMENT

Ion microprobe mass analyzer (IMMA). The IMMA surface analytical facility has been operational for approximately 3 years. During this period three members of the mass spectrometry group have attained proficiency in the application of this method. A variety of unique analytical problems has been addressed, and the results of our major efforts during the past year are presented in the following paragraphs.

In collaboration with C. W. White of the Solid State Division, we have used the unique sensitivity and depth-profiling ability of IMMA to determine the effect of thermal and laser annealing techniques on the distribution of ion-implanted ^{11}B in (100) single crystal silicon. This work is related to the development of improved solar-electrical conversion devices and will be detailed in forthcoming literature reports.[1,2]

Samples of (100) silicon were implanted at dose levels of 10^{14}, 10^{15} and 10^{16} ^{11}B atoms cm^{-2}. The implantation was done at 35 keV and gave a Gaussian implant profile, with the ^{11}B mean depth being around 1320 Å and a half width at half maximum of 585 Å. A typical set of measurements is described for

---

[1] R. T. Young, C. W. White, G. J. Clark, J. Narayan, and W. H. Christie, "Laser Annealing of Boron Implanted Silicon," *Appl. Phys. Lett.* (in press).

[2] R. T. Young, C. W. White, G. J. Clark, J. Narayan, R. D. Westbrook, and W. H. Christie, "Laser Annealed Boron Implanted Silicon Solar Cells," *Proceedings of Int. Conf. on Solar Cells, Luxembourg, Sept. 27-30, 1977* (in press).

an unannealed specimen implanted with ^{11}B to a dose level of 10^{15} atoms cm^{-2}. The peak baron concentration would be about 1 atom %. An electronic aperturing technique was used in pulse counting mode to obtain maximum depth resolution and sensitivity. The unannealed sample was used to calibrate both the depth scale and concentration response of IMMA. The sputtering region from which data were extracted contained approximately 60×10^{-15} g of B or about 3.3×10^{9} atoms. During the 25-min sputter period, about 2.8×10^{6} boron atoms were detected for an absolute efficiency of around 1:1200. Typically, the boron signal was followed down to the 10-ppm level, at which point over 99.99% of the boron had been sputtered from the implanted region.

The effects of laser and thermal annealing on the dopant profile were determined by depth profiling under conditions identical to those used for the unannealed specimen. Thermal annealing at 900 to 1000°C produced only a slight broadening of the implant profile. Pronounced changes occurred in the implant profile distribution as a consequence of laser annealing. The concentration in the near surface region was substantially increased and the profile broadened to greater depth in the crystal. The profile became almost uniform from the surface down to a depth of about 2000 Å in the crystal. The boron profile results determined by IMMA are in qualitative agreement with independent carrier profile electrical-conductivity measurements. It is interesting to note that secondary ion mass spectrometry (SIMS) is the only analytical technique with sufficient sensitivity to profile boron in silicon at the 10^{10}-atoms-cm^{-2} level.

The acknowledged high sensitivity of SIMS makes quantification of the technique desirable. We have continued our efforts in evaluating the quantitative capabilities of SIMS through the analysis of standard materials. Our work with the National Bureau of Standards (NBS) glass and iron standards was detailed in an ORNL TM report[3] and will appear as a journal publication.[4] We have obtained the NBS K-309 standard glass in the form of microspheres as a suspension in ethyl alcohol. To facilitate analysis by IMMA, the microspheres were loaded on pyrolytic graphite planchets. A 19-keV, 10- to 15-μm-diam ^{16}O$^-$ primary beam was used for the analysis. Typically, the beam would be centered on a 5- to 8-μm-diam particle. High Na$^+$ and K$^+$ signals were allowed to decay (2 to 4 min) before taking data. Stable ion signals could then be obtained for 25 to 30 min allowing two to three data sets to be accumulated. Background spectra taken on the planchet in regions adjacent to the microspheres showed no interferences. To calculate the results, we used the SF method. Average SFs derived from a suite of similar materials[3] and previously obtained SFs from the bulk K-309 glass[3] were used. Results from 16 analyses performed on eight microspheres are reported in Table 2.1.

The SFs previously derived from the bulk NBS K-309 glass give analytical results that approach quantitative, whereas average SFs give results that are considered semiquantitative. One-sigma deviations are also included to give some indication of the reproducibility of results.

As a test of the average SF concept, a "blind" glass sample (K-873) was submitted by the NBS to four laboratories, including ORNL, for analysis. The four laboratories did both qualitative and quantitative analysis and reported the results to NBS where the data were compiled. The results of this round-robin

Table 2.1. NBS K-309 microsphere results

Element	Theoretical atom %	Average sensitivity factors			K-309 sensitivity factors		
		Average (atom %)	Deviation (1 σ)	Error (%)	Average (atom %)	Deviation (1 σ)	Error (%)
Al	19.45	22.40	2.25	+15.2	19.91	2.10	+2.4
Si	44.00	33.87	3.40	23.0	40.86	3.66	−7.14
Ca	17.67	19.25	2.44	+8.9	17.63	2.33	−0.23
Fe	12.42	17.85	1.49	+43.7	15.07	1.34	+21.3
Ba	6.47	6.62	1.75	+2.3	6.54	1.72	+1.08

---

[3] D. H. Smith and W. H. Christie, *Investigation of Quantification of SIMS Data: Analysis of NBS Glass and Iron Standards*, ORNL TM-5728 (June 1977).

[4] 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.* (in press).

Table 2.2. Round-robin analysis of "blind" glass K-873

Element	Assay (atom %)	Laboratory			
		A	B	C	ORNL
Al	0.39	0.31	0.35	0.45	0.53
Si	16.16	11.31	14.00	21.95	11.34
Mn	0.23	0.15	0.21	0.15	0.24
Ge	9.28	12.38	8.91	8.42	6.53
Ba	6.33	8.90	9.20	6.83	8.35
Ce	0.12	0.12	0.16		0.16
Ta	0.99	0.20	0.084		0.21
Pb	4.35	4.36	5.25	4.75	9.64

analysis are reported in Table 2.2. Again, semiquantitative results were obtained via SIMS, using average SFs.

The application of SIMS to the analysis of tritium barrier oxide films grown on Incoloy-800 heat-exchanger surfaces continues. In cooperation with Bell, Redman, and Smith of the Chemistry Division, we have used the SF method to quantify elemental depth profiles determined for these films. Two samples of Incoloy-800 were analyzed by optical emission spectrometry to establish nominal elemental composition. These two samples were repetitively analyzed by IMMA to establish SFs and reproducibility limits for the method. Sample 1 was analyzed ten times and sample 2 eight times. The analyses were made over a period of several weeks. The results of this study are reported in Table 2.3.

Table 2.3. Sensitivity factors derived from Incoloy-800

Element	Sample 1 (10)		Sample 2 (8)	
	Wt %	SF ± σ	Wt %	SF ± σ
Al	0.46	4.79 ± 0.39	0.36	4.21 ± 0.12
Si	0.15	0.362 ± 0.044	0.16	0.332 ± 0.012
Ti	0.55	1.23 ± 0.11	0.53	1.19 ± 0.05
V	0.02	0.834 ± 0.076	0.02	0.915 ± 0.019
Mn	0.73	2.53 ± 0.11	0.88	2.30 ± 0.07
Cu	0.42	0.589 ± 0.049	0.38	0.641 ± 0.010
Cr	23.3	1.79 ± 0.09	22.5	1.79 ± 0.06
Ni	28.0	0.749 ± 0.029	28.1	0.824 ± 0.021
Fe	46.37	≡1.0	47.07	≡1.0

The reproducibility of the SFs indicated by the one-sigma limits again indicates that IMMA analysis becomes quantitative when used with a known matrix. We have used the SFs reported above to quantify the composition of experimental oxide films grown on Incoloy surfaces. The sputtering must be done with an oxygen beam to avoid matrix changes as the oxide-metal interface is sputtered through. Using this method, we have shown that the composition of the oxide film is a strong function of the chemical and thermal exposure of the sample. One class of experiments produced films rich in chromium and manganese, whereas another experiment produced films rich in iron. It is paramount that the composition of these oxides be established if their performance as tritium barriers is to be optimized.

Our joint investigation with T. Kollie and R. L. Anderson of the Instrumentation and Controls Division on thermocouple decalibration has continued. Our earlier work with tantalum-sheathed, Al_2O_3-insulated units showed platinum and platinum-rhodium to act as reducing agents for the Al_2O_3 insulation under the reducing conditions set up inside the thermocouple sheath. A detailed account of this study has been accepted for publication.[5] We have now examined platinum-platinum-rhodium thermocouples in a variety of sheath materials in which MgO was employed as the insulator material. In the earlier study,[5] we found intrusion of Al into the Pt and Pt-Rh thermoelements to be the cause of failure. In this study we expected to find magnesium the culprit. We studied transverse cross sections at 5, 15, 25 and 50 cm from the thermocouple measuring junction. The 50-cm section that operated at room temperature showed no appreciable contamination and was used as a standard for the IMMA work. The 5- and 15-cm sections showed high magnesium, as expected, and lower levels of Mn, Al, and Si. Concentration profiles were determined for these elements. Independent optical emission spectrometry showed the platinum wire at 5 cm to contain 6.1 atom % magnesium and 0.18 atom % manganese. These values were used to quantify the IMMA profiles so that the concentration of magnesium and manganese could be evaluated at any point along the wire radius. The outer edge of the wire had approximately 12 and 0.5 atom % magnesium and manganese respectively. The center of the wire contained 0.33 atom % magnesium and about 25 ppma manganese. The aluminum and silicon values were about an order of magnitude lower than for manganese. The magnesium clearly came from the reaction of the thermoelements with the MgO insulation. The aluminum and silicon were originally present as contaminants in the MgO. The manganese was shown to come from the Inconel sheath. In the course of this work, we were

---

[5] T. G. Kollie, W. H. Christie, and R. L. Anderson, "Large Decalibrations in Ta Sheathed, Al_2O_3 Insulated Pt Rh Thermocouple Assemblies During Heating to 1330°C," *J. Less-Common Met.* (in press).

able to show that the reactive sheath material (e.g., stainless steel, Inconel, or Ta) provided the driving force for the platinum or platinum-rhodium-oxide interface reaction. As the oxide insulator decomposed at the metal interface, the sheath material reacted with the liberated oxygen, thereby maintaining the low-oxygen partial pressure that supports the oxide decomposition. To test this supposition, thermocouples clad in nonreactive sheaths (i.e., Pt and Pt-Rh) were prepared and tested. These were found to be significantly more resistant to the kind of failure observed in our work. A detailed description of this study has been submitted for publication.[6]

The recommendations emanating from this work are of significance to high-temperature thermometry. Thermocouples sheathed in reactive metals should not be used above 1000°C for extended times. If exposures above 1000°C are required, a nonreactive sheath material such as platinum or platinum-rhodium should be chosen.

During this period, we have placed purchase orders for a dedicated minicomputer system for IMMA function control, data acquisition, and processing. The system is based on a PDP-11/34 with 32K of core memory, a 2.5-million-word fixed-head magnetic disk, a 1- to 2-million word removable cartridge disk, a DEC writer for input/output, and appropriate peripherals and interfacing hardware.

The computer will control four IMMA functions: x-y sample stage position, primary ion-beam positioning, secondary magnet-scan function, and the electrostatic short-range scan plates. Four variables will be measured: primary ion-beam current, total secondary ion current, mass-resolved secondary ion count, and mass number. A major portion of this effort will be directed toward the automation of depth profiling studies in which the concentration of a particular element is monitored as a function of depth into the surface because manually performed studies of this type are time consuming, tedious, and expensive. *(W. H. Christie, R. E. Eby, R. W. Stelzner)*

Actinides in environmental samples. We have developed a workable method for the IDMS determination of low-level Pu, U, and Th in soils, plants, and animals. The sensitivity obtainable is about 10^{-15} g/g for plutonium and 10^{-9} g/g for uranium and thorium, using pulse counting for ion detection. A triple spike containing ^{242}Pu, ^{233}U, and [illegible]Th is added before chemical treatment is begun.

In this method, samples ashed at 550°C are weighed and spiked with the triple spike. Aqua regia is used to dissolve the samples. The samples are incompletely soluble and are leached according to the procedure developed by Chu.[7] Equilibration of spikes with the desired elements is accomplished in the dissolution steps of the procedure. After dissolving and/or leaching, the actinides are separated by solvent extraction from the bulk material, using a 50% tributyl phosphate (TBP)-Amsco mixture. The organic is scrubbed to remove impurities, and the actinides are then back-extracted into water and evaporated to dryness.

The purified sample is split into two equal parts after dissolving in a small volume of 8 *M* HNO_3. For filament loading, different schemes have been devised to obtain the maximum ion emission during mass analysis. One-half the sample is taken for plutonium adsorption onto anion resin beads according to the published resin-bead filament loading method.[8] The resin-bead loading enhances the plutonium ion emission because the plutonium adsorbs strongly; however, uranium and thorium in nanogram quantities cannot be measured on the same anion resin bead because these elements adsorb weakly. A sequential analysis of Pu, U, and Th is possible if the sample contains about 1 μg of U and Th. Therefore, it is our practice to scan the uranium isotopes during plutonium mass analysis and the thorium isotopes during uranium analysis because the temperatures for thermal emission overlap. If the ion signal for uranium and thorium is too small from the bead loading, the remaining portion of the aqueous sample is evaporated to dryness, redissolved in dilute nitric, and loaded directly onto filaments as the nitrate solution.

The method has been used in experiments designed to measure Pu, U, and Th distribution in plants and animals from contaminated soil. Spike recovery for each element has been measured as between 30 and 70%, using isotope dilution. With these recoveries, excellent ion signals are often obtained. The primary limiting factors are chemical recovery, contamination, and initial spike purity.

---

[6] 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 versus Platinum, Thermocouple Assemblies During Use at 1200°C," *J. Less-Common Met.* (in press).

[7] N. Y. Chu, "Plutonium Determination in Soil by Leaching and Ion-Exchange Separation," *Anal. Chem.* 43, 449 (1971).

[8] R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, "Simultaneous Plutonium and Uranium Isotopic Analysis from a Single Resin Bead: A Simplified Chemical Technique for Assaying Spent Reactor Fuels," *Anal. Lett.* 7, 563 (1974).

In our future developmental work, we plan to investigate the possibility of improving the sensitivity either by a combination of anion and cation resin-bead loading or by a cation bead loading for all three elements. Some preliminary experiments, using cation beads loaded with a triple spike of the elements, have been most encouraging. Also, a lower limit of detection for plutonium would be possible if a spike could be obtained which was free of the major isotope in the sample (i.e., ^{242}Pu or ^{244}Pu free of ^{239}Pu).

An investigation into the feasibility of measuring ^{237}Np by an SF approach is being investigated, using thermal emission mass spectrometry (TEMS) and Pu as an internal standard. Neptunium ionizes efficiently by TEMS; unfortunately, no long-lived isotope of the element exists for isotope dilution analysis. Because neptunium in low-level amounts is difficult to analyze by beta counting, the SF method shows promise as a semiquantitative estimation technique. The mass spectrometry technique involves the integration of the total ions from ^{237}Np, using the ^{242}Pu as an isotope tracer.

Synthetic solutions containing neptunium and plutonium have been analyzed by two loading methods: resin-bead adsorption and solution evaporation. The standards contained neptunium and plutonium in ratios of 100:1, 10:1, 1:1, 1:10, and 1:100, with a maximum of 1 ng for the major isotope. Large integrated ion signals are obtained from 1 ng of plutonium or neptunium, $\cong 5 \times 10^8$ ions ng^{-1}; therefore, the sample size must be limited. Plutonium adsorbs more efficiently than neptunium on anion resin; therefore, a large factor of 9.9 with a relative standard deviation (RSD) of 21% was determined by this method; the factor determined for solution loading was 1.5 with an RSD of 50%. No bias was observed in either method over the concentration ratios studied. Based on these observations, the detection limit of 0.001 ng for neptunium, using 1 ng of ^{242}Pu as internal standard, seems possible with an RSD of about 20 to 50%. *(R. L. Walker, E. G. Miller, H. C. Smith)*

^{99}Tc by isotope dilution mass spectrometry. In a joint effort with the Savannah River Laboratory, ^{99}Tc in environmental samples was to be measured by IDMS. Preliminary tests by using ^{99}Tc indicate that thermal emission and pulse counting for ion detection might have suitable ionization efficiency for developing a sensitive method for measuring ^{99}Tc, assuming a suitable isotope spike of ^{97}Tc can be obtained. We have recently made measurements by using ^{99}Tc to determine the best filament material based on ionization efficiency. Of the three filaments (Re, W, and Ta) tested, ionization is greatest with rhenium; the order based on ionization efficiency is Re > W > Ta.

Molybdenum contamination, even in zone-refined rhenium, causes interference in the measurement of Tc 97/99 because molybdenum has isobaric interference in the *m/z* 97 position. A possible way to eliminate the molybdenum interference is to measure *m/z* 95, 97, and 99 and correct out the ^{97}Mo, based on the natural Mo 95/97 ratio. It is also possible that other interferences will cause problems in the 10^{-13}-g/g range of desired sensitivity.

Improvement in ion emission is under investigation, using an anion resin-bead loading method. Definite improvement has already been shown over solution loading. Ionization efficiency for ^{99}Tc has been measured at about 1 ion/10^6 atoms loaded as the solution. Efficiency measurements for single-resin-bead loadings has shown an enhancement of about 50 over that observed for solution loading. Presumably, this enhancement is due to two factors (1) point source and (2) reduced oxidation states that are less volatile. *(R. L. Walker, E. G. Miller, H. C. Smith)*

Computer interface and sweep controller for multistage mass spectrometer. Extensive modifications of the computer interface/controller for the tandem spectrometers are under development. The changes desired are (1) to expand the mass range available for simultaneous analysis, (2) to increase from 8 to 16 the number of "masses" (subgroups) at which data are collected, (3) to provide a greater number of standard data-collection programs than the two available with the previous model, (4) to allow the operator more freedom in selection of operating conditions, (5) to make the interface/controller capable of operating the spectrometer independent of the computer while retaining the features that permit complete control by the computer, and (6) to replace obsolete data-acquisition equipment.

Incorporation of a John Fluke Mfg. Co. model 5205A power amplifier will permit sweeping the accelerating voltage 2000 V rather than the 500 V previously available; for example, this amplifier will allow the nearly simultaneous collection of data for all isotopes of uranium and plutonium. A calculator chip in conjunction with a 20-key pad is used for entering control parameters into the controller. Each parameter is entered into a register including an appropriate data latch. Some registers remain fixed for an entire analysis. Eight registers, however, might require alteration for each subgroup. The latter registers communicate with a 1K × 16-bit random-access memory in the controller. Coding divides the memory into four "programs" of up to 32 subgroups. These programs can be called from front panel switches. Alternatively, programs can be entered into local memory from the computer. The number of data-collection routines is thus limited solely by the storage capacity of the host computer. Tested programs of future value can also be transferred to the host computer from the controller for storage. A 5-bit address code permits the host computer to address any register and either enter or retrieve data from the register.

Some of the calculator functions have been made available to the operator so that calculations required during setup may be made easily. Often the result can be transferred directly to the appropriate register because the last four digits of the calculator display have been made compatible with the internal bus.

All operations can be initiated or terminated from either the computer or the controller. Thus it is possible to test a program independently of the computer and to switch to the computer only when data are to be collected. One host computer can conceivably serve more than one spectrometer. Alternatively, the computer can control the individual decisions required through a set of flags and or interrupts generated by the controller. The latter mode of operation permits an optimization program to alter the collection scheme during analysis.

The new equipment will replace a multichannel analyzer and homemade peripherals which have become unreliable or totally unusable. It also will update and expand capabilities of equipment designed for IAEA[9] use. After satisfactory performance has been demonstrated with the prototype, we plan to adapt our other multistage instruments for use with the new computer interface controller.

To exploit fully the new sweep-control unit under development for the multistage mass spectrometers, it was necessary to write new computer programs to control data acquisition and processing. With the large voltage (2000 V) now available to be scanned, many more alternatives are available to the analyst for data accumulation. For example, it is possible to scan a metal ion spectrum and to monitor the metal oxide and metal dioxide ion peaks during the same scans. The analyst is therefore able to choose which of the three gives the best results for use in his final report.

Another way the new system can be exploited is to scan several elements simultaneously. In reactor burnup studies, it is possible to monitor Pu, U, and Th throughout the duration of data taking, which should enhance precision and sensitivity.

Development of programs to process the data generated by such data collection schemes is well under way. These programs are being written with a view to maximizing flexibility; that is, data accumulation should not be significantly limited because of the programs. It is envisioned that ultimately we will be able to scan any element with any chosen scanning and ratio calculation scheme. A variety of disk files has been established containing, inter alia, scanning schemes (how many times each mass is swept per scan), ratio calculation information (22 ratios are the current maximum), dead-time and bias-correction parameters, sample information (sample code, sweep rates, number of scans, etc.), mass spectral files containing the point-by-point counts in each data step for the mass spectrum, and an output file containing the averages and standard deviations for each ratio. Data from the last file would be available for printing out in a variety of final report formats.

Bias correction will be monitored daily through analysis of a standard. Results of the most recent ten standards will be kept in a file and updated daily, with the current bias correction reflecting the average of these last ten standards. *(T. R. Mueller, D. H. Smith, R. L. Walker, L. K. Bertram)*

Electro-optical ion detector for SSMS. In an effort to improve data collection in SSMS, we have been working on an electronic ion-detection system by using state-of-the-art components. This system will involve a CEMA having a maximum gain of 10[illegible] with a phosphor screen readout. Light pulses produced when an ion strikes the CEMA will be detected with a TV camera, using a silicon diode vidicon tube. A computer will be used to store these counts along with their position and will reconstruct the mass spectrum or output concentration information directly. This system will allow simultaneous, precise measurements to be made on a small section of the mass spectrum (5 to 15 mass units) and will be used with isotope-dilution techniques to give the optimum accuracy.

Thus far, we have designed the CEMA detector and its holder and the optical port through which the TV camera will view the spectrum. Preliminary design work has been done on the electronic readout and computer interface modules. *(D. L. Donohue)*

---

[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).

Technical assistance to IAEA Safeguards, International Safeguards Project Office (ISPO) Task A.16. As a part of our task to aid the IAEA in Safeguards' measurements, two staff members (Ray Walker and Charles Pritchard) recently spent 3 weeks at the Seibersdorf Safeguards Analytical Laboratory (SAL) training and instructing their personnel on the use of the ORNL two-stage mass spectrometer and on application of the resin-bead procedure for sampling and sequential analysis of plutonium and uranium. The two-stage instrument was built and installed by ORNL more than a year ago, and the resin-bead method was developed in our laboratory. This method offers great potential for Safeguards' analyses because very small samples are required. The main advantages are: reduction of sample preparation costs, reduction of health hazards in the spectrometry laboratory, and greatly reduced risks and costs in shipping highly radioactive samples from operators' sites to Safeguards laboratories.

Procedures for sample preparation, resin-bead handling, and fabrication of microtools for bead manipulation were demonstrated, and detailed procedures were provided to the SAL staff. The operation of the mass spectrometer and its use for analysis of plutonium and uranium from a single bead was demonstreated to the SAL mass spectrometry staff; details for mass analysis were written. During the training period, a procedure for field inspection was drafted and successfully tested during the latter part of the exercise.

As a result of the technology developed here, IAEA's SAL near Vienna is now is a better position to implement an analytical program that can be cost effective, give reliable measurements of plutonium and uranium, and provide the IAEA with the necessary technology to carry out its mission of safeguards analytical measurements. *(R. L. Walker, J. A. Carter, D. H. Smith, C. A. Pritchard)*

Age measurement studies on waste isolation site samples. We are continuing our collaborative effort with Sandia Laboratories, Albuquerque, New Mexico,[10] by assisting them with the mass spectrometric measurement of ^{234}U to ^{238}U alpha ratios on samples from a possible waste isolation area in southeastern New Mexico. The alpha-ratio measurements are used to establish ages of mineral deposits, salts, and brines from the general area. The alpha-ratio disequilibrium method has been used to calculate the age of Caliche or Calcrete from the waste site area. For comparison, we also measured the ^{234}U to ^{238}U ratio in Caliche from the Olduvai Gorge, which had been dated by other techniques such as the K-Ar method. The New Mexico Caliche sample, according to the alpha-uranium-ratio disequilibrium, was about 0.86 as old as the Olduvai Gorge samples, which was in the expected direction.

Additional laboratory experiments with inert atmospheres are being planned to understand some very high alpha ratios that occur in deep well waters. (One brine sample exhibited an alpha ratio of 14:7.) One theory predicts[10] that when the alpha recoil of ^{234}Th (a precursor of ^{234}U in the decay scheme) occurs near a surface or liquid-solid interface, differential solubility can take place, which offers a plausible explanation for the high disequilibrium ratios. Controlled experiments in which hot water was circulated over UO_2 in air for 6 months did not, however, exhibit a discernible change in the alpha ratio. One possible reason for not observing the expected ^{234}Th alpha-recoil effect is that it could have been masked due to the high dissolution rate caused by air oxidation of the UO_2. This experiment is being repeated in an inert atmosphere to elucidate further and to understand the mechanism. *(J. A. Carter, R. L. Walker, E. G. Miller, H. C. Smith)*

ORGANIC MASS SPECTROMETRY

Research and development activities. During the past year we have used the AEI MS50/DS50 high-resolution system and the Du Pont 490B/094B and ORNL low-resolution systems in several research and development projects, some of which will be described. The initial problems in the DS-50 data system which prevented its effective use have been corrected, and the instrument is in full-time operation.

We have spent much time in development of methodology, sample-handling techniques, and computer software for maximum use of the MS-50 system. Qualitative identification of organic compounds is often difficult whenever comparative spectra are not available. In such cases, high-resolution mass spectra and exact-mass measurements make available empirical formulas for each ion in the spectra and thereby assist greatly in identification. In addition, the empirical formulas of fragments lost in the compound fragmentation add valuable information for determination of molecular structures. The ability of the MS-50 system to give information routinely at resolutions higher than

---

[10] J. A. Carter et al., "Age Measurement Studies on Waste Isolation Site Samples," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 29.

10,000 ($m/\Delta m$ for 10% valley) and as low as mass 15 has given us additional capability in solving identification problems.

We can now use resolutions of 10,000 to 40,000 in the computer acquisition mode, although a resolution of 10,000 is usually sufficient to give unambiguous empirical formulas. In a collaborative project with personnel from the Pittsburgh Energy Research Laboratory on the analysis of a nitrogen fraction from the synthoil process, it was necessary to use 40,000 resolution to separate unresolved multiplets because of oxygen, nitrogen, and paraffinic components in the mixture. This resolution was achieved at considerable sensitivity loss. Ion source pressures of about 5×10^{-6} torr, using the direct inlet probe, were required for satisfactory computer data acquisition. We have attained resolutions of about 150,000, using manual peak-matching techniques on individual peaks. This technique requires exact measurement of variations in accelerating potentials and is necessary for separation of very closely spaced multiplets.

An example of a typical application encountered this year will illustrate the utility of the technique and its application to a number of complex identification problems. This problem required the identification of reduction products of acetonitrile. The sample in question was analyzed by direct-probe high-resolution repetitive-scanning techniques while the probe was heated incrementally to 400°C. The computer-reconstructed total-ion-current chromatogram indicated the presence of two volatile components. Experimentally determined molecular ions of m/z 123.0794 and 82.0532 were noted for the two components. These molecular ions corresponded to empirical formulas of $C_6H_9N_3$ and $C_4H_6N_2$ respectively (a trimer and dimer of acetonitrile). Both components exhibited a large fragment ion at m/z 41.0310, corresponding to $CH_3C \equiv N^+$. This information plus fragmentation data suggested a β-iminonitrile structure for the acetonitrile dimer. The trimer was somewhat more difficult to identify, but the *fragmentation pattern and ion empirical* formulas were consistent with a dimethyl-amino-pyrimidine structure. This repetitive scanning technique was also used routinely with the gas chromatographic mass spectrometric (GCMS)-inlet system. About 70 samples were examined by high-resolution repetitive scanning techniques.

The MS-50 has a rather sophisticated capability for determining unambiguous ion fragmentation schemes by various metastable scanning techniques. These methods involve "linking" the accelerating potential, the electrostatic sector voltage, and the collector scintillator potential in various ways. The HV scanning mode identifies parent ions of any daughter ion, and the combined scanning mode identifies daughter ions from any parent ion. This technique was valuable in the analysis of a sample for Russ Knapp of the Health and Safety Research Division, who recently required the determination of the fragmentation scheme for an unusual 58-u loss from the molecular ion of phenyl ω-dimethoxy-ethyl telluride. High-resolution data showed this loss to be C_3H_6O. The combined scanning technique confirmed the loss to be from the molecular ion without intermediate ion formation. A six-membered cyclic transition state was postulated for the 238^+ ion formation. These data have been used in describing the rearrangement for publication. Determination of fragmentation pathways of alkylated phenols is being carried out, using these techniques.

Quantitative gas analyses are now being made with the MS-50. The unique value associated with quantitative high resolution (>1000) analyses is the ability to resolve different components of the same integral mass. Unresolved multiplets are major sources of error in most low-resolution quantitative instruments. Recently a sample containing alkanes and deuterated analogues produced a rather complex series of multiplet ion peaks requiring resolutions of about 10,000 for complete separation. We were successful in identification of the ions and quantification of associated components in this mixture by manual and computer-assisted high-resolution analyses.

One problem associated with the development of high-resolution quantitative gas analyses has been the relatively large loss in sensitivity for low masses (i.e., H_2, D_2, etc.). This problem was corrected by slightly shifting the angle of emission from the ion source for these low masses. This focusing procedure can be done reproducibly and allows a 100-fold improvement in SFs for low masses. Sensitivity factors have been determined for various gases from standard gas mixes, and these factors are used in analyses of the gas samples. This procedure is currently being done manually. However, using the raw-data-acquisition mode available with the DS-50 data system, we have been able to obtain flat-top peaks at a resolution of about 5000 and a dynamic scanning rate of about 100 sec decade. The peak shape suggests that accurate quantification will be possible, using computer processing. Therefore, software has been written to locate raw-data peaks, find the centroid, and determine peak intensities. Other software has been written to construct and maintain a mass spectral library (about 150 compounds) for use in residual calculations, and the residual quantification program is being written.

We have developed several techniques for use with the low-resolution instruments, which we expect to be valuable in future applications. One of these is the use of Tenax adsorption tubes as a means of collecting samples from gas sources containing low-level contaminants. In general, the method involves the collection of organic components on the adsorbent, thermal desorption of the components into the gas chromatographic (GC) inlet, freezing the components on the head of the GC column, and finally, identification of the individual components by GCMS as they are eluted from the column. The advantages gained from this technique include the detection and identification of trace organic components (<1 ppm, depending upon volume of gas pulled through the tube) and the elimination of impurity artifacts, injection difficulties, and other problems associated with solvent collection and sampling.

Since Perkin-Elmer 3920 chromatographs are used on both low-resolution instruments, the glass liners of the injector ports are used as adsorption tubes. They are filled with Tenax and are baked out at 320°C with helium flow prior to use. A device for insertion of the tubes into the heated injection port without interruption of carrier flow has been constructed and has performed satisfactorily.

The Du Pont 490B GCMS has been used to apply the technique to various sample types, including air, cigarette smoke, stack effluents, and "head-space" components. Most of these samples were "frozen" at liquid nitrogen temperatures on the head of a 10-ft Dexsil-400 column before temperature programming from 0 — 320°C. Several interesting, tentative mass spectrometry identifications were noted in this work.

Samples originating from laboratory air contained various alkyl benzenes, alkyl hydrocarbons, acetophenone, naphthalene, methylated silicone oils, and phthalate esters. Each air sample was a composite adsorbed from several thousand liters of air. By contrast, a sample collected from 300 liters of air in a pilot plant process area contained significant amounts of tetrachloroethylene (perclene) as well as elevated levels of many alkyl benzenes and other aromatic compounds.

The latter experiment suggested that this technique could be a valuable aid in monitoring volatile and/or organic particulate matter in certain hazardous processes requiring personnel monitoring. Toward that end, two Spectrex Personal Air Samplers (PAS-2000) were purchased for evaluation, using Tenax polymer as the adsorbent. These personnel monitors are compact/battery operated devices and can maintain a practical flow rate (through our present Tenax tubes) of 100 cc/min. Initial evaluation of these devices revealed that they will prove useful for establishing "exposure" levels of hazardous organic pollutants in work environments.

This sampling technique was of value recently in a health-related problem of concern to the medical staff. Epoxy paint samples that were suspect in the development of skin rashes on several employees were analyzed, using Tenax precolumn adsorption tubes for sampling "head-space volatiles." The individual components were identified, using the Du Pont 490B GCMS. Literally hundreds of GC components were noted in each sample. Major components identified in the primers and finished samples included: methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), alkylated benzenes (C_1-C_5), nonanal, decanal, naphthalene, and alkylated naphthalenes (C_1-C_4), alkanes (C_1-C_{12}), ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, dibutyl cresol, acetaldehyde, ethanol, butanol, low-molecular weight esters, and cyclic aliphatics. Less volatile components included dibutyl phthalate, dibutyl sebacate, dioctyl phthalate, and squalene. These data were submitted to the Health Division staff for correlation with known health effects.

There has been considerable interest and development in organic mass spectrometry recently in various "soft" ionization techniques such as field ionization and chemical ionization. These ionization techniques are especially valuable in qualitative identification problems because much less fragmentation occurs and molecular peaks are usually observed (often impossible in electron bombardment sources). Because of our interest in field ionization phenomena and because ion yields are often low, we have investigated means of improving the overall ionization efficiency of the ORNL low-resolution instrument. This has involved applying different voltages between various plates of the ion source, correlating required drawing-out voltages with case plate-slit dimensions, using additional ion source components (such as ion repeller), studying effects of ionization box position, and installing external ion source magnets. We have succeeded in improving the ionization efficiency by 200 to 400 times, as measured by relative intensities of perfluorokerosene peaks. This improvement was largely due to increasing the potential between the case and draw-out plates from 800 to 2700 V. The measured resolution of the instrument, using 0.15-mm (0.006-in.) source slits, was unaffected by the changes and is 900 to 1000 ($m/\Delta m$ for 10% valley). Noise and background problems are naturally greatly increased, and we are investigating means of eliminating these problems. We determined the sensitivity at usable noise levels to be about 2×10^{-10} C/μg for the molecular peak of cholesterol, comparable to those reported for high-sensitivity commercial spectrometers. With further improvement in noise level, even greater sensitivity will be realized.

Field ionization ion sources require the use of specially activated emitters to develop the high-voltage gradients necessary for ionization. Most currently used emitters are prepared by deposition of needle-like growths on 10-μm tungsten wire. We have assembled the vacuum system to be used in depositing carbon needles from an atmosphere of benzonitrile as originally described by Beckey and Schulten.[11] In addition, we have constructed a plating control for deposition of metallic dendrites on tungsten wire emitters as described by Bursey.[12]

Because the tungsten wire is only marginally visible, we have constructed a spot welder to be used under a microscope for attaching the emitter wire to the supporting legs. After activation by either of the above techniques, these assemblies are mounted in the ion source of the spectrometer. Rearrangement of source voltages is necessary to obtain the normal accelerating voltage (4 kV), while allowing 8 to 12 kV between the emitter and its counter electrode at a distance of 1.5 mm.

We have prepared emitters by using both nickel and cobalt dendrites deposited from heated concentrated solutions of metal salts as suggested by Bursey.[12] The nickel needles were uniformly distributed along the wire, densely packed, and 70 to 90 μm long. The cobalt needles thus far have not been as sharply pointed and were 20 to 30 μm long.

We have obtained field ionization spectra of acetone by using nickel dendrite emitters. We obtained ions with the emitter-electrode voltage as low as 8 kV, and our experiment showed increased ion current with increased voltage. A difference of 10 kV seemed to give satisfactory results without excessive danger of arcing. We found also that we could use draw-out voltages as low as 1.2 kV, simplifying the insulation required between draw-out plate and the counter electrodes. At an acetone pressure of 10^{-5} torr, we obtained a 0.18-V molecular peak, and we estimate that adequate signal-to-noise ratio would have been obtained at 10^{-6} to 10^{-7} torr.

We are now interested in optimizing the efficiency of field ion formation with both carbon and metal dendrite emitters and then in applying the results to development of a field ionization probe for use in desorption and kinetic studies.

Because of the continued interest in polynuclear aromatic hydrocarbon (PAH) analyses, we have been interested in the use of liquid crystal stationary phases for GC separation and for GCMS uses in analysis of these mixtures. The series of substituted *N,N'-bis*(*p*-R-benzilidene)-α,α'-bi-*p*-toluidines were reported by Janini[13] to give excellent separation of isomeric PAHs. We have prepared the higher molecular weight homologs in which *R* is butoxy (BBBT) and phenyl because they are less volatile and result in less spectral background than the lower homologs. Chromatograms made using a 150-cm-long, 2-mm-ID column of 2.5% BBBT on Chromosorb HP (80/100) at 255°C isothermal and helium carrier flow of 23 cc/min showed complete separation of perylene, benzo[*a*]pyrene (BaP), and benzo[*e*]pyrene with retention times of 22, 27, and 30 min respectively. The peaks were symmetrical, and HETP calculations gave about 15 plates per centimeter. The use of this column in the Du Pont 490B GCMS resulted in good spectra from the PAH components, with reasonable column bleed (which could be eliminated, using background subtraction). We have column packing of other homologs and will study their effectiveness in PAH separations as needs occur.

One interesting and different project we completed was of assistance to Environmental Protection Agency (EPA) personnel at Research Triangle Park, North Carolina, in their monitoring program for BaP in air samples collected at industrial sites. Their quantification procedure requires fluorescence measurement of the BaP spot on a thin-layer chromatography (TLC) plate. We were able to prove that the BaP spot contained no contaminants that would lead to significant error in their results. We found only one

---

[11] H. D. Beckey and H.-R. Schulten "Field Desorption Mass Spectrometry," *Angew. Chem. Int. Ed. Engl.* 14(6), 403 (1975).

[12] C. E. Rechsteiner, D. E. Mathis, M. M. Bursey, and R. P. Burk, "A Novel Inexpensive Device for the Electrochemical Generation of Metallic Emitters for Field Desorption," *Biomed. Mass Spectrom.* 4, 52 (1977).

[13] G. M. Janini, G. M. Muschik, J. A. Schroer, and W. L. Zielinski, "Gas-Liquid Chromatographic Evaluation and Gas-Chromatography/Mass Spectrometric Application of New High-Temperature Liquid Crystal Stationary Phases for Polycyclic Aromatic Hydrocarbon Separations," *Anal. Chem.* 48, 1879 (1976).

contaminant (anthathrene), and its presence would not interfere in the fluorescence measurement because it fluoresces at a different wavelength from the BaP. *(W. T. Rainey, D. C. Canada, C. A. Pritchard, E. H. McBay, D. H. Smith)*

Organic mass spectrometry support activities. As in the past, the Organic Mass Spectrometry Group has given support to personnel requiring qualitative and quantitative organic analyses. The major effort has been given to investigators in the Analytical Chemistry Division, with further support to Chemistry, Metals and Ceramics, Chemical Technology, and Health and Safety Research divisions as well as to Y-12 and K-25 plant laboratories.

The Du Pont 490B instrument has been used primarily for collaborative GCMS analyses with personnel in the Bio-Organic Analysis Section of the Analytical Chemistry Division, who requested analyses of a large number of complex mixtures from cigarette smoke, fossil fuels, and subfractions of these. A total of 260 GCMS samples were handled during the past year, and detailed output, often with interpretation, was furnished. The major sample types included: crude oil (aliphatic and PAH fractions), shale oil (PAH, hydrophilic, lypophilic, aromatic, aliphatic and nitrogen fractions), char-coal-energy development (COED), syncrude, synthoil, synfuel, scrubber and process streams, stack gases, cigarette smoke, and animal urinary fractions. Since the major interest in these programs has been on health effects, the PAH components were monitored carefully. Tentative identifications of mutagenic/carcinogenic components included 3-methylcholanthrene, 7,12-dimethylbenzanthrene, benzo[*a*]pyrene, perylene, and many alkyl naphthalenes. The nitrogen fractions from shale oil and synfuels revealed many alkyl pyridines, indoles, carbazoles, and acridines of known physiological activity, plus other nitrogen-containing PAHs of unknown activity.

Considerable effort on both the Du Pont and ORNL instruments has been devoted to samples derived from the Fuel Particle Coating Facility operated by the Metals and Ceramics Division. Their studies of reaction conditions for various coating operations and the perclene recovery operation have required many complex GCMS analyses covering a wide spectrum of aromatic hydrocarbons and alkyl derivatives. Of particular interest has been the presence of $C_{22}H_{46}$ (saturated aliphatic hydrocarbon) as a major component in some samples without accompanying homologs. The origin of this material is still unknown. The analytical results have shown that the perclene recovery operation has been able to remove many of the PAH materials adequately for reuse of the perclene. The perclene residue containing the concentrated PAHs presents a problem in disposal, and we are currently analyzing a series of samples collected from effluent gases during a proposed combustion disposal process. In addition, the time-of-flight mass spectrometer has been used for study of gas streams during these coating operations. This work is reported in detail in the section devoted to HTGR studies.

The ORNL instrument has been used for similar support analyses. About 400 samples (probe and GC) have been processed during the year in addition to use of the instrument to develop field ionization, Tenax adsorption tubes, etc. Many of these were GCMS samples, requiring laborious manual interpretation. Use of the Cyphernet mass spectral search system (MSSS) time-sharing library search options has been of assistance in qualitative identification, but its most valuable feature has been as a source of the complete spectra of compounds to be inserted in the local libraries. In addition, the system now has options to allow subject and author searches of a bibliographical data base containing all Mass Spectrometry Bulletin entries through 1976. We have also entered into a contract with the Cornell University Computing Center for use of the Probability Based Matching program (PBM) and the Self Training and Interpretative Retrieval System (STIRS). These programs were developed by McLafferty and coworkers for qualitative identification of organic compounds and are not available elsewhere. We have been interested in using these systems for identification of compounds that have been impossible to identify by using normal library searching routines and interpretative methods. *(W. T. Rainey, D. C. Canada, C. A. Pritchard, E. H. McBay, D. H. Smith)*

ISOTOPIC AND ELEMENTAL SPECTROMETRY

Spark source mass spectrometry for recycle fuels. A facility is being planned to analyze high-level γ-emitting samples by SSMS. These samples will include LWR and HTGR spent fuels and dissolver solutions. There is currently a facility in Building 2026 for the analysis of high-level α- and β-emitting samples by SSMS, but the upper limit for γ-radiation is 250 mR at contact. This restriction requires samples of higher γ-activity to be diluted by as much as one million-fold before analysis, thus introducing sources of error and contamination. Elemental detection limits under these conditions are relatively poor.

The facility under consideration will be capable of handling samples with up to 100 R of γ-activity. To do this, the entire ion-source region of the mass spectrometer must be enclosed in a lead shielded radiation containment box. Figure 2.1 shows how such an enclosure would be mounted on a commercially available AEI MS-702 spark source mass spectrometer. Both the ion source and the initial stages of the ion flight tube are shown as surrounded by appropriate lead shielding. A viewing window of leaded glass and a remote manipulator will allow the operator to load and unload samples in the ion source.

The operator will be shielded behind a concrete bulkhead during operation of the spectrometer. He will observe the ion source on a closed-circuit TV monitor via a camera located inside the source enclosure. All necessary vacuum and electronics controls will be located on the bulkhead along with remote controls for the movement of the sample electrodes inside the ion source.

To determine what modifications to the SSMS instrument are needed, a feasibility study was conducted in the final quarter of FY 1977. An AEI MS-7 mass spectrometer in Building 9995 was converted to remote operation similar to that shown in Fig. 2.1. This involved removing the front panels of the instrument and setting them up about 5 ft away, using extended electrical cables where necessary. As many components as possible were removed from inside the instrument and placed some distance away.

A Plexiglas mock-up of the shielded source enclosure was fabricated and installed on the front of the instrument. This enclosure has a remote slave manipulator mounted on it as well as several ports for loading samples and ion-source parts. The ion-source parts have been extensively modified to allow for easy handling with the slave manipulator. A TV camera and monitor were used to view the ion source in operation while samples were being sparked. Motorized electrode manipulators were installed to allow for remote control of the electrode position during analysis.

To date the feasibility study is 95% complete. It has shown that all front panel controls can be removed

ORNL DWG 77-6097

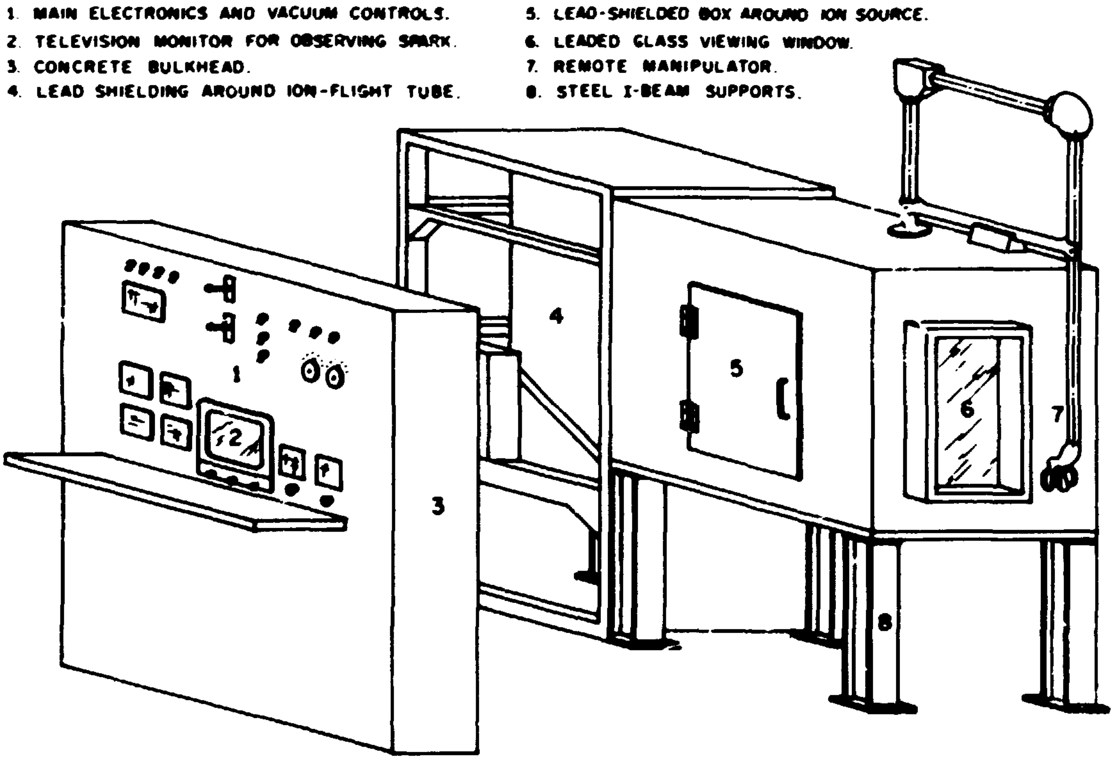


Fig. 2.1. Proposed hot spark source mass spectrometer design.

some distance without affecting their operation. Extended electrical cables were fabricated, and rotary vacuum pumps and auxiliary vacuum valves were placed about 6 ft away. For convenience and to eliminate obsolete equipment, two high-vacuum valves were converted to pneumatic operation. Ion-source parts have been obtained that can be handled by the remote manipulator with sufficient precision to ensure an adequate ion beam. These parts have been designed so that the components that will be most quickly contaminated can be conveniently disposed of and replaced with new parts.

The problem of access to the shielded source enclosure has also been addressed. Because all samples entering the box will be highly radioactive and accumulated waste leaving the box will be even higher, any method used must involve both physical containment and shielding of personnel. Plans are being made to locate this SSMS facility in Building 2026 in close proximity to the hot cells where samples will be prepared. Therefore, some sort of shielded conveyor will be used to connect the source enclosure with the hot cells.

The feasibility study has been useful for cataloging necessary changes to the standard SSMS instrument. Insight has been gained into the unique problems involved in handling samples and ion-source parts by remote control. Decisions about procedures and instrumental modifications have been made, which will facilitate the installation and operation of the proposed instrument. *(J. A. Carter, J. C. Franklin, D. L. Donohue, L. Landau)*

Spectrometry support activities. Emission spectrographic and SSMS analyses were provided to 17 ORNL divisions and related programs. A total of 62,235 analyses were reported during the year. Once again, Metals and Ceramics and Chemical Technology divisions were the largest individual users of these analytical services. In addition, we have provided analytical services to EPA, Y-12, K-25, and Argonne National Laboratory.

The group has been heavily committed to the analysis of Ir-W alloys for impurity elements. The Ir-0.3% W alloy is prepared by Metals and Ceramics as cladding material for ^{238}PuO$_2$ fuel. The impact properties of the alloy are considered to be related to impurity levels, especially W, Th, and Al. The precision of analysis has been improved to about ±25% by use of a reference alloy containing known amounts of thorium and aluminum.

The analysis of radioactive materials by SSMS has continued this year. The ^{233}U work has declined, and we are doing more work on LWR fuel solutions and leachates. At this time we are restricted to radiation levels of 200 mR or less so that we are analyzing submicrogram quantities of some samples. We have maintained an in-house quality control program for the LWR samples by replicate analysis of a synthetic fuel sample. The computer program used to calculate elemental concentration from optical density has been modified so that fission product isotopic abundances are used for elements with atomic numbers between 32 and 66. The program now will use nominal LWR isotopic abundances, depending on the age of the sample.

The direct-reading Paschen optical emission spectrometer (POE) is being modernized. We have replaced 10 channels of the readout system with solid state electronics and are acquiring 20 additional channels. The new readout system is more stable, has automatic dark-current cancellation, and is less difficult to maintain than the old tube circuits. When the installation is complete in FY 1978, we will begin work on a data-acquisition system for the direct reader.

We have altered the emission spectrographic procedure for the analysis of radioactive insoluble solids in the hot cell. Because of air-handling problems, the cell is restricted to samples with a plutonium hazard equivalent (HEP) of 1 g of ^{239}Pu. A procedure for dilution of the samples with a graphite-In$_2$O$_3$ mixture has been used at Building 3019 to provide semiquantitative analyses of radioactive materials. In the past, our data for solids have been semiquantitative. A procedure for the analysis of ^{99}Tc has been established with a detection limit of 0.001%. *(J. C. Franklin, L. Landau, S. A. MacIntyre, W. R. Musick, R. C. Bryant, G. I. Gault, E. H. Waters)*

Inductively coupled plasma (ICP) emission spectrometry. The ICP emission source has been evaluated for the routine analysis of aqueous solutions and organic liquids. The particular problems to which it was applied this year are described elsewhere. We have made certain modifications to the nebulizer-spray chamber and are currently installing a new double monochromator with photomultiplier tube readout.

Our nebulizer[14] is based on the cross-flow design made popular by Kniseley et al. at Ames.[15] However,

---

[14] D. L. Donohue and J. A. Carter, "A Modified Nebulizer for Inductively Coupled Plasma," *Anal. Chem.* (submitted for publication).

[15] R. N. Kniseley, H. Amenson, C. C. Butler, and V. A. Fassel, "An Improved Pneumatic Nebulizer for Use at Low Nebulizing Gas Flows," *Appl. Spectros.* **28**, 285 (1974).

the ORNL design incorporated no metal parts that could be corroded by acids or alkali solutions. The needles are easier to align while operating and are protected for breakage in normal use. A unique feature of this nebulizer allows more than one sample to be aspirated simultaneously, thus making certain types of measurements possible. We have not yet fully investigated the possibilities that this capability affords.

The spectrometer used to evaluate the ICP's performance was a 0.5-m Ebert configuration. We decided to replace this spectrometer with one having higher stray-light rejection. This is necessary for analyzing trace impurities in the presence of high levels of alkaline earth elements such as Mg, Ca, Ba, and Sr and other strongly emitting elements such as Fe, Al, Si, and Ti. We therefore chose a Jarrell-Ash 0.5-m double monochromator (model 82-440) consisting of two 0.25-m monochromators in tandem. This is an economical system in which scattered light is reduced to less than one part in ten million. It also can be converted to two separate monochromators for sample and reference beam measurements.

The ICP emission source with single channel readout has been shown to be a satisfactory method for analyzing trace elements in organic liquids.[16] We have used it for the analysis of as many as 20 elements in No. 2 and No. 6 fuel oils and light crude oils from the Middle East and the United States. The availability of organic-soluble trace-element standards has limited our choice of elements. This analysis is more difficult than analyses with aqueous solutions because of the higher power levels required (1.75-2 kW) and the tendency to form carbon streamers in the plasma. With appropriate precautions and techniques, however, the analysis of organics can be as rapid (10 to 15 elements per hour for as many as four samples) and precise (±5 to 10%) as the analysis of aqueous samples.

The fuel oils analyzed were submitted by Metals and Ceramics Division and were of very different viscosities, which made it necessary to dilute them with large amounts (10:1) of a pure solvent such as kerosene or decane. This same solvent was used to make up the standard and blank solutions. Even with this dilution, detection limits were below 1 ppm for all but two of the elements studied. In some cases, less sensitive emission lines were used to avoid carbon-band interference.

The analysis of light crude oils was accomplished in a similar fashion. In this case, a viscometer was used to measure the individual samples and to achieve the same viscosity as the kerosene blank by diluting them with decane. The major elements found in the Middle East light crude were: Ni, Zn, Fe, Si, and Mg, whereas V and Ni were the major elements found in the U.S. sample. These results were verified by SSMS after the oils were ashed at 550°C to remove organics. The analysis technique is convenient and less subject to contamination than methods requiring extensive sample pretreatment.

The ICP was also used to evaluate detection limits for five elements (Ta, Ti, Sb, Nb and Ru) in concentrated nickel solutions. In a test of the system under worst-case conditions, sample solutions were submitted containing as much as 12 wt % of nickel (as the nitrate). The object was to determine the detection limits for these five elements in synthetic mixtures containing various amount of nickel as well as to determine the actual amounts present in the submitted samples.

The detection limits obtained with as much as 1000 ppm of nickel were essentially the same as in pure aqueous solutions. Analytical lines were chosen to be free of interference from lines of nickel, which was not a significant problem below 1000 ppm. However, at 10,000 ppm of nickel, the background signal rose by an amount approximately equal to the signal from 1 ppm of each element. This effect was particularly bad for antimony (259.8 nm), whereas it affected titanium (334.9 nm) the least. The detection limits in most cases deteriorated by 10 to 20%, which meant that the analytical signal for a particular element could still be distinguished from the background, provided the "blank" and sample contained the same amount of nickel.

For the real samples, data were taken at a nickel concentration of 50,000 ppm, using a blank of the same concentration. Photo current was read on a strip chart recorder, and the analytical data were obtained by comparing the blank, samples, and synthetic standards, all at the same nominal nickel concentration. The results were checked with SSMS, and the agreement was reasonably good for the most sensitive elements (Ti, Nb, and Ru) but poor for Ta and Sb, caused by their initially poor detection limits and perhaps by their greater spectral overlap with the nickel lines. It was concluded that to increase *precision and accuracy, the nickel level should be* kept below 1% through some form of separation

---

[16] V. A. Fassel, C. A. Peterson, F. N. Abercrombie, and R. N. Kniseley, "Simultaneous Determination of Wear Metals in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry," *Anal. Chem.* **48**, 516 (1976).

method, which would not affect the five elements of interest. Ion exchange separation was studied and showed some promise for this application. *(D. L. Donohue, J. A. Carter)*

Fly ash elemental characterization. The environmental concern over coal-burning electric generating plants has caused a number of coal-related samples to be brought to our laboratory in recent years. Among the most challenging of these are fly ash, bottom ash, and electrostatic precipitator ash. These materials account for nearly all of the inorganic elements in the feed coal, with significant differences between them indicating that elemental segregation or separation has occurred. It is therefore often necessary to characterize the elemental composition of such samples with reference to the trace, minor, and major elements present.

To achieve the objective, our laboratory has taken a multitechnique approach, involving OE spectroscopy and SSMS to give a survey analysis of all elements on a semiquantitative basis. Once the approximate concentrations have been established, more refined techniques are used to determine the concentrations accurately. These include POE and ICP spectrometry, which are used to measure the major elements present (Si, Ca, Fe, Al, Mg, Mn, and Ti). In addition, "dry-mix" isotope dilution SSMS is used for certain minor and trace elements of environmental interest (Tl, Pb, Ba, In, Cd, Mo, Sr, Zn, Cu, Ni, and Cr).[17] All other elements present can be reported semiquantitatively from the initial OE and SSMS survey analysis, and elements not detected are assigned a value of "less than" the detection limit.

In the OE and SSMS analyses, samples are run as received, either as the powdered fly ash for OE or mixed with a conducting powder and pressed into electrodes for SSMS. This procedure reduces the possibility of contamination and greatly speeds the analysis. National Bureau of Standards SRMs 1632 (coal) and 1633 (fly ash) are used for quality control. The other methods of analysis (POE and ICP) require a solution sample. Fly ash is high in oxides of silicon and aluminum, which will not dissolve under normal HNO_3:HCl treatment. Less desirable acids must be used such as HF, $HClO_4$, or H_2SO_4, which cause higher blank levels and spectral interferences. Fusion with KOH or $KHSO_4$ has been used to dissolve fly ash, but this method results in high blanks and undesirable alkali salt concentrations. Thus solution techniques are employed for the major elements present at concentrations >0.5%.

The multitechnique approach taken in our laboratory uses several optical and mass spectral techniques to characterize fully the sample, with emphasis on certain important elements. Whenever possible, concentrations are determined by two separate techniques, and any discrepancies are followed up until the best value is obtained. With the broad elemental coverage of OE and SSMS, nearly every element can be estimated, and in many cases quantification can be performed to better than ±10% RSD.

Geothermal brines. We have participated in the analysis of geothermal round-robin (GRR) samples 1 and 2 (GRR-1, GRR-2). Data were reported for 26 elements in these samples. To cover the concentration and elemental ranges required, we used ICP, IDSSMS, SSMS, and POE for this analysis. ICP and/or POE were used to determine Al, B, Ca, K, Li, Mg, Rb, and Sr, whereas IDSSMS was used for Pb, W, Ba, Te, Si, Rb, Se, Zn, Ni, Fe, Cr, K, and B. Other element (As, V, Bi, Co, Cs, Mn, Cu, and Sb) reported were determined by using an enriched isotope as an internal standard. The concentration of the alkali and alkaline earth elements in GRR-2 is much higher than in GRR-1. Therefore, spectral interferences for all techniques are much worse in GRR-2 than GRR-1 sample sets. *(J. C. Franklin, D. L. Donohue, S. A. MacIntyre, L. Landau)*

Low-level gas mass spectrometry. An ultra-high-vacuum mass spectrometer operating in a static mode is being evaluated for establishing identification of gases in traveling wave tubes (TWT). An interagency agreement between the U.S. Air Force and DOE was established so that the Mass Spectrometry Section could provide technical assistance with space-related hardware. The U.S. Air Force, through Aerospace, Inc., requested the identification of the residual gases in several TWTs.

The TWT was attached to the sample system of our ultra-high-vacuum spectrometer with a bakeable copper-gasketed flange. The entire spectrometer, sample, and sample system were baked for several hours at 250°C. The mass spectrometer was operated in the "static mode" by isolating the analyzer from the pumping system because the sample volume was extremely small ($<10^{-6}$ cc STP). Otherwise a small gas sample in a dynamically pumped mass spectrometer would be pumped away before all the components of the sample could be measured. The TWT seal was penetrated by a mechanism fabricated

---

[17] D. L. Donohue, J. A. Carter, and J. C. Franklin, "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry," *Anal. Lett.* 10(5), 371-79 (1977).

by Aerospace, Inc., and the analyses of the residual gases were determined as follows: H_2, 5.06%; He, 1.38%; CH_4, 70.31%; N_2 + CO, 22.99%; and Ar, 0.26%. An estimate of the total volume of the gases was 10^{-13} liter.

After the residual gases were pumped away, the sample tube was reheated to 150°C and an analysis made of the gases released from the internal tube components. Typical results were H_2, 74.16%; He, 11.58%; CH_4, 4.03%; N_2 + CO, 10.04%; Ar, 0.01%; CO_2, <0.01%; and H_2O, 0.17%.

These results have been useful to Aerospace, Inc., and the Air Force in establishing quality criteria for the traveling wave tubes. *(J. R. Walton, J. A. Carter)*

Nitrogen isotope ratios in lung tissues. The $^{15}N/^{14}N$ reduction pyrolysis system [18] was used for the analysis of freeze-dried lung tissues from small mammals in a research program being performed at the Stanford Research Institute (SRI). In their experiments, animals were exposed to enriched $^{15}NO_2$; other animals, used as controls, were exposed to normal NO_2. By use of this technique and the isotopic ratio ^{15}N:^{14}N (determined by the reduction pyrolysis system), SRI can determine the nitrogen exchange rate in the lung tissues and perhaps predict NO_x within the lung tissue. The reduction pyrolysis system was also used to determine the amount of nitrogen-containing high-molecular-weight organic compounds.

Computer program modifications for SSMS. A computer program was written to accommodate data from SSMS samples with nonnormal isotopic compositions. The calculation of the weight percentage of an element in an SSMS sample requires the knowledge of the isotopic distribution of each element of interest as well as of each element whose isotopes may have the same m/z as some of the isotopes of the elements of interest. When the sample is normal, natural distributions are used. For samples that have been irradiated or samples produced by nuclear fission, the isotopic distributions are no longer normal, and corrections have to be made by hand to the values computed by our IBM 1130 computer.

Modifications were made to the computer program, which calculated the weight percentage of an element from the optical density of a mass spectral line on a photographic plate. The new version was written to accommodate fission product elements that do not have normal isotopic abundances. Subroutines were written to analyze both LWR fuel material that had been irradiated for 2 years and cooled for 2 years and experimental breeder-reactor material irradiated for 65 MWd and cooled for 3 years. These additions have enabled us to process samples much more rapidly by eliminating most of the hand calculation necessary for the analysis of material, using unusual isotopic distributions. Other types of samples can be handled by adding a table of isotopic distributions and making minor modifications. The program has also been modified to make use of multiply charged ions, and the simple addition of a sensitivity card will permit the sensitivity factors to be changed as the experimental conditions demand. *(L. Landau, J. C. Franklin, W. H. Christie)*

Mass spectrometry analysis. This laboratory performs mass spectrometric measurements on a wide variety of solids and gases. During this past year, about 19,800 results were reported, about the same as for the previous year. Again, our major support has been for the Chemical Technology Division, including the various Coal Technology and the Stable Isotopes programs. We have continued supporting many programs described in last year's annual report. These include the determinations of U and Th by IDMS for the HTGR Thorium Utilization Program; H_2, HD, and D_2 mixtures from solubility studies of mixed hydrogen isotopes in lithium for the Fusion Energy Division; Cm, Am, and Cf isotopic analysis for the TRU Facility programs; the purity of He, Ar, and N_2 for certification of gas cylinders for ORNL and Y-12 Stores; ^{85}Kr samples from the thermal diffusion enriching facility; ^{133}Xe samples from fuel dissolutions; many sets of samples of mixed hydrocarbons from the various projects in the Coal Technology Program; preliminary, returned, and inventory samples of separated stable isotopes of 33 different elements, mostly Ag, Ca, Se, Sn, Te, and Zn.

Special gas analyses were done in support of NASA's Mars atmospheric program. Calibration gas mixtures simulating the atmosphere of Mars were certified in our laboratory; gas composition and isotopic analysis of N_2 and Ar were measured. A freezing-out technique was used to determine low levels (0.2%) of CO in CO_2.

A major analytical effort is under way to determine accurately U and Pu in LWR spent fuels. Sample preparations are being made in the High Level Radiation Laboratory in Building 2026 because the samples are highly radioactive. Procedures for sampling, spiking, and sample spike equilibration

---

[18] J. A. Carter, D. R. Matthews, R. L. Walker, and J. R. Walton, "Measurement of Nitrogen and Nitrogen Isotopic Ratios Using Reduction Pyrolysis Coupled with Mass Spectrometry," *Anal. Lett.* **6**(10), 951–60 (1973).

have been written to establish the basic requirements of the isotope dilution method. Mass measurement of Pu and U is done, using the resin-bead loading method and the two-stage mass spectrometer. In addition, IDMS is being used for burnup measurements in other fuel cycle programs.

We have recently received a graded set of fission-produced xenon samples from R. W. Schaich of the Operations Division. These samples were isotopically analyzed, and our results were then used as "standard" values to recalibrate the Operations Division xenon analyzer. This instrument is used to establish xenon content in samples going to customers from the Isotope Sales Office. *(J. R. Sites, M. M. Honaker, L. Guinn, R. L. Walker)*

3. Analytical Services

L. T. Corbin, Head

This has been a year of both consolidation and expansion within the Analytical Services Section. The establishment of a separate Radiochemistry Section within the division and the subsequent transfer of a number of activities to this section resulted in a consolidation of our service efforts into primarily those of inorganic analyses. The radiochemical work remaining in the section now involves mainly hot-cell and TRU operations. We have expanded our developmental activities related to the reactor programs at ORNL as well as our service functions such as those required in the enlarging coal program.

Development continues on a number of reactor programs, ranging from immediate measurements for ongoing programs (e.g., in-line monitoring of gaseous effluents from fuel microsphere preparation) to the exhaustive historical surveys being made of the dismantled Peach Bottom Reactor components and fuel elements. A number of challenging and unusual problems have emerged from the Advanced Fuel Recycle Program, which include studies of solids, liquids, and gases. Among the latter are measurements of both tritium and carbon-14, two very difficult-to-assay low-energy beta emitters. We believe we are the first group to make repetitive measurements for ^{14}C on small replicate samples from a single LWR fuel rod.

An achievement that promises to increase efficiency and promote greater accuracy in the service laboratories is the establishment of our computer-based data-management system. The system not only processes requests and work and time sheets, but it also performs the calculations necessary for reporting final analytical data. Final reports for customers are automatically printed on completion of work, while time charges are accumulated for later distribution by the section.

A number of improvements have been made to existing analytical equipment, and several new instruments have been obtained. The section continues to expand in the variety of analytical determinations performed, which are spread over a number of ORNL divisions. In addition, 17 outside organizations submitted over 1500 test specimens for evaluation of coatings or paint to be used in reactor environments. Thus the unique capabilities of the Analytical Services Section continue to be recognized and used, both within the Laboratory and outside in the private sector.

REACTOR PROJECTS

D. A. Costanzo, Group Leader

Gas-Cooled Reactor Program Studies

Monitoring of gaseous effluents from HTGR fuel-preparation reactions by time-of-flight mass spectrometry. The effluent gases from the chemical reactions occurring during the preparation of HTGR fuel microspheres have been monitored, in-line, with a time-of-flight mass spectrometer (TOFMS).[1] These studies have been used to optimize conditions for development of HTGR fuel-fabrication procedures in the Thorium Utilization Program. Carbonization of uranium-loaded, weak-acid ion exchange resin

---

[1] D. A. Lee, "Monitoring Gaseous Effluents from HTGR Fuel Preparation Reactions Using a Time-of-Flight Mass Spectrometer," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp 40-41.

(U-WAR), one of the processes in the manufacture of fuel microspheres, has been studied in a series of experiments. This series of temperature-programming experiments used the TOFMS to collect the thermochemical data necessary to make a kinetic analysis of the pyrolysis products and to propose mechanisms for the decomposition of the ion exchange resin matrix. Isothermal step programming was used to determine the gaseous products evolved at various stages of decomposition of the polymeric matrix. A paper describing this work was presented at the American Ceramic Society Meeting.[2]

Another phase of the carbonization process was experiments in which the composition of the gas used to levitate the microspheres in a fluidized bed was varied. The gases used for each experiment were argon, nitrogen, carbon dioxide, 4% hydrogen-96% argon, and 10% methane-90% argon. Resin-bed temperatures were plotted against time for each experiment. Mass spectra of the evolved gaseous products were taken every 3 min throughout the heating period from 20 to 700° C. Peak heights were measured from these spectra for each of 21 significant masses. The peak heights of each mass were plotted against time, and profiles of the plots were examined relative to the resin-bed temperature profiles. Analyses of the carbon-to-uranium ratios in the carbonized products were also used to select the optimum levitating gas. From these experiments, nitrogen was the choice of the gases. These data will be used to optimize the conditions for the carbonization of U-WAR. *(D. A. Lee)*

Tritium monitoring for irradiation capsule GB-10. Experimental tritium monitoring for the Gas-Cooled Fast Reactor (GCFR) irradiation capsule GB-10 has been completed.[3] During the past year experimental data have been reduced, evaluated, and compiled in an ORNL topical report, which is scheduled for release in December 1977.[4] *(M. E. Pruitt)*

Surveillance of fission products in the Peach Bottom Reactor. We continue to collaborate with the Chemical Technology Division in the HTGR Fission Product Surveillance Program.[5] In this program, terminated at the end of FY 1977, the behavior of fission products in both the primary coolant circuit and the fuel elements of the Peach Bottom HTGR was studied. The purpose of this work was to compare measured and predicted behavior of fission products in an HTGR.

During this year a report[6] was published that described work on the primary coolant circuit, and this phase of the study was presented at an American Nuclear Society meeting.[7] In studies of fuel elements, examinations of the final four elements irradiated to the end-of-life (EOL) of reactor core 2 (899 equivalent full-power days) were completed. Two reports[8,9] describing the examinations of elements E11-07 and E14-01 were published, and another[10] presenting findings for element F03-01 is being reviewed for publication. Preparation of reports describing the examinations of elements E01-01 and F05-05 are nearing completion.[11,12] An additional presentation describes the behavior of fission products in Peach Bottom fuel elements.[13]

Examination of Peach Bottom fuel elements, which was begun in 1972 with the examination of element E06-01 irradiated for 384 equivalent full-power days (EFPD),[14] included one 791-EFPD element E11-07[8] and four 898-EFPD elements

---

[2] J. A. Carpenter and D. A. Lee, "Kinetics and Mechanisms of the Carbonization of Uranium-Loaded Weak Acid Resin HTGR Fuel Microspheres," *Am. Ceram. Soc. Bull.* **56**, 343 (1976).

[3] M. E. Pruitt, "Tritium Monitoring for Capsule GB-10," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, pp. 41-42.

[4] M. E. Pruitt and A. W. Longest, *In-Line Tritium Monitoring in the GCFR Vented Irradiation Capsule GB-10*, ORNL-5256 (to be published).

[5] F. F. Dyer, "Peach Bottom Reactor Studies," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 42.

[6] F. F. Dyer, R. P. Wichner, W. J. Martin, and H. J. de Nordwall, *Distribution of Radionuclides in the Peach Bottom HTGR Primary Circuit During Core 2 Operation*, ORNL-5188 (March 1977).

[7] F. F. Dyer, R. P. Wichner, and A. P. Malinauskas, "A Study of Radionuclides in the Peach Bottom Primary Circuit during Core 2 Operation," *Trans. Am. Nucl. Soc.* **26**, 314 (1977).

[8] R. P. Wichner, F. F. Dyer, W. J. Martin, and L. C. Bate, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element E11-07*, ORNL-5214 (April 1977).

[9] R. P. Wichner, F. F. Dyer, W. J. Martin, and L. L. Fairchild, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element E14-01*, ORNL TM-5730 (August 1977).

[10] 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 (to be published).

[11] 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 report (to be published).

[12] F. F. Dyer, R. P. Wichner, W. J. Martin, and L. L. Fairchild, *Distribution of Fission Products in Peach Bottom HTGR Fuel Element F05-05*, ORNL TM report (to be published).

[13] R. P. Wichner, F. F. Dyer, and A. P. Malinauskas, "Distribution of Cesium and Other Fission Products in Peach Bottom HTGR Fuel Elements," *Trans. Am. Nucl. Soc.* **26**, 313 (1977).

[14] F. F. Dyer, R. P. Wichner, W. J. Martin, L. L. Fairchild, R. J. Kedl, and H. J. de Nordwall, *Post Irradiation Examination of Peach Bottom HTGR Driver Fuel Element E06-01*, ORNL-5126 (April 1976).

E14-01[17], F03-01[17], E01-01[17], and F04-05[17]. Experimentally, the examinations were concerned with the following determinations:

(1) dimensional changes and component integrity,

(2) fission product inventory and distribution in the fuel,

(3) transport of fission products to the graphite and migration of fission products along the element,

(4) radial distributions of radionuclides in the graphite, and

(5) fraction of fuel particles which developed failed pyrocarbon coatings.

Some highlights of the examinations follow. Of the gamma-emitting radionuclides (including ^{95}Zr, ^{103}Ru, ^{106}Ru, ^{110m}Ag, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{141}Ce, ^{144}Ce, ^{154}Eu, and ^{233}Pa) that were observed in the fuel, only ^{110m}Ag, ^{134}Cs, ^{137}Cs, and ^{154}Eu exhibited a significant tendency to migrate from the fuel and into the graphite. Silver-110*m* appeared to be much more volatile than the others; the behavior of ^{154}Eu was similar to the two cesium isotopes. Axial distributions of radionuclides in both the fuel and graphite components showed the effects of the purge gas, which flowed down the element in gaps between the fuel and sleeve and between the fuel and spine, to transport the four volatile nuclides toward the bottom of the element. The fraction of particles having failed pyrocarbon coatings was found by the hot-chlorine leach method to be in the range of 2 to 5%.

Full details of the examination procedures and results are presented in previously cited literature. *(F. F. Dyer)*

Radial sectioning of Peach Bottom fuel element sleeves and spines. The lathe, which was modified for hot-cell machining and was described previously,[16] has been used to machine Peach Bottom graphite sleeves and spines for determination of the radial distribution of the fission products. Four sections of each sleeve and spine from elements E11-07, E14-01, F03-01, E01-01, and F05-05 have been completed. Cuts ranging from 5 to 60 mils were transferred to double bottles for weighing. The double bottle was used for in-cell handling; when it was removed from the hot cell, the outer contaminated bottle was left in the hot cell and was replaced by a new outer bottle. This prevented the contamination of samples and bottles and allowed the measurement of the gamma-emitting fission products without changing the samples from the original bottle. The data obtained from the radial cuts showed a rapid decrease in radioactivity as a function of distance into the sleeve or spine from the fuel region of the element. The radioactivity remained at a low level to the center of the spine or to the outer surface of the sleeve, except for some increase caused by external contamination. *(L. C. Bate)*

Peach Bottom Reactor graphite analyses. Analyses of strontium-90, tritium, and carbon-14 were made to evaluate the penetration patterns into graphite in the Peach Bottom Reactor experiment. Components of interest were the graphite spine core and the graphite sleeve that surrounds the fuel.[15] Sampling was carried out by collecting machined turnings, which ranged from 5 to 60 mils in thickness, and was designed to reveal the radial distribution through the graphite. Some samples were low enough in radioactivity to permit the analyses to be carried out on the bench top; others required the use of a hot cell. In the analysis of the turnings, the strontium-90 was determined radiochemically after dissolution in a nitric sulfuric acid mixture. A separate portion of the graphite was combusted at 850°C in a stream of wet oxygen to convert the carbon-14 to $^{14}CO_2$ and tritium to HTO. The resulting gases were trapped separately and determined by liquid scintillation beta counting. When samples of activated charcoal from the fission product trap of the purge gas were analyzed, it was found that radiocesium caused interference in the tritium and carbon-14 analysis. This problem was overcome by inserting a 40-mesh Al_2O_3 trap, heated to 100°C, just downstream from the combustion furnace.

As the graphite increased in radioactivity, it was necessary to adapt the existing methods to hot-cell operation. Little change was required in the dissolution technique. The combustion procedure was modified so that the oxidizing and carrier gases, regulated by capillary flow, were introduced into the hot cell where the actual combustion occurs. The gases to be analyzed were withdrawn from the hot cell via heated nickel tubing that contained Al_2O_3; the

---

[15] J. L. Botts, "Reactor Projects," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 43.

[16] L. C. Bate, "Lathe Modifications for Hot-Cell Machining," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 43.

[17] R. P. Wichner, F. F. Dyer, W. J. Martin, and L. C. Bate, *Distribution of Fission Products in Peach Bottom HTGR Fuel Elements E11-07*, ORNL-5214 (April 1977).

HTO and $^{14}CO_2$ were trapped separately as before. As a safety precaution, the traps were enclosed in a Plexiglas cabinet equipped with a negative-pressure vent line that exited into the hot cell.

In both bench-top and hot-cell analyses, there has been a consistent pattern of penetration into the graphite. The reproducibility, based on the recovery of standards prepared to simulate actual samples, is in the order of ±5%. *(R. F. Apple)*

Radiation effects on ^{233}U-loaded weak acid resin. A study is being conducted jointly with the Metals and Ceramics and Chemical Technology divisions to assess the possible effects of self-radiolysis on the performance of carboxylic acid resin fully loaded with ^{233}U during fabrication of HTGR fuel particles. Two tests are being made to evaluate the effects of radiation damage. The first evaluates the U-loaded resin performance during carbonization and conversion. The second measures the residual uranium on the aged resin after stripping with 6 *N* nitric acid.

Two polyacrylic acid type resins (Amberlite IRC-72 and Duolite C-464) are being tested. The U-loaded resins were analyzed immediately after loading and after storage periods of 1, 3, and 6 months. Different conditions for storage of the resins between various process steps are also being tested. Samples are stored in three ways: (1) water-soaked (submerged in distilled water), (2) dried to 10 to 14 wt % H_2O, and (3) dried to 2 to 6 wt % H_2O. The uranium-loaded resin is being analyzed for water content by the determination of loss on drying at 110°C for 16 hr. The uranium content of the dried resin is determined gravimetrically by combustion of the material at 900°C in oxygen for 2 hr. The uranium is calculated from the residue weight, assuming it to be stoichiometric U_3O_8.

After carbonization at 900°C and partial conversion to UC_2 at 1500°C, the particles are analyzed for uranium and carbon. The uranium content is determined from the residue weight as described above, and the carbon is determined gravimetrically by converting the carbon to CO_2 in an oxygen atmosphere at 900°C and trapping and weighing it. The gravimetric methods used to determine the uranium and carbon contents were evaluated by using $^{238}UC_2$ WAR material, 65% converted. Fifteen determinations from the same material batch were made for uranium and carbon. The uranium content was 80.78 wt % (RSD = 0.11%), and the carbon content was 15.27 wt % (RSD = 0.63%). The residual quantity of uranium on the aged resin is determined by washing the loaded resin with 6 *N* HNO_3 and burning the leached resin in oxygen at 900°C for 2 hr. The residue is then dissolved in 8 *M* HNO_3, and the uranium determined by alpha counting. *(J. L. Botts)*

Assessment of the analytical requirements for the Hot Engineering Test Facility. The Hot Engineering Test (HET) Facility will demonstrate and verify pertinent technology necessary for a commercial high-temperature gas-cooled reactor (HTGR) fuel recycle plant. The HET Project plans are to use TURF (Building 7930) to begin reprocessing Fort St. Vrain fuel in 1982–83. We prepared a report on analytical aspects of the project, which includes (1) a brief description of the existing analytical facilities that will be used to support the project, (2) a proposed HET sample scheme and projected sample load, (3) estimates for the cost of analyses and analytical manpower required for the operation of HET, (4) identification of proposed analytical development activities, (5) total development manpower effort, and (6) a cost estimate for capital equipment. The report is being reviewed by HTGR project management. *(F. L. Layton)*

Methods Development

Determination of the defective particle fraction in HTGR fuels. The routine detection of defective coatings by high-temperature (1500°C) chlorination has been limited to the Biso particle,[18] which has only a single dense pyrolytic carbon layer over the porous carbon buffer coat that surrounds a fuel kernel. A procedure has now been developed for the Triso particle, which has a SiC coating sandwiched between two dense pyrolytic carbon coatings. Chlorination in combination with radiography was found to reveal defects in outer coatings. In a 3-hr chorination, a defective outer pyrolytic carbon layer results in the destruction of the intermediate SiC layer by volatilization of the Si as $SiCl_4$, leaving the carbon behind as a porous layer. This fact is easily revealed in radiographs. If the inner pyrolytic carbon layer is also defective, the usual transport of the kernel mass occurs as with the Biso particle.

High-temperature chlorination has also been applied to the detection of Biso particles with permeable coatings. Use of Ne-He gas permeation techniques for this problem have not always been

---

[18] D. E. LaValle, "Reactor Projects," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 43.

effective, nor is a simple 2-hr chlorination at 1500°C. The present procedure used chlorination for two 3-hr periods to reveal gross defects and for two 6-hr periods to expose permeability a total of 18 hr of chlorination at 1500°C. This method has revealed all degrees of permeability.

A paper describing this work has been published.[19] (*D. E. LaValle, F. L. Layton*)

Determination of sulfur in green and fired HTGR fuel rods. In the past the determination of sulfur in HTGR fuel rods was done by means of a Leco sulfur determinator. Because of the inability of the Leco apparatus to handle large amounts of off-gases, only small samples (~60 mg) of the fuel rods could be used for analysis. Because the rods weigh approximately 12 g, there is a great possibility of sampling error. At the 60-mg sample level, the precision of sampling was determined to be ±30%.

A method was investigated whereby larger samples could be used. The procedure consisted of slowly igniting the sample in an argon-oxygen stream to a final temperature of ~1400°C. The sulfur present is oxidized to SO_2. The off-gases are bubbled through an acidic starch-potassium iodide solution to which a drop or two of 0.002 *N* potassium iodate has been added. The SO_2 reduces the free iodine present and decolorizes the blue of the solution. By titrating with a standard solution of potassium iodate, the quantity of SO_2 evolved can be measured. The use of this procedure allows an increase in the sample size of green fuel rods from about 60 mg to about 500 mg and of fired rods from about 60 mg to about 12 g. Sampling errors are greatly reduced and precision is improved. In the case of green fuel rods, the sampling precision was ±30% for a 60-mg sample and ±3% for a 500-mg sample. For the fired fuel rods, sampling errors are eliminated because the entire rod is used for analysis. The accuracy of the method as determined by the analysis of standard coal samples and inorganic sulfate salts is 97 ± 4%. (*F. L. Layton*)

Advanced Fuel Recycle Program Studies

Chromatographic separation capabilities. Gas and liquid chromatographic capabilities are being established for analytical development studies related to advanced fuel reprocessing. A liquid chromatograph has been assembled, which consists of a Milton Roy minipump, Cheminert model R6031SV sample injection valve, jacketed glass Cheminert columns and a laboratory data control model SF770 spectroflow uv monitor. The chromatograms are displayed on a Health-Schlumberger model SR206 dual-scan recorder.

The first liquid chromatographic experiments were feasibility studies on the separation of nitrate-nitrite and nitrate-azide mixtures, which can exist in hydrazine-stabilized solutions of plutonium(III) during Purex processing. A column (6.3-mm diam × 170-mm long) of Aminex A25 strong-base anion exchange resin with a particle size of 17 ± 2 μm was used. Also a solution of potassium chloride was chosen as the eluent to maintain the resin in the chloride form, which minimizes column dimension changes caused by resin swelling and contracting. Working pressures depended primarily on the eluent flow rate and approached 500 psi at about 2 ml/min. Good separations of nitrate-nitrite and nitrate-azide mixtures were obtained, using aqueous standards and 0.5 *M* KCl eluent. At a flow rate of 1.76 ml/min (400 psi pressure), retention times for nitrite, azide, and nitrate ions are about 13, 30, and 38 min respectively. These experiments are continuing to establish optimum experimental conditions (flow rate, solvent strength, etc.) for these chromatographic separations. (*D. L. Manning*)

Analysis of advanced reactor fuels. Indications are that a discrepancy exists in the data obtained when conventional coulometric methods[20] are used to characterize advanced reactor fuels containing uranium and plutonium. An accurately determined chemical factor must be used to eliminate the interference caused mutually by the two heavy metals. A correction must also be made for iron. To eliminate these problems, an investigation is being made in which the uranium is determined by the Davies-Gray volumetric titration method[21] and the plutonium is determined by an amperometric titration method using Fe^{2+} to reduce Pu^{6+}.[22] The

---

[19] D. E. LaValle, D. A. Costanzo, W. J. Lackey, and A. J. Caputo, "The Determination of Defective Particle Fraction in High-Temperature Gas-Cooled Reactor Fuels," *Nucl. Technol.* 33, 290 (1977).

[20] W. D. Shults, "Coulometric Methods," chap. 23 in *Standard Methods of Chemical Analysis*, vol. III, 6th ed., ed. by F. J. Welcher, D. Van Nostrand Co., Inc., Princeton, N.J., 1966.

[21] W. Davies and W. Gray, "A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium Using Iron(II) Sulfate as Reductant," *Talanta* 11, 1203 (1976).

[22] C. A. Seils, Jr., R. J. Meyer, and R. P. Larsen, "Amperometric Titration of Plutonium(VI) and Iron(II)," *Anal. Chem.* 35, 1673 (1963).

isotope dilution mass spectrometric (IDMS) method is also being evaluated for the analysis of uranium and plutonium by using the resin-bead technique.[23] In addition, a series of uranium and plutonium control standards have been prepared, which simulate the reactor fuel samples. These controls are analyzed by the same procedure as the samples to obtain data for establishing the reliability of the method. (*J. L. Botts*)

Tritium removal from LWR fuel. Experiments are under way to determine if tritium will be released from irradiated Robinson Reactor UO_2 fuel at elevated temperatures (1000°C) either under vacuum or with a purge of 1% H_2 in helium. These scoping experiments are in support of LWR voloxidation studies in the Chemical Technology Division. The hot-cell apparatus to be used consists of a clam-shell resistance furnace for heating the UO_2 and can be connected either to a vacuum pump or to the 1% H_2 in helium purge. The release of tritium will be measured by "before" and "after" analyses of the fuel. The fuel will be dissolved in 7 *M* HNO_3 and the tritium separated by distillation. (*L. C. Bate*)

GENERAL ANALYSIS LABORATORY

W. R. Laing, Group Leader

Development and Special Projects

The General Analysis Laboratory characteristically carries out a wide variety of chemical analyses for many customers, both inside and outside ORNL. Much of this work is developmental in nature. Several of the more important special projects are reported here.

Because of the diversity of samples that are run on our Technicon AutoAnalyzer, it is difficult to select sample sizes or aliquots prior to a given run. Accordingly, we used a least-squares curve-fitting routine to extend the range of the ammonium thiocyanate spectrophotometric method for the Technicon AutoAnalyzer into the nonlinear area. The calibration curve covered 0.1 to 2.2 mg U/ml. Quality control samples analyzed over this range gave results within ±3%.

In the investigation of methods for monobutylphosphoric acid (MBP) and dibutylphosphoric acid (DBP) in tributylphosphoric acid (TBP), both gas chromatography and nonaqueous titrations were used. Either methylation or silylation was used to provide more volatile compounds for the gas chromatographic separation. Each method worked equally well, and there was little basis to choose one over the other. Sensitivity was 0.05 μg for MPB or DBP. Nonaqueous titration of MBP and DBP in 90% acetone was used for higher levels of these compounds.

An atomic absorption method for ruthenium in organic (TBP) solution was developed. Ruthenium is easily volatilized, so procedures for wet ashing of organic samples could not be used. It was found that the TBP solution could be diluted with a mixture of ethyl and butyl alcohols, which would allow the addition of aqueous solutions containing releasing agents, radiation buffers, and known spike additions. These TBP samples were analyzed by the standard addition technique with sensitivities of 1 ppm. This same technique was used to analyze other organic solutions for neodymium and iron.

In a study of ruthenium chemistry, several complex ruthenium compounds were prepared from degradation products of tributylphosphoric acid. An atomic absorption method was used for the ruthenium determination, and a perchloric acid reflux was used to convert organic phosphorous compounds to PO_4^{3-} for spectrophotometric measurement.

In studies of the mechanism of the chemical reduction of Pu(VI), solutions were analyzed for HN_3, NH_2OH, N_2H_4, NO_2^-, NO_3^-, and NH_4^+ in various combinations. A spectrophotometric method was used for HN_3, and ion-selective electrodes were used for NH_4^+ and NO_3^-. Ceric and iodine titrations were used for HN_3, NH_2OH, and N_2H_4.

Tests of off-gas scrubbers required the measurement of NO_x in the gas phase, NO_3^- and NO_2^- in aqueous solution, and OH^- measurement of the scrubber solutions. The gas samples were equilibrated with 1% H_2O_2, and the resulting HNO_3 titrated. Nitrite in solution was measured by reaction with ceric sulfate; the total nitrogen content was determined by the Kjeldahl method. More than 750 caustic scrubber solutions were titrated, using the Fisher automatic titrator.

A large effort was made to extract useful materials from fly ash. In some tests the ash was sintered with Na_2CO_3 and then leached by Na_2CO_3 solutions or water. In others the ash was refluxed

---

[23] R. L. Walker, C. H. Pritchard, J. A. Carter, and D. H. Smith, *Practical Aspects of the Resin Bead Technique for Mass Spectrometric Loading*, ORNL TM-5505 (1976).

with inorganic acids. Elements of interest were Al, Fe, Ti, and U; these were determined by atomic absorption or fluorometry. Standard addition was used on all samples to avoid matrix problems.

Sealed-tube dissolutions have been used for several years to prepare iridium alloys for analysis. Some alloys, however, have resisted this treatment even after 7 days at 300°C. A switch to an HCl-HClO$_4$ dissolution medium rather than an HCl-HNO$_3$ mixture showed improvement in dissolution of these samples. An Ir-Th alloy, which had not dissolved at all in the HCl-HNO$_3$ mixture, was successfully prepared.

In support of Office of Waste Isolation programs, a series of NBS cement standards was prepared under the same conditions that were used for OWI samples. Standards were then selected which closely bracketed sample concentrations so that the microprocessor on the Perkin-Elmer 460 AA instrument could be used to linearize the working concentration range. Sample concentration could be read directly from the instrument display. Cement samples have been analyzed for CaO, SiO$_2$, Al$_2$O$_3$, Na$_2$O, K$_2$O, Fe$_2$O$_3$, and MgO, using this technique. Analysis time for a cement sample was 2 days instead of a week, using the classical ASTM procedure.

RADIOACTIVE MATERIALS ANALYSIS LABORATORIES

J. H. Cooper, Group Leader

Analytical chemistry support for the LWBR Assistance Program was completed early this year, and current work has been directed strongly toward fuel reprocessing studies. The Transuranium Analysis Laboratory, in addition to its support of transuranium-element production, has been active in the analyses of synthetic fuel reprocessing samples. Analyses of these samples emphasized the determination of uranium, plutonium, plutonium oxidation state, and acidity. Spectrophotometric methods were used for detemining uranium, radiometric methods were used for plutonium, and potentiometric methods were used for acidity. Plutonium oxidation states (as well as plutonium polymer) were studied by solution spectrophotometry, using a Cary recording spectrophotometer. Rapid estimates of Pu(IV) were made by extracting the Pu(IV) into thenoyltrifluoroacetone (TTA) and counting the plutonium alpha activity. The Pu(III) and (VI) do not extract into TTA from 1.0 *M* acid.

Estimation of Radiolytic Degradation Products in Tributylphosphate

In processing spent reactor fuels by the Purex process, the TBP extractant undergoes radiolytic degradation. The degradation products are mainly DBP, MBP, and phosphoric acid (H$_3$PO$_4$). The compounds DBP and MBP form stable complexes with U, Pu, Zr, and Ru; these adducts are retained in the organic phase during stripping and washing steps. The ability to determine both DBP and MBP in recycled TBP solutions is important to understanding the extraction process.

Portions of TBP-dodecane extractant that had been contacted several hours with a dissolver solution of an LMFBR fuel rod were decontaminated and submitted for the measurement of TBP radiolytic decomposition products. Aliquots were silylated and analyzed by gas chromatography. The silylation step was necessary to convert DBP and MBP into volatile derivatives. Chromatographic peaks that corresponded to DBP and MBP as well as TBP were obtained on all the irradiated samples. Unirradiated solutions of TBP-dodecane did not reveal significant DBP or MBP peaks. The concentrations of these degradation products in irradiated samples ranged from 500 to 3000 ppm with the level of DBP being somewhat higher than MBP. The results from these first irradiated samples were encouraging. It appears that we can detect TBP degradation products by silylation followed by gas chromatography. Additional experiments are planned.

Determination of ^{14}C in LWR Spent Fuels

An apparatus was fabricated and assembled for repetitive hot-cell dissolutions of LWR spent fuel to assess the reproducibility and reliability of ^{14}C measurements. The apparatus has glass connections and provides both for acid reflux dissolution of the LWR fuel and for sweeping the off-gas through sodium hydroxide scrubbers before and after it passes through a hot copper oxide bed. Following a dissolution test, the scrubber solutions were assayed for ^{14}C.

The apparatus was first checked in the hot-cell mock-up by processing ^{14}C standards (Ba^{14}CO$_3$ and labeled benzoic acid) through the dissolution procedure. For seven experiments the recovery of the ^{14}C was 99 ± 5% at the 10^4 dis/sec level, which was chosen to simulate LWR estimates. This indicated that all of the ^{14}CO$_2$ was swept from the dissolver flask to the NaOH traps and that all of the ^{14}CO$_2$ was removed by the first trap. The ^{14}C activity in the second trap was not significantly different from the background. The apparatus was then reassembled in the hot cell, and eight experiments (with 3-g portions of an LWR spent fuel rod) were conducted under conditions designed to achieve complete dissolution of the sample. The ^{14}C content was found to be $1.95 \pm 0.16 \times 10^{3}$ dis sec^{-1} g^{-1}.

The temperature of the dissolver flask was maintained at 80 to 90°C, and the CuO bed at 600°C; each $^{14}CO_2$ trap contained 75 ml of 2 *M* NaOH. The time for sample dissolution and recovery of the $^{14}CO_2$ was about 3 hr. The samples were completely dissolved in 50 to 75 ml of solution containing one part 4 *M* HCl and two parts 4 *M* HNO_3. In 4 *M* HNO_3 alone, however, a small amount of residue remained after 3 hr of reflux, but it could be dissolved by the addition of HCl. The HNO_3 treatment appeared to release about 80% of the ^{14}C. The LWR fuel also dissolved in concentrated $HClO_4$, but ruthenium distilled into the first NaOH trap, and hence a redistillation was required prior to counting. To our knowledge, these are the first repetitive ^{14}C measurements on small samples of the same LWR fuel rod. The reproducibility of the results and the quantitative ^{14}C recovery, based on standards, indicate that the measurements are realistic.

LWR dissolver solutions were also analyzed for residual ^{14}C by refluxing an aliquot of the dissolver solution, using the procedure for the LWR samples with added perchloric acid. No significant quantities of additional ^{14}C were found. This indicated that organics and other substances that may retain ^{14}C were not present in any appreciable quantities following the initial dissolution of the LWR fuel in nitric acid.

ENVIRONMENTAL ANALYSIS LABORATORY

R. R. Rickard, Group Leader

During the past year there was a 25% reduction in the number of analytical results reported as a consequence of programmatic changes within the Environmental Sciences Division. The EPA Microcosm Project was terminated last spring, the Walker Branch Watershed study was undertaken at a lower sampling level, and the NSF–Almaden Mercury Program required fewer analyses. Nevertheless, the Microcosm Project was sizeable. Numerous analyses were made for the alkali and alkaline earth elements and anions such as nitrate, phosphate, and sulfate. In a study of the fate of arsenic when microcosms were subjected to water leaches, we explored the feasibility of a direct-measurement atomic absorption technique, using the graphite furnace. A control-area sample, a sample with an intermediate level of arsenic, and a sample with a relatively high level of arsenic were analyzed by this method. In all three samples, good agreement was found with the results obtained by the more time-consuming AsH_3 method. The graphite furnace coupled with the standard addition technique was found to be quite reliable for determining arsenic in fly ash. The fly ash was dissolved, using the vapor-phase method reported by Feldman.[24]

Attempts to use the gas-chromatographic microwave-excitation system (GCMES) to measure selenium in processed coal, fish, and water samples were abandoned in favor of flameless atomic absorption. A piaselenol complex was derived from the chelation of Se(IV) with 5-nitroso-*o*-phenylenediamine and was extracted into toluene. Good agreement was found with NBS coal and liver standards and an EPA water standard.

As part of a study to determine the environmental behavior of nickel and fluoride, selected vegetation was sampled and analyzed. Nickel analyses required sample ashing at 550°C, followed by leaching with high-purity 1 *N* nitric acid before atomic absorption measurements were made. Separate samples of vegetation were digested with a potassium hydroxide solution before measuring the fluoride content, using an ion-selective electrode. Fluoride concentrations were found from 1 to 100 μg/g.

To obtain suitable base-line information for trace elements in foods, the Environmental Surveillance Evaluation Section of the Industrial Safety and Applied Health Physics Division purchased typical processed and fresh foods at a local supermarket. The foods were homogenized, sampled, and wet-ashed in the clean laboratory to reduce the possibility of trace-metal contamination. The concentration of mercury in all of these foods was found to be well below 1 μg/g.

Iodine-impregnated charcoal is used by the Environmental Sciences Division for extracting mercury from air streams. Air samples were taken from control areas and regions near manufacturing sites, salt domes, and a mercury mine. The presence of iodine in the charcoal severely distorted the mercury absorption signal used for analytical purposes. We found that pretreatment of the charcoal

---

[24] C. Feldman, "Determination of Traces of Arsenic in Siliceous Materials," *Anal. Chem.* **49**, 825 (1977).

with sulfuric acid at 300°C, followed by the conventional nitric-perchloric acid–dichromate treatment, was an effective way to circumvent the problem. Standards prepared and analyzed substantiated this finding.

An Omron video terminal was placed in the Environmental Analysis Laboratory to provide access to the ORNL DEC System 10 computer and hence to implement the division's data-management system. There was immediate improvement in both data handling and quality of reports. The system also provides rapid retrieval of time data used for the preparation of the monthly cost distribution.

SPECIAL SERVICES

Custom Synthesis

As in previous years, most of the preparations for this synthesis were made for research groups in the Solid State Division. For the Neutron Diffraction Group, two ferrites were made—$BaNi_2Fe_{16}O_{27}$ and $BaNi_2Sc_4Fe_{12}O_{27}$—by methods previously described.[25] They were blended to make 50 g of the ferrite $BaNi_2Sc_2Fe_{14}O_{27}$. Another batch of the isotopic compound $^7Li^2H$ was made because of unexplained anomalies in the first material. Another isotopic compound provided was $Na_2SO_4 \cdot 10^2H_2O$. An extensive project was begun for the preparation of large crystals of the highly conducting charge transfer salt, tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ). The electrical properties of this compound, including possible superconductivity, are highly sensitive to crystal imperfections, which are attributed to impurities. All starting materials are being prepared in high purity prior to synthesis of the TTF-TCNQ. For the Neutron Spectrometry Group, 500 g of palladium was recovered from various alloys to give a product containing as the only impurity, 600 ppm of cobalt To remove the cobalt, a method was developed in which the palladium, as soluble H_2PdCl_3, is reduced to the metal with formic acid and filtered, leaving the cobalt in solution. Other work included preparation of the alloys $Pd_{0.99}Fe_{0.01}$, $Pd_{0.98}Fe_{0.01}{}^{160}Gd_{0.01}$, and $Pd_{0.99}{}^{160}Gd_{0.01}$. The preparation of the isotopic compound $^{154}Sm^{11}B_6$ was accomplished by conversion of the samarium metal to a powder by hydriding, blending with ^{11}B powder, and heating to 900°C. A further grinding, compressing, and firing at 1300°C gave the pure single-phase cubic $^{154}Sm^{11}B_6$. For the Isotopic Research Materials Laboratory (IRML), 25 g of $^{175}Lu_2O_3$ was converted to the metal by reduction of the intermediate $^{175}LuF_3$ with calcium at 1700°C. Also 6 g of $^{160}GdF_3$, prepared from oxide, was supplied to IRML for reduction to ^{160}Gd metal.

For LWR reprocessing studies in the Chemical Technology Division, the chloride-free ruthenium compound $Na_2[RuNO(NO_2)_4OH]$ was supplied in periodic 25-g batches. For the Magnetic Energy Fusion Program of the Metals and Ceramics Division, 25 g of Li_2O was prepared by heating Li_2CO_3 in a high vacuum at 700° until no more gas evolved (~60 hr). (*D. E. Lavalle*)

Testing of Coatings

The number of requests for the testing of paints and coatings for use in nuclear reactor primary containment areas increased markedly this year. Sample specimens (steel panels and concrete blocks) were submitted by a total of 17 manufacturers and nuclear utility companies. About 200 coating systems were tested and evaluated. Included among the more than 1500 test specimens were 70 systems for ease-of-decontamination testing, 360 specimens for radiation-resistance testing, and the remainder, including the irradiated specimens, for simulated loss-of-coolant-accident (LOCA) tests. Several radiations of special test specimens were made for ORNL divisions.

The decontamination tests were conducted in Building 3019. The irradiation was done, using spent fuel assemblies at the HFIR fuel storage pool. The autoclave used for the LOCA test is located in Building 2026. Currently, ORNL is the only installation qualified to conduct all three tests at one company site as required by the test specifications. *(G. Goldberg)*

---

[25] D. E. LaValle, "Materials Preparation," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 47.

4. Bio-Organic Analysis

M. R. Guerin, Head

The Bio-Organic Analysis Section continues to use a matrix-type organization with four discipline-oriented groups responding to technical commitments of two major programs. These programs consist of 12 individual projects. The commonality of this effort continues to be the life sciences orientation of our organic analytical research and services. With the exception of a small involvement in providing special analytical in-house services, section activities are committed to providing tools (hardware, materials, and methods) for biological and environmental testing and data for defining and interpreting the results of these tests. About 60% of our effort is allocated to health effects of cigarette smoke; the remaining 40% is allocated to environmental and health effects, primarily of advanced fossil-fuel technologies.

Projects addressing the relationship between smoking and health now emphasize inhalation exposure to the virtual exclusion of other routes of smoke administration. We have demonstrated the efficacy of a group responsible for quality control of and for assisting personnel involved in routine inhalation bioassays of cigarette smokes at other institutions. A state-of-the-art tobacco smoke inhalation exposure device that incorporates automatic continuous exposure documentation is now available to the scientific community. We have quantitatively determined the effectiveness of such devices to dose the respiratory tract of experimental animals and have postulated a generally applicable mathematical relationship between exposure parameters and retained dose of tar. Research efforts are now focused on methods to (1) establish the fate of individual smoke constituents after deposition in the animal, (2) allow a cost-effective improved documentation of exposure, and (3) allow an early assessment of the physiological impact of smoke exposure. Routine analyses of cigarette smokes are currently limited to (1) the comparison of whole smokes offered for inhalation with condensed smokes that were previously offered for skin testing and to (2) the characterization of commercial cigarettes for translating the findings of the National Cancer Institute Smoking and Health Program to procedures and policies applicable to the human smoking population.

Energy-related studies have focused on the relationship between chemical composition and biological significance. Particular attention has been given to the relationship between microbial mutagenesis, whole animal carcinogenesis, and chemical composition. The mutagenically active (presumably indicative of carcinogenesis) alkaline constituents of synthetic crude oils have been isolated in a fraction of about 0.5 wt % of the oil and found to contain predominantly azaarenes, including azacoronenes. We have generated and supplied materials to Biology Division collaborators for assessing the role of polycyclic aromatic hydrocarbons in occupational carcinogenesis related to coal- and shale-oil production. A method has been developed for the separation of synthetic oils into chemically defined classes for further chemical, biological, and/or environmental testing, which incorporates the required applicability to large sample sizes and minimizes contacts with materials that exhibit a high probability for chemical alteration.

BLANK PAGE

Renewed attention is being given to basic analytical methodologies to ensure that quantitative results and organic structural identifications are reliable. We have found that because of its volatility, radiolabeled naphthalene is a poor indicator of the fate of diaromatics during chemical and chromatographic isolation as well as during evaporative concentration. We have also confirmed that polycyclic aromatic hydrocarbons labeled with ^{14}C and with ^{3}H do not behave equally well as indicators of chemical recovery because of tritium exchange with chromatographic adsorbents and possibly because of other constituents of complex mixtures. These and related observations are being used to develop more reliable and rapid methods for the chemical characterization of natural and synthesized materials.

The reports presented have been chosen by the task leaders as representative of our current activities and indicative of our ability to provide instrumentation, methods, materials, and/or data required to define the relationship between chemical composition and biological impact.

SEPARATIONS AND IDENTIFICATIONS

Isolation of mutagenic constituents of synthetic crudes. The development and use of bioassays to pinpoint dangerous chemicals, especially carcinogens, is an important component of the ORNL Synthetic Fuels Life Sciences Program. Recent studies[1,2] have demonstrated that microbial mutagenicity assays have especially useful features; for example, they are inexpensive, fast, reasonably reproducible, and yield results that correlate well with the carcinogenic potentials of pure compounds. Less certainty exists concerning the ability of such tests to identify reliably hazardous components of complex mixtures.

During the past 2 years we have worked with colleagues in the Biology Division to design and carry out experiments for establishing and validating bioassays for incorporation into a general toxicity-screening program at ORNL. A data base of biological activities, determined using the microbial mutagenesis assay, has been generated for a wide variety of fossil-derived materials. Our experimental role in these mutually designed studies has been to fractionate crude materials into distinguishable chemical classes and identify constituents of biologically active fractions. Ether-soluble base (ESB) fractions of several crudes and aqueous wastes, which were fractionated by an extractive separation procedure,[3] exhibit high biological activities as measured by the Ames microbial mutagenesis test. The ESB was therefore chosen for subfractionation to isolate and identify the biologically active components.

A subfractionation procedure was developed to isolate the mutagenic components of the ESBs of a shale oil and a coal-derived crude oil. No particular guidance was available in the literature. Biologically active compounds might fall into several chemical classes, and a successful subfractionation scheme had to be worked out in parallel with the bioassays of subfractions to determine if active components are being separated.

Biologically active subfractions were sought, using liquid chromatography with several packing-solvent combinations. Bioassays indicated the extent of separation of the active components and, in effect, served as the chromatographic detector. We found that the best isolation was achieved by a two-step process: (1) an alumina (Activity I) column eluted with benzene, followed by (2) a Sephadex LH-20 column eluted first with isopropanol and then with acetone. Columns were constructed by modifying standard burets and were eluted by gravity flow.

The effective isolation of mutagenic components in the acetone fraction is apparent from the data in Table 4.1. The acetone subfraction contains about ten relative weight percent of the ESB, and the ESB fraction represents only about 5 wt % of the starting material; the overall isolation of the principal mutagenic components is therefore about 0.5 wt % of the crude oil. The benzene and isopropanol eluates contain only negligible biological activities but represent 90% of the material. The nonactive components are separated extremely well from the active components by this elution sequence.

Mass balance calculations indicate quantitative recoveries of the ESB components. Biological activities

---

[1] Council of the Environmental Mutagen Society, Committee 17, *Science* 187, 503 (1975).

[2] "Simple Test May Establish Carcinogenicity," *Chem. Eng. News*, Dec. 22, 1975, pp. 19 20.

[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. Distribution of mutagenic activity among subfractions of synfuel ether-soluble base fractions[a]

Subfraction	Synthoil base fraction Relative weight (%)	Synthoil base fraction Specific activity (rev/mg)[b]	Synthoil base fraction Relative activity (%)[c]	Shale-oil base fraction Relative weight (%)	Shale-oil base fraction Specific activity (rev/mg)[b]	Shale-oil base fraction Relative activity (%)[c]
Benzene	76	850	2	78	0	0
Isopropanol	12	0	0	12.5	226	1
Acetone	12	220,000	88	9.2	25,000	92
Total	100		90	99.7		93
Ether-soluble base fraction		30,000			2,500	

[a] Data from J. L. Epler et al., Biology Division.

[b] Revertants per milligram (rev/mg), the number of histidine revertants from *Salmonella* strain TA98 by use of the plate assay with 2×10^8 bacteria per plate. Values are derived from the slope of the induction curve extrapolated to a milligram value.

[c] Percent of relative activity of each subfraction referred to mutagenic activity of the original base fraction, calculated by: specific activity of each subfraction (rev/mg) × % of relative weight of each subfraction/specific activity of original base fraction (rev/mg).

are also nearly quantitatively recovered. If the weight percentages of the three fractions are multiplied by their specific activities and these are summed, the additive activities of the subfractions yield predicted specific activities of 27,000 revertants per milligram (rev/mg) for the synthoil ESB and 2300 rev/mg for the shale-oil ESB. These compare with 30,000 and 2500 for the synthoil and shale-oil ESBs, respectively, before subfractionation; calculated recoveries are 90 and 93% of the original activities respectively. The loss of about 10% of the biological activity in these cases might have some significance; that is, absence of synergistic activity following fractionation might account for the difference. However, the reproducibility of bioassays also falls in this range. The mutagenic activity of the synthoil-derived ESB is comparable to that of pure benzo[*a*]pyrene (BaP), whereas that from the shale oil is an order of magnitude smaller.

Gas chromatography and combined gas chromatography-mass spectrometry (GCMS) have been applied to each of the subfractions. Compounds ranging from low-molecular-weight diazenes and pyridines in the benzene fractions to heterocyclic azacoronenes in the acetone fraction have been observed. Ninety percent of the peaks in the gas chromatographic (GC) profiles of all fractions have been tentatively identified by GCMS. The highly mutagenic acetone subfraction contains principally azaarenes such as azabenzoperylenes, azaindopyrenes, and azacoronenes. These compounds may be the components that produce the high biological activity. Mutagenesis testing of pure compounds representative of high molecular weight azaarenes is required to confirm this suspicion.

Detailed characterization of the acetone subfraction requires analysis on an analytical-scale liquid chromatographic column and capillary column GC. This is being pursued, but positive identifications of components will continue to be limited because of the small amounts that can be isolated and the lack of commercially available compounds for reference purposes. (*C.-h Ho, J. G. Dorsey,*[4] *T. K. Rao,*[5] *B. R. Clark*)

Isolation and characterization of polycyclic aromatic hydrocarbons (PAH) for skin carcinogenicity testing. Coal tars have long been known to contain highly carcinogenic components. Certain PAHs are among the most carcinogenic compounds known and continue to be the focus of extensive research in carcinogenesis. Among the basic questions that remain unanswered regarding these compounds are (1) what synergistic effects might exist among PAHs or PAHs and other chemical classes and (2) to what extent do the PAHs in fossil-derived tars contribute

---

[4] On loan from Y-12 Product Certification Division.

[5] Biology Division.

to the overall carcinogenicity of these substances? In an attempt to address these questions, we have isolated the PAHs from four fossil-derived crude oils. J. M. Holland (ORNL Biology Division) is using the mouse dermal bioassay to determine the relative carcinogenicities of the isolates and their parent crudes. Data on rate of tumor development vs dose and sample type will provide some valuable answers to the above questions. In addition, mouse dermal assay data can be compared with other bioassays on these materials. Whether or not the Ames test can identify carcinogenic *mixtures* is still in question and can be answered to a limited extent by comparing these data.

Isolation of PAHs from the crude oils was carried out by using a modification of a procedure[6] traditionally applied to cigarette smoke condensates. Since PAHs are among the neutral class of components, neutral fractions were first generated by extracting acidic and basic components from ether solutions of the crudes with aqueous solutions of hydrochloric acid and sodium hydroxide. The neutral fraction was dissolved in cyclohexane, and the cyclohexane was extracted with dimethylsulfoxide (DMSO), back-extracted from the DMSO with fresh cyclohexane after adding water (40%) to the DMSO, eluted through Florisil and alumina columns (Activity II) with hexane-benzene, and finally evaporated to constant weight at room temperature. The isolates thus produced from a shale oil, two liquified coal products, and a mixture of natural petroleums were distributed into glass vials, each vial containing enough material for one week of skin painting.

Four dose levels for each crude material and three levels for each isolate have each been applied to test groups of 50 animals each. Current results indicate that the dose levels chosen may be at the low end of the dose-response curve. An additional experiment is being considered which would use substantially increased doses of crudes and isolates; the experiment would follow additional testing of the crudes to determine the appropriate dose.

An important part of these experiments is to establish both the compositions and the stabilities of the isolates. Gas chromatographic analyses of the isolates during the course of the bioassay have shown no significant changes in peak heights or retention times since the beginning of the experiment. All materials are stored in the dark in a freezer (−18C°) until used. All of the isolates have been screened by GCMS using a 10-ft × $^1/_8$-in. OD glass column packed with 3% Dexsil 400 on 100/120 mesh Chromosorb W-AW programmed from 100 to 320°C at 2°/min after an 8-min hold. Thirty-seven compounds for which a standard mixture exists were quantified by peak-area integration. Other compounds have been identified by mass spectrometry but have not been quantified. Generalizations from these analyses are (1) low-molecular weight, naphthalenic materials were largely lost during room temperature solvent stripping—only 10 to 20% of the diaromatics present in the crude oils remains in the isolates; (2) the coal-derived isolates have greater amounts of high-molecular weight components than do the shale-derived or petroleum isolates; (3) coal-derived isolates have a greater variety of PAHs than do petroleum or shale-derived isolates, probably as a result of having more alkylated species; (4) the coal-derived crudes have a higher total PAH content (5 to 6 wt %) than do either the shale oil (2.0%) or the petroleum blend (2.6%).

Another important aspect of this work is the development of capabilities for determining the exact isomeric identification of particular compounds. From the viewpoint of biological activity, the isomeric form of the compound is crucial. Mass spectrometric data cannot easily differentiate among compounds of identical molecular weights, for example, the various methyl isomers of the same parent compound. To use other, less sensitive, means for identification requires a substantial amount of subfractionation and purification to concentrate the analyte, which necessitates starting with large amounts of whole isolate. In the present study, not enough isolates were produced for a detailed identification of this sort. However, an attempt was made to identify the major PAH constituents of one coal-derived isolate by liquid chromatographic subfractionation on alumina. About 1 mg of material was finally obtained after combining the same subfractions from repetitive runs. Nuclear magnetic resonance spectroscopy was used to attempt identifying the "pure" compound but proved too insensitive at this level, even with overnight signal averging. Ultraviolet fluorescence spectroscopy indicated a mixture still existed, and this was confirmed by thin-layer chromatographic separation into at least two major components. Another fluorescence measurement indicated pyrene as the likely compound we had isolated. This identification was essentially established, even before the isolation work, from the GC

---

[6] 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).

retention time and GCMS molecular weight data. The isolation and identification was carried out to investigate this approach for obtaining "pure" compounds from the PAH isolate. What has been shown is that even a major component of an isolate is not easily separated and identified unambiguously. (*B. R. Clark, H. Kubota, R. R. Reagan, R. W. Harvey, I. B. Rubin, E. H. McBay, E. C. Siebold,[7] M. R. Guerin*)

Sephadex LH-20 class fractionation of synthetic crudes. Crude oils produced from coal and oil shale are not readily class fractionated by methods designed to fractionate petroleum crudes. The first steps toward a more suitable method were outlined in the previous progress report.[8] The most promising procedure uses Sephadex LH-20 gel in three different separation modes in succession. This separation method,[9] schematically illustrated in Fig. 4.1, has the advantages that large samples can be handled easily, no harsh chemicals are used, no physical stresses are employed, no degradation of the gel is encountered, and yields during the fractionation procedure are virtually quantitative.

A shale oil has been used to study the reproducibility and separations behavior of the three-step elution scheme that has evolved. The steps employed are outlined briefly as follows:

Step 1: The gel is swollen with methanol (85 vol %) and water (15 vol %) and is equilibrated with hexane. The sample is eluted with hexane until little material is found in the eluate as determined gravimetrically. This step produces a separation equivalent to that of solvent-solvent partitioning. In this case, the hydrophilic materials remain on the column, whereas the lipophilic materials are eluted with the hexane. Although work to date has incorporated this solvent system, no major problems are foreseen in using similar polar and nonpolar solvent combinations for cases in which hexane does not provide sufficient solubility of the starting material.

Step 2: The lipophilic material from the previous step is placed on a column which has been swollen with tetrahydrofuran (THF) and the column is eluted with THF. This step results in the elution of three distinct fractions—a "polymeric" fraction eluted approximately with the void volume, a nonpolar fraction containing aliphatics and aromatics and eluted in reverse order of molecular size, and a "hydrogen-bonding" fraction containing lipophilic constituents with polar functionalities.

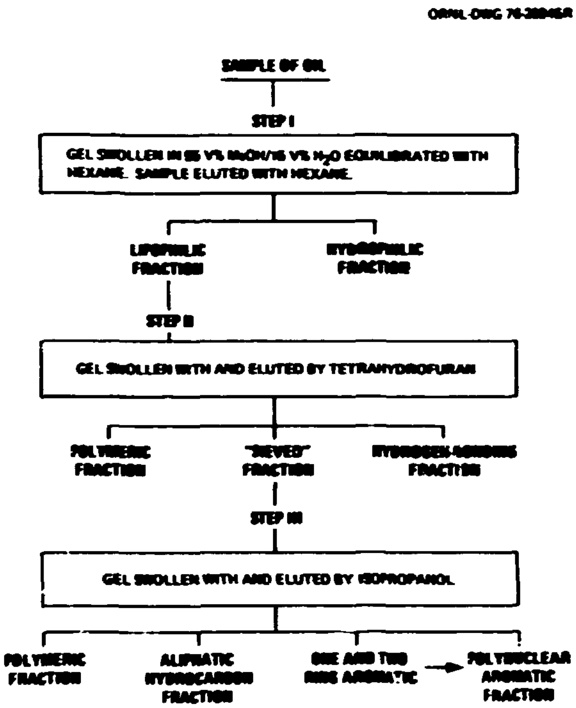


Fig. 4.1. Separation scheme using Sephadex LH-20 gel.

Step 3: The aromatic-aliphatic fraction from step 2 is further fractionated on a column that has been swollen and eluted with isopropanol. A void-volume fraction is obtained which consists of additional polymeric material that separates in this step because of the slightly diminished pore size of the gel in isopropanol. The second fraction is distinctly aliphatic, with the aliphatic compounds eluting in the reverse order of their molecular weights. The remaining fractions are aromatic and less distinct. Except for aromatics that contain ring substitutes, the elution is clearly in the order of increasing molecular weights. If the aromatic compounds are substituted with alkyl and/or polar functional groups, their elution volumes are lowered, and overlaps will occur. Because polar constituents have been separated by earlier steps, only alkyl substitution of aromatic compounds should affect the elution volumes. Experimental data indicate that, even with extensive alkyl substitution (e.g., phenylcyclohexane), a large elution volume remains between the elution of the lowest molecular weight aliphatic and a highly alkyl-substituted aromatic.

---

[7] Southern Colleges and Universities Union (SCUU) spring semester student and summer NSF student participant.

[8] A. R. Jones and B. R. Clark, "Large-Scale Chemical Class Fractionation of Synthetic Crude Oils," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 69.

[9] 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).

Separations performed on a shale oil and charcoal-energy development (COED) syncrude oil were reproducible over a wide range of sample sizes and showed distinctly different distributions among the chemical classes obtained by this procedure. The principal difference lies in the aliphatic-aromatic contents. The shale oil is much more aliphatic than is the COED oil. The procedure and these observations have been reported.[9]

An important objective of this work is to devise a procedure of wide applicability. Several other materials have now been tested or are in the process of being tested by use of this procedure with appropriate modifications in solvent systems for the first step to accommodate solubility differences of whole samples. A synthoil and a solvent-refined coal product are being fractionated. The greatest difficulty encountered in the general application of this procedure lies in selecting an appropriate solvent-gel treatment for use in the first step. Shale oil and COED syncrude oils contain relatively small amounts of hydrophilic materials, making them sufficiently soluble in hexane that no difficulty is encountered. Materials such as synthoil, which contains about 30 wt % polar components, and the solvent-refined coal product, which has a high polymeric component, cannot be dissolved adequately in hexane. Furthermore, elution with hexane causes the formation of insoluble, viscous plugs at the top of the column which makes this separation impossible. Different solvent and solvent-gel systems should circumvent this problem and are being explored. Because THF appears to be the best overall solvent for the widest variety of fossil-derived materials, one might begin with the second step or first carry out the conventional solvent extraction of the polar components.

Mutagenic activities of each fraction derived from applying the procedure to a shale oil have been determined. These results are interesting in several respects. First, there is no loss of biological activity with progression through the separation steps. The average specific activity of the whole crude oil was 223 rev/mg. Summation of the final fraction activities yielded 229 rev/mg. This yield suggests that there is no extensive synergistic relationship between compound classes found in different fractions. Secondly, the most active fractions are the polynuclear, the hydrogen-bonding, and the hydrophilic. These data agree extremely well with the observed activities of corresponding fractions generated by acid-base solvent extractions. This implies that acid-base treatment does not affect mutagenic activity.

The work of Determann and Lampert[10] demonstrated that different degrees of hydrophobic interactions occur in LH-20 gel as a function of the ionic strength of aqueous eluting solutions. We are using this observation to develop a means of subfractionating the hydrophilic fraction produced in the first step of the procedure. Preliminary results have shown that the gel, when swollen with water and eluted with 0.1 to 10.0 *N* acetic acid solutions, can separate a test solution into basic, neutral, phenolic, and carboxylic acid fractions. A simple separation between bases and all other classes of compounds is obtained by using 6 *N* acetic acid. Aliphatic alcohols, ketones, and low-molecular weight carboxylic acids are poorly separated from the other hydrophilic constituents. (*A. R. Jones, B. R. Clark*)

QUANTITATIVE METHODS AND PROJECTS

Development of methods for analysis of polycyclic aromatic hydrocarbons (PAH) in the aquatic environment. PAHs have long been recognized as a particularly bioactive class of compounds. The determination of their identities and distribution in the aqueous environment is important in assessing the environmental impact of processes that release such compounds. A method for the analysis of sediment and water for PAH content is being developed in a cooperative study with the Environmental Sciences Division on the distribution and fate of polycyclic aromatics released into the environment by a coal-coking plant.

The first stage in the development of this procedure involved determination of optimum conditions for quantitative extraction of PAHs from sediment and water. One-hundred-gram samples of sediment were spiked with either carbon-14-labeled naphthalene or BaP and were subjected to Soxhlet extraction with acetone. Liquid scintillation counting of aliquots withdrawn at regular intervals indicated quantitative recovery of these two representative PAHs after 48 hr of extraction. Water samples were similarly spiked and were partitioned with one-tenth volume aliquots of cyclohexane. Liquid scintillation counting of aliquots of each extraction showed that quantitative recovery was achieved by four extractions.

The next step was to determine the optimum level of purification necessary to isolate the PAHs

---

[10] H. Determann and K. Lampert, "Hydrophobic Interaction in Gel Adsorption Chromatography," *J. Chromatogr.* **69**, 123 (1972).

extracted from the samples. Because the sediment extracts were more complex, developmental work focused on these samples. Preliminary examination of a suite of samples collected at the actual coking-plant field site was carried out by a modified Kubota procedure.[11] The acetone sediment extracts were concentrated, diluted with water, and extracted into cyclohexane. The combined cyclohexane layers were concentrated and partitioned with DMSO. The latter was diluted with water and back-extracted with fresh cyclohexane to obtain a PAH-enriched fraction. After concentration, the fraction was passed through Florisil and alumina columns to prepare diaromatic and polyaromatic (3- to 6-ring PAH) isolates.

Each isolate was sampled separately for recovery measurements by liquid scintillation counting for quantitative analysis by gas-liquid chromatography (GLC). Diaromatics were analyzed using a 22-m OV-25 glass capillary column, while the 3- to 6-ring PAHs were separated on a 20-ft Dexsil 400 glass packed column. Approximately 86 chromatographic peaks were obtained for the 3- to 6-ring PAH isolate. Mass spectral (MS) examination of this isolate indicated that it contained the expected PAHs, essentially free of nitrogen and sulfur-containing heterocyclics. The mass spectra of the GLC peaks showed that at least 128 separate species were present. Among the more biologically active of the PAHs tentatively identified by GLC and MS in the sediment of a stream receiving the waste water outfall from the coking plant were the carcinogens benzo[*c*]phenanthrene (2.1 µg/g of dry sediment), benzo[*b*, *j*, and/or *k*]fluoranthene (23 µg/g), *o*-phenylene pyrene plus dibenz[*a*, *c*, and/or *a*, *h*]anthracene (total ~9 µg/g), and benzo[*a* plus *e*]pyrene (19 µg/g). The diaromatic isolate was found to contain the expected naphthalenes. More than 65 GLC peaks contained at least 75 identifiable alkyl naphthalenes and acenaphthalenes.

Although the combination of serial solvent partitioning and adsorption column chromatography was successful in preparing a suitably pure PAH isolate, it was very manpower-intensive; consequently, developmental efforts focused next on reducing and optimizing the isolation procedure. Accordingly, a set of four sediment acetone extracts was pooled to provide a sufficient supply of common starting material for two isolation procedures. Two aliquots were carried through the entire solvent-partitioning and column-chromatography procedure, and two were carried through an abbreviated procedure. The last procedure consisted of concentrating the acetone extracts, diluting with water, and partitioning with cyclohexane. The concentrated cyclohexane layers were then passed directly through Florisil and alumina columns to generate the isolates. The GLC profiles of the isolates prepared by the full and abbreviated procedures were qualitatively identical, and mass spectroscopy indicated that the peaks contained the same species. Thus the abbreviated purification procedure appeared to be equally effective and considerably more efficient in producing an isolate. However, there were quantitative differences between the two isolates. These differences were attributed to the liquid-liquid partitioning steps of the full procedure and to possible differences in partition coefficients among the PAHs, particularly of the alkylated derivatives.

The accuracy and precision of the abbreviated procedure is currently under study. PAH-free sediments were spiked with known quantities of 34 PAHs and subjected to analysis. In the 3- to 6-ring PAH fraction, with a few exceptions, recoveries of the PAHs averaged 102%, with an average standard deviation of 6.27%. Recoveries were biased negatively for phenanthrene and anthracene, 87.9 and 92.7%, respectively, because of their greater volatilities and their appearance in both the diaromatic and 3- to 6-ring PAH isolates. Interestingly, although fluorene was about evenly split between the two isolates, 9-methyl fluorene appeared mainly in the diaromatic isolate, and 1-methyl fluorene was found mainly in the 3- to 6-ring PAH isolate. In contrast, recoveries for the 4-ring and higher PAHs were biased positively with an average recovery of 106%. This positive bias is attributed in part to the uncertainties in the corrections for liquid scintillation quenching in tracer recovery measurements.

Two PAHs, o-phenylene pyrene and picene, were lost entirely from the 3- to 6-ring PAH isolate. Insufficient elution of the columns is ruled out because two similarly large or larger PAHs, benzo[*g*,*h*,*i*]perylene and anthanthrene were recovered to the extent of 102 and 91% respectively. A specific adsorption or chemical reaction of these two PAHs during some extraction or isolation step is implied. The cause of these specific losses remains to be determined.

The analysis of the diaromatic isolate is complicated by the fact that naphthalene (carbon-14 tracer) is more volatile than the other constituents of the isolate. Recoveries calculated for the spiked PAHs, including corrections for handling losses based on the tracer, ranged from 61 to 249%, with most consider-

---

[11] H. Kubota, W. H. Griest, and M. R. Guerin, in *Trace Substances in Environmental Health IX*, D. D. Hemphill, ed., University of Missouri, Columbia (1975).

ably above 100%. Actual recoveries were in the range of 21 to 68%. Thus a more realistic tracer such as a carbon-14 labeled dimethyl naphthalene or a dual tracer system incorporating an additional tritium-labeled alkyl naphthalene will be necessary. Preliminary work with tritium-labeled tracers suggests that tritium-hydrogen exchange with the sediment and adsorption column packings might prevent the use of dual tracers. Research is continuing on this problem.

A reliable procedure for the analysis of 3- to 6-ring PAHs in sediment and water is in final stages of development, but further work will be required before alkyl naphthalenes can be confidently measured. The fully developed and validated method should have important applications to other sample matrices. (*W. H. Griest, R. R. Reagan*)

Occupational exposure to airborne polycyclic aromatic hydrocarbons. The last annual report[12] contained preliminary results on the characterization of PAH-containing fugitive emissions that result from the production of graphite from petroleum pitches in the Navy Graphite Program. Air-sample collection and analytical procedures were developed and applied to locate the specific work operations associated with significant BaP-containing fugitive emissions. This report summarizes the results of a more detailed characterization of these emissions.

A detailed examination was made of the fugitive emissions generated by chopping, grinding, and sieving operations carried out in a small workroom during the course of a normal workshift to characterize "typical" occupational exposure. Three stationary air samplers followed the generation and spread of emissions across the workroom. Samples were collected in 1-hr intervals. During a particularly dusty series of grinding and sieving operations, one of the hourly air concentrations of total particulates and BaP reached 1.46 mg/g^3 and 0.72 $\mu g/m^3$, respectively, at an air sampler located adjacent to the equipment in use. A sampler located across the workroom detected 0.13 mg/m^3 of total particulates and <0.03 $\mu g/m^3$ of BaP in the same time interval, demonstrating a considerable gradient in the emissions concentration. Significantly, however, a personal breathing-zone air monitor carried by the worker indicated that potential personal exposure was three to five times greater than that predicted by the stationary air samplers. The greater apparent emissions concentration detected by the personal monitor versus the stationary air samplers is attributed to two factors (1) the personal monitor is carried by the worker and hence is closer to the actual source of emissions, that is, the work operation being carried out by the worker, and (2) the personal monitor moves with the worker in and out of emission clouds as he works around the room.

Breathing-zone air concentrations of total particulates reached 5.6 mg/m^3, and BaP ran as high as 1.36 $\mu g/m^3$ during one hourly sampling in a peak emission period. The 6.4-hr time-weighted exposure to airborne BaP during the working hours was estimated to be in the range of 0.6 to 0.7 $\mu g/m^3$. Thus, the 8-hr time-weighted exposure would be 0.5 to 0.6 $\mu g/m^3$ if BaP exposure during nonworking hours was insignificant. The suggested 8-hr time-weighted exposure limit to airborne BaP is 0.2 $\mu g/m^3$.[13]

Particle size was examined next. This parameter is an emissions characteristic that determines the inhalability and possibility of retention of particles in the lungs. Particle-size analysis by scanning electron microscopic examination of breathing-zone air particulates collected on air-filter pads during grinding operations demonstrated that about 70 wt % of the airborne particulates were less than 10 μ in diameter and, hence, respirable. Only 1 %, however, fell in the range of approximately 0.8 to 1.6 μ, corresponding to maximum particulate deposition in the alveoli and fine bronchioles.

BaP is only one PAH of the many possible species associated with the particulates. An analysis was carried out in search of other potentially bioactive PAHs. Multicomponent PAH analysis by GCMS of a PAH isolate from particulates collected in a 24-hr air-sampling period led to the tentative identification of 28 PAHs. These PAHs constituted an air concentration of approximately 12 $\mu g/m^3$ (24-hr average) and about 4 wt % of the particulates. Chrysene (and/or triphenylene) was the major PAH. It was present at an air concentration of 1.91 $\mu g/m^3$ and a particulate concentration of 6.43 mg/g. Among the more bioactive of the other species identified were BaP (<0.25 $\mu g/m^3$), benzo[*g,h,i*]perylene (0.2 $\mu g/m^3$), benzo[*b* and/or *j* and/or *k*]fluoranthene (0.79 $\mu g/m^3$), fluoranthene (0.15 $\mu g/m^3$), and pyrene (0.40 $\mu g/m^3$). Four sulfur-containing heterocyclics also were tentatively identified in the particulates.

The results indicate that grinding, chopping, and sieving operations in the production of graphite can

---

[12] W. H. Griest et al., "Characterization of Occupational Exposure to PAH-Containing Fugitive Emissions," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 57.

[13] Standards Advisory Committee on Coke Oven Emissions, *Occup. Safety and Health Rep.* 4(50), 639 (1975).

result in the release of significant amounts of respirable, PAH-containing fugitive emissions. As a direct result of this study, worker protection equipment is now in use, and fugitive emission containment devices are being designed. (*W. H. Griest, H. Kubota, G. Olerich, R. W. Holmberg, L. B. Yeatts, Jr.*)

Hierarchical approach to the quantitative measurement of benzo[*a*]pyrene (BaP) in synthetic fuels samples. Benzo[*a*]pyrene is a classical carcinogen, and thus its specific determination in materials potentially affecting personal health and environmental quality is important, as, for example, in the design of coal-conversion plants and waste-treatment or disposal facilities. BaP measurements are used often as rough indicators of total PAH content, although the validity of such assumptions is questionable and must be demonstrated for each sample matrix.

Because the purification steps in a traditional BaP analysis are usually time consuming and manpower intensive, we are constantly seeking means of reducing the effort without compromising analytical reliability. Each different sample matrix need not require the same level of treatment before final BaP analysis; hence a means for quickly determining the optimum treatment would be most desirable. A hierarchical approach to BaP analysis appears to meet this requirement most effectively.

Basically, the hierarchical approach is a framework of procedural steps leading to a final BaP determination. At critical steps in the procedure, the choice of further treatment depends on decision-making observations. In its present stage of development, the hierarchical process begins with an observation of the physical state of the sample: solid or liquid. Liquid samples are then classified as either clear and colorless or colored. The first few steps in the treatment depend on the category in which the sample fits. Solid samples (0.5 to 1.0 g) are dissolved with methylene chloride and diluted to 100 ml. After standing overnight, 10- to 20-ml aliquots are centrifuged, and the supernatant is purified on a column of Florisil (6 g), using 35 ml of methylene chloride as eluent. Highly colored liquid samples are diluted to 100 ml with methylene chloride, and aliquots are treated similarly. The total eluant from the Florisil column in either case is collected, and the solvent is evaporated with dry nitrogen under reduced pressure.

The appearance of the residue determines the course of succeeding steps. A dry residue is dissolved in 3 ml of benzene, and then 6 ml of hexane is added. The solution is spiked with carbon-14-labeled BaP and is passed through a composite column prepared from 12 g of Activity II neutral alumina, layered under 1 to 6 g of Florisil. The amount of Florisil depends on the depth of color of the residue solution; darker colors require more Florisil. The column is washed with 80 ml of 2:1 (volume to volume) hexane:benzene, and the eluant is collected in 5-ml fractions after the first 20 ml. The BaP subfractions located by liquid scintillation counting are composited and concentrated to 10 ml for analysis by fluorescence spectrometry.

A wet residue from the initial Florisil column usually signifies the presence of high-boiling aliphatic hydrocarbons. This type of residue is dissolved in hexane, spiked, and passed through the composite Florisil-alumina column described above, but with a step-gradient solvent program consisting of 50 ml of hexane followed by 80 ml of 2:1 hexane:benzene. The first 50 ml of eluant are discarded, and the remainder is collected in 5-ml fractions. The BaP subfractions are located by liquid scintillation counting, composited, and concentrated to 10 ml for fluorimetry.

Fluorimetric analysis consists of scanning the sample emission spectrum from 370 to about 440 nm with an excitation wavelength of 368 nm. The spectrum is examined to estimate the purity of the sample. An apparently pure sample is aliquoted for liquid-scintillation-counting recovery determination, and the remainder is concentrated to 0.1 ml for confirmatory analysis by GC using a liquid cystal stationary phase. The sample is again aliquoted for recovery measurements.

A sample with an impure BaP spectrum or one for which the GC and fluorimetric analyses do not reasonably agree is subjected to further purification on an acetylated cellulose column (50 g) with 200 ml of an ethanol:toluene:water (17:7:1) solvent. The first 105-ml eluant is discarded, and the remainder is collected and concentrated for the final fluorimetric and GC analyses as above.

Clear and colorless liquid samples are spiked and purified on a 10- to 20-g alumina column using 200 to 300 ml of 2:1 hexane:benzene as the solvent. The BaP-containing subfractions of the eluant are composited, concentrated, and analyzed by fluorimetry and GC. Further purification, if necessary, can be carried out on the acetylated cellulose column.

The initial application of this hierarchical approach to determine BaP was to eight samples collected at various steps in the solvent refined coal process. These samples consisted of solids, slurries, liquids, and tars. Data generated on these samples can be compared in a limited manner with results obtained by other laboratories on samples collected at different times. Gross disagreements in data for similar samples might indicate analytical problems for a particular type of sample matrix.

The solvent-refined coal product was found to contain the highest level of BaP, 197 ppm. This result is in good agreement with a value of 171 ppm of BaP determined at another laboratory. The hierarchical procedure indicated 41 ppm of BaP in a process solvent, which again falls into the range of results obtained elsewhere, 29 to 96 ppm. Our value of 0.5 ppm for BaP in a light oil distillate compares favorably with a value of 0.11 ppm measured in another laboratory. However, differences in the distillation cuts of the oil samples can drastically affect the BaP content, and other samples have been reported to contain 0.02 and 28 ppm of BaP.

Considerable differences exist for results on wash solvents. The hierarchical procedure suggested a BaP content of 7.5 ppm, whereas measurements at other laboratories on different wash solvent samples suggested 0.04 to 0.65 ppm of BaP. Comparative data do not exist for the other samples in this suite. Differences in analytical results among the different laboratories can be resolved only by mutual exchange and analysis of sample materials. Arrangements are being made for these studies. (*H. Kubota*)

Characterization of smokes from domestic commerical cigarettes. A recent publication[14] suggested that health risks associated with cigarette smoking might be equated with exposure to a select group of toxic smoke constituents: tar, nicotine, carbon monoxide, oxides of nitrogen, hydrogen cyanide, and acrolein. Etiological studies have provided evidence that links these smoke constituents with certain diseases and dysfunctions of the pulmonary and cardiovascular systems. Tar, nicotine, and carbon monoxide probably exert the greatest health effects of smoke. Both nicotine and carbon monoxide are implicated in cardiovascular disease. The former is a toxic alkaloid; the latter is a respiratory enzyme poison. The tar contains most of the carcinogens found in tobacco smoke plus a host of irritating and toxic constituents. The nitrogen oxides might be associated with obstructive pulmonary disease. Both hydrogen cyanide and acrolein are ciliatoxic; the former also is a respiratory enzyme poison.

Dose-response analyses of epidemiological studies have provided estimated "critical values" for daily intake of these smoke constituents. Thus cigarettes can be ranked according to the deliveries of these smoke constituents, and predictions can be made as to the maximum number of cigarettes of each brand that could be smoked daily before the smoker would exceed the critical values of these constituents and reach a statistically significant greater risk of disease than the nonsmoking portion of the population. To provide the data necessary to calculate this maximum "acceptable" number of cigarettes for each brand, we were requested by the National Cancer Institute Smoking and Health Program to perform analyses on the deliveries of these smoke constituents by a group of domestic commercially available low-tar and -nicotine cigarettes.

Thirty brands, all of relatively low-smoke delivery compared to the most popular brands, were characterized over the course of a year. Two manufacturing lots of three brands were partially characterized. Data for seven representative brands are shown in Table 4.2. Tar values of these 30 brands ranged from a low of 1.2 mg per cigarette (Carlton Menthol) to 14.5 mg per cigarette (Fact); nicotine deliveries generally paralleled those of the tar, 0.14 mg per cigarette (Carlton Menthol) to 1.03 mg per cigarette (Fact). Similarly large ranges were found for the deliveries of the other smoke constituents. Cigarettes with high tar and nicotine also delivered relatively high amounts of the other constituents. Generally, but not always, the mentholated version of a given brand delivered 5 to 10% less tar and/or nicotine than the nonmentholated version. Differences in the deliveries of other constituents were more variable, some being about the same in the two varieties and others being considerably greater in the nonmentholated variety, de-

Table 4.2. Smoke constituent data for seven representative low-tar and -nicotine brands

Brand	Per cigarette delivery					
	Tar (mg)	Nicotine (mg)	CO (mg)	HCN (μg)	NO_x (μg)	Acrolein (μg)
Fact						
Batch 1	14.5	1.03	17.2	147	233	109
Batch 2				124	220	83.0
Fact Menthol						
Batch 1	13.0	0.98	15.1	150	238	109
Batch 2				106	241	79.5
Real	10.2	1.01	12.9	155	98.9	75.5
Tempo	6.9	0.56	10.1	98	166	31.0
Stride	3.3	0.36	1.8	<10	5.3	11.8
Now Menthol						
Batch 1	1.8	0.16	2.1	9.3	29.6	12.5
Batch 2	0.8	0.09		7.9	22.4	
Carlton Menthol	1.2	0.14	2.0	12	12.0	9.8

---

[14] G. B. Gori, "Low-Risk Cigarettes: A Prescription," *Science* 194, 1243 (1976).

pending on the particular brand. Fact produced the highest carbon monoxide delivery (17.2 mg per cigarette) and a new brand, Stride, the least (1.8 mg per cigarette). Hydrogen cyanide was highest in Real (155 μg per cigarette) and lowest in Now Menthol and Stride (both <10 μg per cigarette). Oxides of nitrogen and acrolein were both delivered in highest amounts by Fact and Fact Menthol (238 and 109 μg per cigarette respectively) and in the least amounts by Stride (5.3 μg of NO_x per cigarette) and Carlton Menthol (9.8 μg of acrolein per cigarette).

Not surprisingly, the manufacturing date was found (Table 4.2) to have a major influence on the deliveries of some constituents. Analysis of two samples of Fact Menthol manufactured 7 months apart indicated a 42% increase in hydrogen cyanide and a 37% decrease in acrolein deliveries in the more recent product. Two samples of Fact (6 months difference) showed increases of 31 and 19% for these constituents respectively. It is possible that the resin peculiar to this brand in the filter might have been less active in the more recent production batch. Tar deliveries of two batches of Now Menthol—an exceptionally low-delivery, air-dilution filter brand—differing by only 2 months in production time varied by 56%. "Acceptable" levels of smoking for any given brands will thus vary with the production batch of the cigarettes.

It must be emphasized that all of the brands subjected to this study deliver smaller quantities of tar and nicotine than do the most popular brands. As such, a larger number of the relatively high delivery products (Fact and Real) can be smoked before reaching the "critical value" than the currently most popular brands. It must also be noted that "acceptable" levels of smoking do not imply "safe" levels but, rather, levels at which current epidemiological methods are insufficiently sensitive to detect an increased health risk as compared with the nonsmoking population.

Results routinely generated by the Federal Trade Commission of tar and nicotine analysis of smokes delivered by all American commercial cigarettes can be used to compute "acceptable" levels of smoking for each product. The battery of analyses used here takes into account the potential contribution of gas-phase constituents to health risk. Manufacturing practices designed to reduce tar and nicotine deliveries do not necessarily reduce gas-phase components. "Super-low" delivery brands such as Now and Carlton, however, are generally observed to be consistently low in delivery of gas-phase components. (*R. B. Quincy, W. H. Griest, A. H. Marshall*)

INHALATION EXPOSURE CHEMISTRY AND INSTRUMENTATION

Operational and chemical monitoring of inhalation bioassay experiments. The Smoking and Health Program of the National Cancer Institute (NCI) is developing and employing inhalation bioassays to determine the relative biological impact of tobacco smoke 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. NCI is currently sponsoring several inhalation bioassay projects. The study at the Veteran's Administration Hospital, East Orange, New Jersey, has recently concluded its chronic exposure phase. Three bioassays, one at Battelle Pacific Northwest Laboratories, Richland, Washington, one at Borriston Research Laboratories, Inc., Temple Hills, Maryland, and one at Hazleton Laboratories America, Reston, Virginia, are now in the chronic exposure phase. Two additional studies are in preliminary testing phases. 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 and nitrogen dioxide in tobacco-smoke associated atherogenesis, and 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 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 environment) 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 conclusions concerning the smoke doses that the animals are offered in these chronic studies. For example:

1. An indication that the chemical composition of the particulate phase of the smoke of one type of cigarette used in a particular study was radically different from that of the same cigarette smoked under analytical conditions.
2. Few of the important components of the particulate gas phase of the experimental cigarette smoke were enriched or depleted after passage through the dog exposure systems.
3. Carbon monoxide concentrations in the smoke offered to dogs in one study verified that these animals were receiving a smoke dose that was highly depleted in particulate-phase constituents.
4. The dose of an anticilia toxin additive from one type of experimental cigarette was found to be highly variable.
5. A high degree of variability was observed in gas-phase output of one cigarette code, which could result in widely varying blood carboxyhemoglobin levels in the experimental animals exposed to those cigarettes.

Careful documentation of these and other situations are essential for valid interlaboratory comparison of bioassay results. Documentation also illustrates the need for more frequent monitoring of exposures. Ideally, routine monitoring operations should be performed by the bioassay laboratory at a much greater frequency than that possible with periodic site visits. During the past year, a modest effort has been under way to construct and evaluate a prototype portable monitoring device, based on the measurement of infrared light backscattered from smoke particulates, which can be used to instrumentally determine the amount of smoke offered to the animal for inhalation. The sensor concept, developed as part of a contract with the Council of Tobacco Research-USA, Inc., was discussed in detail in last year's annual report.[15] The system consists of a sensor head that is mounted at the tracheal cannula on a dog-exposure system. A flow-controlled vacuum pump, capable of withdrawing the contents of the smoke-stand tube through the cannula past the sensor head, is built into the electronics control package. As particulates pass through the sensor, backscattered light is converted to voltage, integrated, and displayed.

The portable sensor was field tested on a recent bioassay site visit. After only minimal calibration, the offered smoke dose as measured by the particulate sensor was found to be in excellent agreement with that found gravimetrically. We are preparing to add an air-flow measuring device to the sensor system so that the amount of particulates delivered can be measured during actual animal inhalation. The flow device, properly interfaced, will automatically compensate for flow-rate changes in the sensor which are caused by animal respiration.

A survey was made of the particle-size distributions of the smoke from the three dog-exposure systems used in NCI-sponsored bioassays this year. All of these devices deliver a puff of undiluted smoke to a stand tube, where it remains until inhaled intratracheally by the animal. The residence time of the smoke in the system depends on the animal's inspiration rate in relation to the machine puffing cycle. Smoke particulate size distributions were determined by the methylcyanoacrylate fixation-scanning electron microscopy technique described in last year's report.[16] Results indicated that, for all three devices, there was substantial particle-size growth (when compared to freshly generated smoke), even for smoke that is inhaled immediately after the puff is made available. This is caused by rapid particulate coagulation during the time the smoke resides in the generation region of the device. In addition, there is continued growth in the particle size several seconds following introduction of the smoke into the system stand tube. Thus a large fraction of the smoke particulates inhaled by the animals range in size between 0.6 and 1.7 μm in diameter.

NCI is testing, via inhalation bioassay, experimental cigarette variants used in the mouse-skin-painting carcinogenesis studies. To investigate the comparability of the materials tested in these two types of bioassay experiments, a study was conducted

---

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

[16] R. W. Holmberg and L. B. Yeatts, Jr., "Particle Size Characteristics of Tobacco Smoke," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 72.

to compare the chemical composition of the condensable smoke constituents exiting from the tracheal cannula of the dog exposure devices with the smoke condensate from one cigarette code used in the skin-painting bioassays. To compare materials that were physically similar, smoke withdrawn from the dog exposure system by use of a respirator was collected in a condenser that employed both dry ice acetone and refluxing solvent traps. The resulting fractions were combined and reduced in volume to produce a material similar to the skin-painting condensate. Gas chromatographic profiling and specific constituent analysis of major particulate phase components suggested similar composition of the two materials. However, many of the components, including benzo[*a*]pyrene and benzo[*a*]anthracene, were twice as concentrated in the condensate obtained from the dog exposure device as in the Series IV condensate. This suggests that important chemical differences beyond those of the noncondensable gas phase constituents might exist between the condensate skin painting and whole-smoke inhalation bioassays. *(R. A. Jenkins, B. E. Gill, D. D. Pair)*

Chemistry of cigarette smoke produced by an inhalation exposure device. The smoke exposure machine model two (SEM II), developed for the Council for Tobacco Research-USA, Inc. (CTR USA) by Process and Instruments Corp. and ORNL, is a unique smoke-exposure device in that it produces an essentially continuous stream of cigarette smoke for delivery to animal exposure chambers. Briefly (a detailed description has been given previously),[17] cigarettes are loaded at 2-sec intervals from a hopper into a rotating drum containing 30 ports for the cigarettes. The cigarettes move with drum rotation to a position where they are automatically lighted and puffed. A sealed dome surrounds the cigarette-handling mechanism and is maintained at a slight positive air pressure to provide the driving force for the puffs. Each of the 30 cigarettes is puffed sequentially for a 2-sec period to produce the stream of smoke. After a prescribed number of puffs have been taken, the spent butts are automatically ejected, and the machine is either shut down or recycled for a second exposure. Because the machine differs markedly from other smoke exposure systems that deliver smoke from a single cigarette, one puff at a time, extensive testing of the chemical makeup of the smoke is required to evaluate its performance.

The SEM II operates with constant dome pressure and therefore does not generate puffs of constant volume, the established standard, but generates puff volumes that are inversely related to the resistance-to-draw (RTD) of the tobacco rod. Research cigarettes exhibit considerable variation in RTD values; relative standard deviations of 15% within a given batch are typical. The resistance of a burning cigarette, however, depends on the length of the unconsumed tobacco rod and a back-resistance developed by the fire cone during the puffing process. It might therefore be expected that puff volumes would exhibit little memory of the RTD of the unlit cigarette. We have found, however, that puff volumes delivered by the SEM II are strongly correlated with this RTD. This correlation persists from first to last puff even though only a fraction of the original rod remains. Although one might expect that the puff volume would increase markedly as the tobacco rod shortens, we found only a slight correlation between puff volume and puff number.

High-resolution gas-chromatographic profiling techniques[18] have been applied to the study of the smoke delivered from the SEM II. This technique has been used to resolve a large number of the semivolatile components present in the gas phase of the smoke. Generally, components with boiling points ranging from 30 to 180°C were scanned. The profile from undiluted cigarette smoke (Kentucky reference 2A1 cigarette) from the SEM II is compared in Fig. 4.2 with that obtained from an ORNL single-port machine operating under analytical conditions in a free-smoking mode. Only minor differences in component concentrations are evident. Studies were also made of SEM II smoke as a function of dome pressure and as a function of cigarette RTD, thereby varying the puff volumes from the cigarettes in two ways. An analysis of the peak heights from these GC profiles shows that there is little effect of puff volume on the concentrations of semivolatile constituents of the smoke.

Preliminary measurements have been made on the amounts of noncondensable gases and the components of particulate matter delivered from 2A1 cigarettes. Gas-phase samples were collected by a syringe-withdrawal system, sampling the smoke from

---

[17] J. H. Moneyhun and J. R. Stokely, "SEM II Tobacco Smoke Inhalation System," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 69.

[18] M. R. Guerin et al., "Multicomponent Profiling and the Blind Assay," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 59.

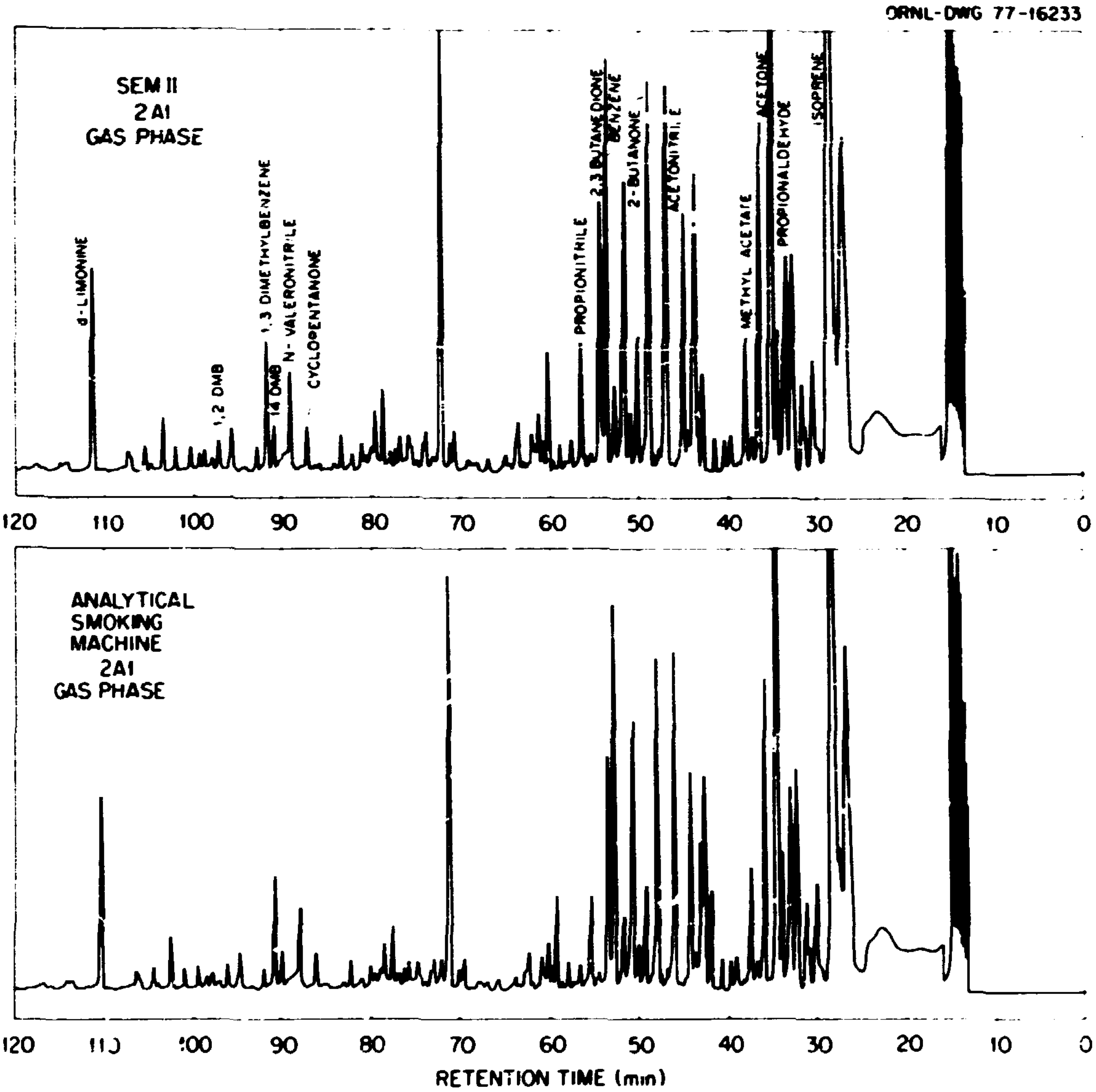


Fig. 4.2. Gas chromatograms comparing gas-phase fraction of cigarette tobacco smoke from SEM II smoking machine (top) with that from analytical smoking machine (bottom).

30 randomly selected cigarettes as they were smoked through ten puffs on the SEM II. For comparison, similar samples were collected from the same lot of 2A1 cigarettes that were selected for average weight and RTD as they were smoked on an analytical machine (Phipps and Bird). Delivery of three of the gas-phase components, CO, CO_2 and CH_4, were essentially the same by both machines, whereas hydrogen was found to be 17% higher for the SEM II.

It was not feasible to collect particulates from a full complement of 30 cigarettes. Samples were taken from four cigarettes that were weight and RTD selected and loaded in adjacent drum positions on the SEM. The collecting filter was mounted immediately behind the slider block of the SEM to preclude losses that might occur in the delivery system. Again, similar samples were collected from the analytical machine for comparison. Total particulates were found to be only 5% higher in SEM II smoke, but individual chemical components varied more significantly. For example, free fatty acids were 17% higher in the SEM; neophytadiene, 22% higher; nicotine, phenol and cresols, about 32% higher; glycerol and catechol, about 7% higher. Only the water content of the particulates was found to be lower (~23%) in smoke from the SEM. It should be noted that these comparative values do not necessarily reflect adversely on the SEM II as a smoke-exposure machine. In particular, the comparisons shown here are of smoke from a free-smoker (SEM II) on the one hand and a restricted smoker (Phipps and Bird) on the other. Free smoking (butt of cigarette open to surrounding air between puffs) has been shown to deliver higher concentrations of smoke constituents than restricted smoking (butt closed).

The SEM II operates continuously at a significantly higher than normal environmental temperature and in normal operation, because of cigarette variability, uses cigarettes with RTD values considerably different from the average. Plans are being made to investigate the effect of these variables on the chemistry of the smoke. *(C. E. Higgins, R. W. Holmberg, J. H. Moneyhun, J. R. Stokely)*

Programmable control of a tobacco smoke-inhalation exposure device. The SEM II smoking machine has been described in the preceding section. In a typical exposure regimen, animals are exposed to smoke for 30 sec, and then to air for 30 sec. The animals thus sample successively each of the cigarette puffs at 1-min intervals; 10-min exposures representing ten-puff cigarettes are typical. This type of exposure regimen has a potentially serious drawback. After short exposures to smoke, mice tend to inspire at a much reduced rate – this is sometimes described as "breathholding." As a consequence, the later puffs of a cigarette are not sampled by the mice with the same efficiency as the earlier puffs. Because significant differences in both the amount and chemistry of the smoke occur with puff number (e.g., later puffs are much richer in smoke particulate constituents), the mice might not sample smoke typical of the cigarette being tested. A better exposure regimen would be to deliver, from successive cigarettes in the drum, smoke from successive puffs, thereby averaging the output of smoke from the entire cigarette in a much shorter time interval.

The SEM II is mechanically adequate to provide smoke averaged in this manner, but the hard-wired-switch logic of the machine is not adaptable to the task. A Texas Instruments Co. 5TI programmable controller was selected and has been interfaced and programmed to control the SEM. It is a low-cost (~$2000) system, easily programmed and simply interfaced to the relays, solenoids, etc., of the existing system and is capable of controlling complex systems whose function can be defined by switch logic, counters, and timers. This instrument system consists basically of a programming keyboard from which the steps of conventional ladder logic diagrams, including counters and timers, are entered; a sequencer for storage and logical interpretation of the program steps; and input output modules that respond to input switch closures to give programmatically controlled output pulses that actuate the various functions of the SEM. The device has been interfaced to control the drum motor, blow system, loader, lighter, distribution valve, and ejector of the SEM. A program has been developed to control the SEM both in its conventional mode and in the "puff-averaging" mode described above.

A comparison of smoke particulate output from the two modes of smoking as detected by the Gayle particulate sensor is shown in Fig. 4.3. Output from the conventional mode in which smoke from each successive puff is delivered for 1-min duration is shown in Fig. 4.3*a*. The concentration of particulates in the smoke increases approximately fourfold from the first to tenth puff. Output from the puff-averaging mode is shown in Fig. 4.3*b*. Although there are large short-term variations, particularly from the first or lighting puff, the overall concentration remains essentially constant over the entire exposure.

The system has been demonstrated to officials of CTR USA (the sponsoring agency) and to officials of Process and Instruments Corp. (the manufacturer of the SEM II) with the recommendation that it be included in new models and retrofitted to models now being used at bioassay laboratories. In addition to its applicability to the puff-averaging problem, it lends itself to easily programmable changes in SEM

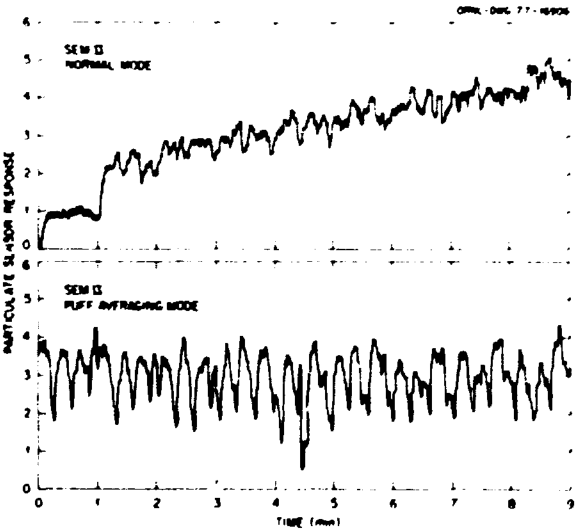


Fig. 4.3. Comparison of smoke particulate concentrations from SEM II as operated in two puffing modes.

exposure operations which are suggested by operating experience. *(R. W. Holmberg, M. T. Kelley)*

Aerosolization of bioactive chemicals for inhalation testing. Systems for exposing rodents to aerosols of known or suspected bioactive chemicals via inhalation are being developed for the CTR/USA for use in biological studies at the Microbiological Associates Laboratories' inhalation testing facility in Bethesda, Maryland. It is the aim of this study to develop exposure systems that deliver aerosols whose chemical and physical properties are well characterized and whose concentration is known or can be monitored. Initially, aerosolization of the tumor promoter 12-*0*-tetradecanoyl phorbol 13-acetate (TPA) and the carcinogen methylcholanthrene are being considered. While it is apparent that no single aerosolization technique will be applicable to all compounds, compressed air nebulization of solutes dissolved in biologically tolerable, volatile solvents (e.g., water, ethanol) will be the most generally useful. This technique is being applied to the production of TPA aerosols from ethanol solutions. Because TPA is expensive, labile, and hazardous, it is highly desirable to have a generator that will operate on small amounts (1 or 2 ml) of solution. A number of compressed air nebulizers are available commercially but are not adequate for this purpose. A simple, efficient nebulizer has been designed and constructed for this requirement and has been tested, using methylene blue and phenolphthalein as nonhazardous prototypes for TPA. When operating at 21 psig, it will provide 10 min of exposure, using 10 mg of TPA dissolved in 2 ml of ethanol. The TPA aerosol concentration is approximately 250 μg per liter of air at a flow rate of 3 liters per minute. Ethanol vapors provide some physiological insult to the animals, but its vapor-phase concentration is minimized by cooling the solution in an ice bath.

The nebulizer has been interfaced to a standard stock-type exposure chamber through a section of piping long enough to permit the complete evaporation of the alcohol particles that are generated; consequently, only dry TPA particles enter the exposure chamber. Provisions are made for the introduction of an impacting stage to control the sizes of the aerosol particles. With the concentration of TPA being used, however, preliminary measurements indicate that essentially all of the particles will be less than 1 μm without such an impactor. A Gayle light-scattering particulate sensor,[19] developed for measuring the concentration of the much more concentrated tobacco smoke aerosols, has been adapted for the continuous monitoring of these aerosols. It has been calibrated with both methylene blue and phenolphthalein and has been found to give a linear response over the concentration range of 50 to 400 μg per liter.

Initially, it is intended that the animals be exposed to a continuous stream of aerosol. Longer and more cost-efficient exposures can be made by operating in a pulsed mode. Modifications of the animal-exposure chambers to increase their containment volume will be necessary, however, to operate in this manner. The system is being installed in a glove box, which has been approved for handling carcinogenic materials, for final testing by use of TPA solutions. In addition to estimating aerosol concentration from particulate sensor response, samples will be collected for subsequent liquid chromatographic analyses. Such analyses will be performed to differentiate TPA from possible degradation products. *(R. W. Holmberg, J. H. Moneyhun)*

A helium glow discharge, element-selective detector for gas chromatography. The need for a sensitive, simple, multielement detection capability for gas chromatography has led many people to investigate various element-specific detectors. We have been evaluating a helium glow discharge detector (GDD) for multielement specificity during the past 2 years. Formerly referred to as an arc emission detector (AED), the GDD operates by fragmenting sample molecules with ionized helium. The electronically excited atomic fragments emit visible or uv radiation, which is quantified after passage through a monochromator. By splitting the GC effluent and recording simultaneously the response of the conventional flame ionization detector (FID) and that of the GDD, a dual trace chromatogram is obtained, with one trace being sensitive to all hydrocarbons and the other trace being selective for the element in question. In last year's report,[20] construction of a background-correction system was discussed, which eliminates many false positive responses due to broad-banded radiation from hydrocarbon fragments. This year we have made some specific improvements in the system which are directed toward achieving a more reproducible and

---

[19] T. M. Gayle and C. E. Higgins, "Smoke-Concentration Sensor," *Inst. and Contr. Div. Annu. Prog. Rep. Sept. 11, 1976*, ORNL-5196, p. 17.

[20] C. E. Higgins and J. R. Stokely, "Application of a Light-Scattering Device for Detection of Smoke Particulates in the Walton Smoke Exposure System," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1976*, ORNL-5244, p. 71.

sensitive response. These improvements include design modification to the chamber to insure reproducible electrode alignment and an improved optical system to permit more light to enter the monochromator.

Fundamental studies with the GDD are discussed in Chap. 1 of this report. During the past year, our studies with the GDD have been directed toward applications of silicon- and arsenic-selective detection. By observing silicon emission at 288.2 nm, we were able to follow incorporation of silicon into molecules with replaceable hydrogens during trimethylsilylation. The results indicated that, for complex mixtures of certain chemical types, it was necessary to use much larger amounts of silylating reagent and catalyst than normally would have been anticipated to accomplish complete replacement of the removable hydrogen atoms. In addition, it was found necessary to carry out the reaction at more elevated temperatures.

As part of our work in support of fossil fuel programs, this section has been preparing chemical class fractions from fossil-fuel-related samples for bioactivity testing. For interpretation of results of biological activity, it is valuable to know if certain fractions contain only compounds of a given class. We undertook a pilot study to determine if the element specificity of the GDD could be used for rapid screening of acidic fractions for the presence of neutral species. Because both weak- and strong-acid components possess replaceable hydrogens, it is possible to "tag" the acidic components with trimethylsilyl groups. By chromatographically resolving the fractions, using both the conventional FID and the GDD in a silicon-specific mode, the acidic components are visualized on both detectors, whereas components that are nonderivatizable give no response on the GDD trace. We demonstrated by use of this approach that the weak-acid fraction of shale-oil product water contained only components with a true acidic character but that the strong-acid fraction of the same sample contained several nonderivatizable species, especially in the higher molecular-weight range. By using this approach, fractions that may warrant more detailed chemical definition can be identified.

We have initiated studies on the application of the GDD to the determination of arsine in complex gas-phase mixtures such as cigarette smoke, synthetic natural gas, or emissions from fossil-fuel-combustion processes. For this work, numerous GC stationary phases were evaluated before one was found that could pass nanogram quantities of arsine without irreversible adsorption at temperatures suitable for the separation of low-molecular-weight organic compounds. Use of Porapak N as a stationary phase currently appears to be the most promising. Added trace quantities of arsine in natural gas can be resolved from the major organic constituents by use of the aforementioned background corrector. The detection limit for AsH_3 is about 30 ng per sample injection. To evaluate potential interferences to arsine determination in highly complex mixtures, we are investigating the resolution of AsH_3 in the gas phase of cigarette smoke. Carbon dioxide present in large quantities is a major interference because it elutes simultaneously with added traces of arsine. Broad-banded emissions from excited CO_2 fragments cannot be completely suppressed with the background corrector. Thus, it will be necessary to establish new chromatographic conditions to separate CO_2 from arsine. *(A. D. Horton, C. Feldman)*

Trapping of organic gas phase pollutants for gas chromatographic analyses. Quantitative studies are being made of absorptive sampling techniques to collect the organic constituents present in environmentally important gaseous effluents for subsequent gas chromatographic analyses. A qualitative evaluation of adsorptive sampling was reported previously.[21] Such techniques have distinct advantages over the usual direct gas sampling, both in preserving labile components and eliminating the necessity of collecting and transporting large gaseous samples. It is planned to apply this methodology to the study of flue gases from the combustion of shale oil and other coal-derived liquid fuels.

Tenax-GC has been investigated as a trapping agent, using cigarette smoke as a rich and well defined source of semivolatile organic constituents. Trap shape and size, sampling flow rates, and desorption conditions have been studied. To be effective as a remote device, the trap should be of simple construction and should not require cryogenic equipment or elaborate manifolds and pumping. We have found simple glass tubes filled with 60/80 mesh Tenax-GC to be effective. Generally, resolution of GC peaks were found to increase as tube diameter was decreased, but this phenomenon was accompanied by a commensurate loss of capacity. For the studies reported here, 5-1/4-in.-long, 5-mm-ID tubes were used. For some of the gases absorbed (e.g., isoprene), an optimum flow rate for sampling was

---

[21] W. T. Rainey, C. A. Pritchard, and D. C. Canada, "Organic Mass Spectrometry Support Activities," *Anal. Chem. Div. Annu. Prog. Rept. Nov. 30, 1976*, ORNL-5244, p. 31.

found; for others (e.g., acetaldehyde), absorption efficiency decreased slowly with increasing flow rate.

Previous investigators[22] found it necessary to desorb the gases from the Tenax column onto a small-volume cryothermal trap in the oven of the gas chromatograph and then transfer the sample to the column. We have been able to obtain adequate peak resolution while desorbing the trap contents directly onto the column through a specially modified, heated injector port. The column was cooled to −70°C by back flushing through the Tenax trap, heated to 250°C. Desorption by forward flow produced virtually unrecognizable chromatograms because of peak broadening.

Cigarette smoke was sampled by standard techniques and carried onto the Tenax traps with nitrogen as a carrier gas. For comparison, similar samples were injected directly onto the column in the GC. In both cases GC profiles were made and were found to be quite similar; all peaks resolved by direct sampling were found when desorbed from Tenax.

Three constituents, isoprene, acetaldehyde, and acrolein, were chosen for quantitative evaluation. Essentially 100% of the isoprene and acrolein were collected on and desorbed from the Tenax columns. Significant losses of acetaldehyde occurred; only about 80% of the amount directly sampled was detected after desorption from the Tenax. The stability of these constituents as adsorbed on Tenax was also investigated. In 72 hr, no net losses of acetaldehyde and acrolein were found, but there was a 10% loss of isoprene. *(A. D. Horton, S. G. Zeldes[23])*

BIOANALYTICAL METHODS AND PROJECTS

Determination of radiolabeled cigarette-smoke tracers in physiological specimens. During the past 2 years, we have been providing analytical chemistry support for a series of experiments designed to study the induction of respiratory or cardiovascular disease in mice as a result of exposure to cigarette-smoke aerosols. These studies are supported by the CTR/USA and are being carried out jointly by ORNL and Microbiological Associates of Bethesda, Maryland. Such studies are greatly dependent on chemical analysis to characterize the exposure system and to provide reliable estimates of the amount of the aerosol reaching various parts of the respiratory tract. The most reliable method for measuring smoke particulates deposited after inhalation is the addition of a tracer compound such as ^{14}C-dotriacontane (DTC) to the cigarette and subsequent examination of the target tissue for ^{14}C-activity.[24–27] Because a large number of tissue samples (more than 15,000) was generated by these studies, it was necessary to design analytical methods that would minimize the analysis time for each sample. Thus a procedure was devised that allowed most smaller tissue samples to be placed in a scintillation vial at autopsy and then carried through the entire analytical procedure without removal from the vial.

In the case of samples from mice, all individual organs can be treated exclusively in scintillation vials; only larger samples such as the carcass or the hide must be disintegrated in larger volumes with an aliquot from a known volume subsequently being analyzed. For the tissue specimens that could be accommodated by a scintillation vial, the sample was disintegrated by digestion with an ethanol-potassium hydroxide mixture, followed by bleaching with hydrogen peroxide, adding a liquid scintillator solution, and analyzing on a Packard Tri-Carb liquid scintillation spectrometer, model C 2425 (Packard Instrument Company, Downers Grove, Illinois).

Although this procedure represents a significant improvement in economy, there were two potential problems which had to be addressed (1) whether the counting efficiency would be adequate for samples in which fragmented biological material (bone, undi-

---

[22] A. Zlatkis, H. A. Lichtenstein, and A. Tisbee, "Concentration and Analysis of Trace Volatile Organics in Gases and Biological Fluids with a New Solid Adsorbent," *Chromatographia* 6(2), 67 (1973).

[23] ORAU Summer Research Participant, Centre College, Danville, Ky. 40422.

[24] B. R. Davis, T. H. Houseman, and H. R. Roderick, "Studies of cigarette smoke transfer using radioisotopically labeled tobacco constituents. Part III. The use of dotriacontane-16,17-c as a marker for the deposition of cigarette smoke in the respiratory system of experimental animals," *Beitr. Tabakforsch.* 7, 148 (1973).

[25] I. B. Rubin, "A simplified method for the determination of labeled alkane hydrocarbons in mammalian tissue and blood after exposure to radiolabeled cigarette smoke," *Anal. Lett.* 6, 387 (1973).

[26] R. Binns, J. L. Beven, L. V. Wilton, and W. G. D. Lugton, "Inhalation toxicity studies on cigarette smoke II. Tobacco smoke inhalation dosimetry studies on small laboratory animals," *Toxicology* 6, 197 (1976).

[27] J. E. Caton, W. E. Dalbey, P. Nettesheim, and M. R. Guerin, "Tobacco smoke inhalation exposure dosimetry," *Symposium on Bioassay Models and Inhalation Toxicology, Tampa, Florida, October 19-22, 1976* (in press).

gested food, etc.) and ethanol-potassium hydroxide still remained in the vial and (2) whether the remaining fragmented material or the ethanol-potassium hydroxide would cause a change in the counting efficiency with the passage of time after disintegration. Fortunately, the automatic external standard (AES) feature of the model C 2425 liquid scintillation spectrometer provided an ideal means for studying the above problems by allowing the counting efficiency to be determined at the same time that the sample was assayed.

A study of the counting efficiency for such samples using both the AES ratio and recounting after addition of a known amount of activity indicated that between 60 and 80% of the activity could be detected. For most tissue specimens, the counting efficiency did not change with time. However, the counting efficiency for larynx samples decreased rapidly with time elapsed after bleaching. In addition, this study showed that counting efficiency should be evaluated for all samples on an individual basis rather than employing an average efficiency for a given type of tissue. For example, in a given experiment, the average efficiency for all lung samples would be about 71%. The majority of these lung samples would have efficiencies in the range from 68 to 73%. However, a small percentage of the samples would exhibit lower counting efficiencies. Such lowered counting efficiencies might have been caused by a greater amount of blood being incorporated with the sample at autopsy; but in any case, the evaluation of counting efficiency at the initial assay improved both accuracy and precision of results.

To evaluate the efficiency at the time of counting, a relationship between the AES ratio and efficiency was generated for each batch of scintillator solution. This relationship had the form

$$\text{efficiency} = \sum_{i=0}^{i=n} A_i(\text{AES ratio})^i ,$$

where A_i is a constant. The data to establish this relationship were obtained by adding a known amount of activity to the volume of scintillation solution used in tissue assays. The counting efficiency for this solution of known activity was then incrementally reduced by adding small volumes of pyridine. A least-squares fit of these data to the above expression indicated that the deviation between the experimental values and the efficency predicted by the expression becomes minimal for values of $n = 3$. Subsequently, this method of evaluating individual sample efficiencies has been incorporated into the determination of all tissue activities. This procedure not only eliminates the time-consuming procedure of establishing efficiencies by recounting the sample after the addition of a known amount of activity ("spiking") but it also eliminates two sources of error associated with "spiking" (1) errors introduced by changes in counting efficiency occurring during the time elapsed between initial counting and recounting and (2) errors associated with using an average efficiency value for all samples of a given type of tissue. Because of the error associated with the addition of measured small volumes, efficiency values for a given type of tissue must generally be averaged when the "spiking" method is employed for large numbers of samples. *(J. E. Caton, G. M. Henderson, C. S. Alley)*

Prediction of smoke deposition in mice. The joint studies with Microbiological Associates have resulted in a comprehensive assessment of cigarette-smoke particulate deposition in mice as indicated by the tracer, ^{14}C-DTC. These studies involved the exposure of mice to cigarette smoke generated by a Walton horizontal smoking machine[28] smoking cigarettes that had previously been labeled with ^{14}C-DTC. This smoke exposure system can take a 2-sec, 35-ml puff from one, two, or three cigarettes and deliver the smoke to either a 384- or a 768-ml exposure chamber from which up to 20 mice must obtain their breathing air. Therefore, by varying the number of cigarettes smoked and the size of the exposure chamber, the concentration of cigarette smoke to which animals are exposed can be varied from 4.5% (one cigarette smoked into a 768-ml chamber) to 27% (three cigarettes smoked into a 384-ml chamber). The smoke aerosol was generated at the rate of one puff per minute and was held in the exposure chamber for any portion of that minute selected by the operator.

The quantity of smoke particulates deposited into exposed mice was measured as a function of smoke-exposure time and smoke concentration. It was found that deposition is a linear function of smoke concentration but not a linear function of exposure time. Particulate deposition appeared to almost double for each 10-sec increase in exposure time.

To better understand cigarette smoke inhalation dosimetry in mice, efforts have been made to develop models that will predict particulate deposition. The

---

28. J. R. Stokely, C. E. Higgins, J. H. Moneyhun, M. R. Guerin, L. Florant, and J. Greenspan, "A system for inhalation exposure of small laboratory animals to tobacco smoke," *Beitr. Tabakforsch.* (to be published).

most successful model at this writing relates smoke-particulate deposition in an individual mouse to the total smoke-exposure time by fitting data from individual exposures to the polynomial expression

$$F = A_0 + A_1T + A_2T^2 + A_3T^3,$$

where F is the fraction of the total ^{14}C activity available in the exposure chamber that is retained by an individual mouse; T is the total exposure time in seconds ($T = 300$ for a 30 sec/puff exposure to a cigarette smoked for 10 puffs); and A_0, A_1, A_2, and A_3 are constants. This expression can be considered to have a linear ($A_0 + A_1T$) and a nonlinear ($A_2T^2 + A_3T^3$) component. The linear component can be removed and the nonlinear portion can be fitted to the exponential expression

$$BT^M,$$

where B and M are constants. Thus the expression for the fraction of the total available activity retained by an individual mouse becomes

$$F = A_0 + A_1T + BT^M .$$

Both the fraction of the total available activity retained by the lung and by the whole mouse can be fitted to this expression, yielding the following equations:

$$F_{lung} = [15 + 0.51T + 0.0016T^2] \times 10^{-5}$$

$$F_{total} = [19 + 1.1T + (3.0 \times 10^{-8})T^4] \times 10^{-5} .$$

Using these expressions one can predict smoke deposition results in an individual mouse by simply calculating the predicted fraction and multiplying times the total amount of particulate matter available in the exposure chamber. The curves calculated from these expressions are plotted in Fig. 4.4, wherein they are compared with observed data points. The linear contribution to each curve is also plotted in Fig. 4.4 to emphasize the increasing importance of the nonlinear contribution at greater exposure times. This increasing nonlinear contribution reflects the decreasing ability of the mice to restrict their breathing as exposure time increases. The greater increase in total body deposition relative to total lung deposition at higher exposure times indicates that the smoke aerosol has grown in particle size, thus creating more difficulty in reaching the lower respiratory tract. This decreased respirability is evidenced by greatly increased deposition observed in the upper airways and larynx. The model results in a correlation between observed and calculated values of 0.98 for the total internal deposition of smoke particulates in the lung and of 0.95 for the total internal deposition of smoke particulates. *(J. E. Caton)*

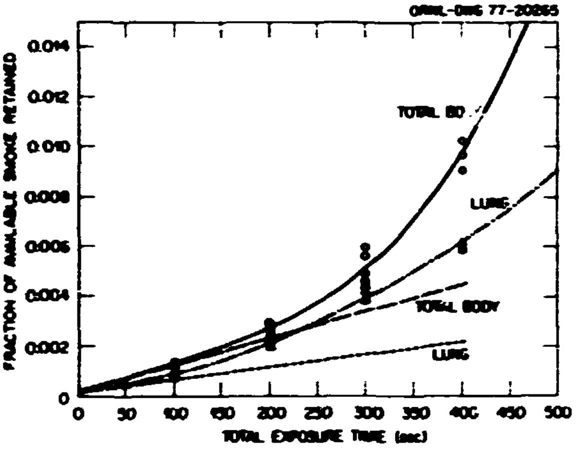


Fig. 4.4. Plot of predicted particulate deposition in mouse lungs (— - —) and total mouse body (———) as a function of exposure time on Walton horizontal smoking machine. Plotted points are experimentally observed values (●, total body; Δ, lung). Straight lines show linear contribution to the model (- - -, lung; — — —, total body).

Distribution and retention of various compounds in mice after inhaling cigarette smoke. In addition to determining the deposition site of smoke particulates in mice by use of ^{14}C-DTC, we have examined the distribution and fate of some of the more active constituents of the cigarette smoke. Cigarettes were labeled with ^{14}C-CTC, ^{14}C-BaP, or ^{14}C-nicotine. Mice were then exposed to the smoke generated by these labeled cigarettes, using the Walton horizontal smoking machine. The mice were sacrificed at time intervals ranging from a few seconds to several days after completion of the smoke exposure.

The clearance rates for DTC were studied to establish baseline information for a fairly inert component of the smoke aerosol. About 40 hr were required for the total ^{14}C-DTC activity in the body to decrease to one-half the value found immediately after exposure. This rate of clearance was assumed to indicate the mechanical clearance rate of smoke particulates. In contrast, compounds that cleared considerably faster than DTC were considered active constituents, whose clearance rates were more dependent on processes such as enzyme-catalyzed chemical changes and transport-across-membrane barriers than on mechanical clearance.

The clearance rates for both BaP and nicotine were fast compared with DTC when these compounds were added as tracer components in cigarette smoke that entered the respiratory tract of the mouse. Under such conditions, the half-life for BaP was less than 1 hr. Nicotine was cleared from the lung and body even faster than BaP. Rapid clearance of BaP and nicotine is also reflected in body distribution changes of the tracers. For the relatively inert DTC, 70% of the total body burden remained in the lungs for hours after inhalation. Redistribution of nicotine and BaP through the mouse system, however, was quite rapid. Ten percent or less of the total-body ^{14}C activity was found in the lower respiratory tract several minutes after exposure to the smoke of a single cigarette. The observance of this rapid redistribution led to experiments in which mice were exposed for 20 sec to a standard puff of cigarette smoke containing either ^{14}C BaP or ^{14}C nicotine. The proportion of tracer found in the lower respiratory tract immediately after exposure to a single puff was higher than that found after exposure to a whole cigarette but never approached the 70% observed for DTC.

Perhaps the most significant result of these studies is the rapid clearance observed for BaP. It is well known that BaP administered to the respiratory tract in a nonaerosol form (suspension in aqueous solvent) leads to much cellular damage. The mechanism for this cellular damage is generally thought to be the enzyme-catalyzed conversion of the BaP to an epoxide that can react with cellular material. Although cigarette smoke is known to induce the proper enzyme activity, the time interval following smoking that is required for induction of significant enzyme activity is greater than the time interval required by the mouse to clear more than 90% of the ^{14}C-BaP that enters the lung in a cigarette smoke aerosol. This observation raises some doubts concerning the validity of determining the biological activity of a compound in the respiratory tract when the compound being tested enters the respiratory tract in a physical form that is significantly different from the form in which it is naturally encountered.

Experiments have been designed to study the relationship between the physical form of the insult (suspension or aerosols of various particle sizes) and system functions such as clearance, elimination, and metabolism. (*J. E. Caton, G. M. Henderson*)

5. Nuclear and Radiochemical Analysis

J. R. Stokely

The Nuclear and Radiochemical Analysis Section was formed as a new organizational unit in July 1977 to bring together much of the radiochemical development and sample-analysis effort in the division. Consolidation of radiochemical work in the new section allows more effective use of our facilities and expertise as well as close interaction between developmental and service activities. An effort is being made to expand capabilities and to diversify work involvements. Initial activities include acquiring new instrumentation, establishing developmental activities in support of existing sample-analysis programs, and initiating new projects and work activities. Our goal is to provide the best possible radiochemical analysis support for ORNL programs and simultaneously to make relevant scientific contributions to the field of radiochemical analysis.

As structured, the section consists of three groups: intermediate-level radiochemistry, low-level radiochemistry, and neutron activation analysis. Our low-level radiochemical analysis group provides analytical development and sample analysis on materials containing picocurie to nanocurie levels of radioactivity. The group is growing because of increased interest in low levels of radioactivity in the environment. Our laboratory facilities and equipment are proving inadequate for the increased work load, and we are in the process of expanding our chemical laboratory facilities and upgrading our instrumentation and technical expertise for low-level analysis of radionuclides. Three chemical laboratories and a counting room are being equipped for low-level analysis. New instrumentation has been acquired to provide increased alpha- and gamma-spectrometry capabilities, and equipment has been added for preparation of environmental samples for analysis. A portable spectrometer has been put into service for extra-laboratory identification and quantitation of gamma-emitting radionuclides. A developmental program has been initiated with the Industrial Safety and Applied Health Physics Division to devise new methodology for environmental monitoring and surveillance.

The intermediate-level radiochemistry group performs development and sample analysis on materials containing microcurie to millicurie levels of radioactivity. The group is involved in a large sample-analysis program in support of work performed in other divisions. Associated with the sample analysis program is a small developmental effort aimed at the upgrading of capabilities and special sample analysis. During the past year, the group has acquired and put into operation a new computer-multichannel analyzer system (Nuclear Data 6620), which has resulted in significant improvements in analysis by gamma-ray spectrometry. Initial steps have been taken in the group to implement the division's data management system. Full implementation is expected within the next few months and will result in more efficient and reliable processing of large amounts of sample-analysis data generated by the group.

The neutron activation analysis (NAA) group provides analysis and development work for laboratory programs and assists others outside ORNL in special projects that draw upon our expertise or use our special facilities. For NAA work, we have sample-irradiation facilities at three reactors. During the past year, we have continued to be

BLANK PAGE

involved in the National Uranium Resources Evaluation (NURE) program. Our current involvement in this program is in the NAA of sediments for uranium by irradiation and delayed neutron counting. In addition to this program, general NAA services are provided as requested by investigators at ORNL; approximately 7500 determinations were made over the past year to assist other programs. Neutron irradiation and counting measurements for investigators in the Neutron Physics Division have also been carried out to determine the heat generated from the decay of radioactive fission products after reactor shutdown. Some expansion of NAA work is expected within the next year. We are now installing a new neutron-detection system for uranium analysis, which will result in greater sensitivity and improved efficiency. Efforts are under way to use fully our high-flux irradiation facility at the HFIR. Plans are being made to automate counting measurements for multielement NAA.

LOW-LEVEL RADIOCHEMICAL ANALYSIS

Sample Analysis Program

The low-level radiochemical analysis group performs analyses on a variety of materials in support of programs in other ORNL divisions. The principal interests in low-level analysis are related to environmental research, monitoring, inventory, and survey programs that are conducted by the Environmental Sciences, Health and Safety Research, Industrial Safety and Applied Health Physics, and Operations divisions. Table 5.1 lists frequently analyzed materials and radionuclides determined. In general, detection limits for alpha-emitting radionuclides are of the order of 10^{-2} to 10^{-4} dis min^{-1} g^{-1} and for beta emitters, 10^{-3} to 10^{-1} dis min^{-1} g^{-1}, depending largely on the sample matrix and size. Most analyses are performed by isolation of the nuclide followed by alpha, beta, or gamma measurements in special low-background counting equipment. Selected sample-analysis efforts described below illustrate our involvement in programs concerned with low levels of radionuclides in the environment.

Personnel of the Environmental Sciences Division have made extensive studies of transuranium element contamination of the White Oak Creek floodplain.

Table 5.1. Some analyses performed routinely by low-level radiochemical group

Radionuclide	Vegetation	Soil	Animal tissue	Mill tails	Solutions	Filters
Am-241	X	X	X		X	
Cm-244	X	X	X		X	
I-131					X	
Np-237	X	X			X	
Pb-210		X		X	X	X
Po-210				X	X	
Pu-239	X	X	X		X	X
Pu-238	X	X	X		X	X
Ra-223		X	X	X	X	X
Ra-224		X	X	X	X	X
Ra-226		X	X	X	X	X
Ra-228		X	X	X	X	X
Sr-89		X	X		X	X
Sr-90		X	X		X	X
Tc-99	X	X	X		X	
Th-228	X	X		X	X	X
Th-230	X	X		X	X	X
Th-232	X	X		X	X	X
U-234	X	X	X	X	X	X
U-235	X	X	X	X	X	X
U-238	X	X	X	X	X	X

which drains the ORNL area. Several hundred radiochemical analyses have been performed for plutonium, americium, and curium in soil, garden vegetables (tomatoes, carrots, beets, potatoes, beans), and small animals (opossum, groundhog, earthworms, snakes). Typical concentrations found for plutonium were 140 dis min^{-1} g^{-1} in soil, 10 dis min^{-1} g^{-1} in litter, 0.4 dis min^{-1} g^{-1} in ground cover, 0.01 dis min^{-1} g^{-1} in leaves, and 0.01 dis min^{-1} g^{-1} in small animals. Plutonium-238 values were 5 to 10% of ^{239}Pu values.

In the routine monitoring of White Oak Dam water samples, an increase in alpha activity was observed recently. Because the levels of activity were reaching the maximum permissible, it was necessary to determine the source and identity of the alpha emitters. In conjunction with the Industrial Safety and Applied Health Physics and Operations divisions, we identified the main alpha emitter as ^{244}Cm; by repeated sampling of White Oak Creek, the source was soon located and controlled.

The Environmental Sciences Division is using a retention pond to characterize and inventory transuranics and other radionuclides in an aquatic ecosystem. To date, this study has generated samples of water, sediment, invertebrates, insects, fish, frogs, and algae. Typical levels for alpha activity are 10^3 dis min^{-1} g^{-1} in sediment, 10^{-2} to 10^{-3} dis min^{-1} ml^{-1} in water, and 10^{-4} to 10 dis min^{-1} g^{-1} in biota. In some of these samples the unusual behavior of uranium caused interference problems in the analysis for thorium and americium. This problem is being studied. Small animals (primarily cotton rats) that inhabit the pond area are being analyzed for plutonium, americium, and curium. Concentrations of these nuclides were 0.01 dis min^{-1} g^{-1} of ^{239}Pu (whole carcasses), 1 dis min^{-1} g^{-1} of ^{239}Pu (stomach), and 0.1 dis min^{-1} g^{-1} of combined americium and curium (whole carcasses). These results indicate that americium and curium can be retained to a greater extent by the animals.

Samples of about everything imaginable have been submitted by the Health and Safety Research Division from sites at Cleveland, Ohio, Canonsburg, Pennsylvania, St. Louis, Missouri, and Middlesex, New Jersey. Radium, thorium, lead, and uranium determinations reveal concentrations from background levels as high as 10^3 dis min^{-1} g^{-1} of these materials. Again, uranium in some water samples was found to display unusual behavior. Samples from phosphate mining in Florida presented problems for the analysis of lead-210; however, changes in procedure alleviated the problems. (*T. G. Scott, A. L. Crook*)

Development in Support of Sample Analysis

Work has continued on identification and determination of low levels of radioactive species in environmental materials. This work is in collaboration with members of other divisions, notably the Environmental Sciences, Industrial Safety and Applied Health Physics, and Health and Safety Research divisions. Such collaboration has resulted in several publications, and more are in preparation. We also participate in the efforts of organizations such as ASTM and ANSI, whose objective is to improve radiochemical methodology.

A variety of naturally active species must be identified and measured as part of the Excess Site program. Methods were devised for ^{231}Pa and for ^{230}Th and daughters of ^{227}Ac, which require chemical separations and alpha-spectrometric measurements. Particles from the Nevada Test Site were examined by alpha spectrometry. Though degraded, the spectrum above 0.9 MeV permitted identification of plutonium and americium, which was verified by x-ray and gamma-ray spectrometry. Self-absorption was estimated to be equivalent to that in a single 40- to 50-μm spherical particle. Alpha spectra of ^{239}Pu with various amounts of PrF_3 were obtained to assist in the particle study and for possible computer resolution of spectra.

In a local sample of interstitial water from sediment, uranium behaved anomalously in that it coprecipitated with PrF_3. This behavior was prevented by first heating with HNO_3. It was surmised that reduction of U(VI) to U(V) or U(IV) had taken place. The sample was analyzed for thorium, uranium, neptunium, plutonium, and transplutonics; only uranium was found. (*S. A. Reynolds, T. G. Scott*)

Environmental Surveillance

The local perimeter and remote air-monitoring networks of the Industrial Safety and Applied Health Physics Division provide special samples along with rainwater samples from rain collectors for the study of airborne radioactivity by air filtration techniques. In addition, soil and vegetation samples are collected annually from locations near the perimeter air monitor (PAM) stations. At each PAM station, a 1-m^2 grid is laid out to define the collection area. The vegetation within the defined area is harvested by hand clipping at the roots. The resulting sample is chopped into small segments and packed into a Marinelli beaker for γ-spectrometric measurement. Samples of vegetation are measured "as received" to prevent the loss of volatile radionuclides such as ^{131}I, or ^{106}Ru during drying. In each PAM sampling location devoid of vegetation, nine soil samples are collected. The resulting samples are analyzed with the Ge(Li) system, using calibrations obtained from New Brunswick Laboratory certified samples.

A special initial survey of grass samples at PAM stations took place at two main stations—one about 8 km east and one about 8 km northwest of ORNL. Samples from both stations showed the presence of fission product radionuclides above the expected levels. The samples contained ^{95}Zr, ^{103}Ru, ^{140}Ba-^{140}La, and ^{141}Ce at levels of 3 to 20 pCi/m^2, in addition to the natural radioelements, K, Th, and U. These activity levels were determined with short counting periods of 1000 sec. Using additional information obtained from air-filter samples at other PAM stations, it was determined that the fission product nuclides originated from the Chinese bomb test of September 26, 1976, some 55 days earlier. By using longer counting intervals, it was possible to determine quantitatively ^{131}I and ^{137}Cs at 0.6 and 0.2 pCi/m^2 (in addition to the other fallout radionuclides).

These results of the initial survey of perimeter soil samples at the nine stations took place during the last quarter of 1976 and in February of this year. Results of the soil survey are presented in Table 5.2. Radionuclide concentrations are expressed in units of picocuries per gram. The ^{137}Cs and ^{125}Sb contributions probably came from global fallout from previous nuclear weapons testing, whereas the shorter lived fission products, ^{95}Zr and ^{103}Ru, were probably contributed by the September 1976 Chinese bomb test.

Airborne radioactivity is sampled at all three networks for quarterly and annual reports. For baseline measurements, weekly collections were made at a single PAM station about 8 km east of ORNL. The purpose of this special study was to obtain a temporal variation of the Chinese bomb fallout. A graphical presentation of the change in three fallout nuclides and ^{7}Be for a 6-month period is shown in Fig. 5.1. The counting rate of the photopeak characteristic of the four radionuclides is plotted vs the week number of 1976 and 1977. The relative constancy of ^{7}Be for the entire period serves as an internal standard for the analytical method. The initial steep decrease in levels of the fallout nuclides correlates well with an increased rainfall during weeks 41 and 42, resulting in a "washout" of the fallout. The sharp increase in ^{141}Ce levels following week 10 of 1977 coupled with the gradual increase of ^{95}Nb and ^{103}Ru levels prior to that time provides a possible explanation for a 15-fold increase in gross beta levels reported in some western states' air monitors in the middle of March. These studies have been reported at a conference.[1] (*J. S. Eldridge, T. W. Oakes*[2])

Table 5.2. Annual perimeter soil analyses, 1976

In picocuries per gram

Station No.	^{40}K	^{226}Ra	^{228}Th	^{137}Cs	^{125}Sb	^{95}Zr	^{103}Ru
P-31	11.2	0.9	1.1	1.4	0.3		
P-32	35.0	0.8	1.1	1.8	0.3		0.02
P-33	11.6	0.9	0.8	1.4			
P-34	19.2	0.8	1.3	2.8			
P-35	5.1	0.8	0.9	1.5	0.2		0.05
P-36	7.9	0.8	1.0	2.4			
P-37	11.4	0.6	0.7	0.3		0.06	0.04
P-38	5.8	1.0	0.8	1.1	0.2		0.02
P-39	12.9	1.1	1.0	1.7	0.3		

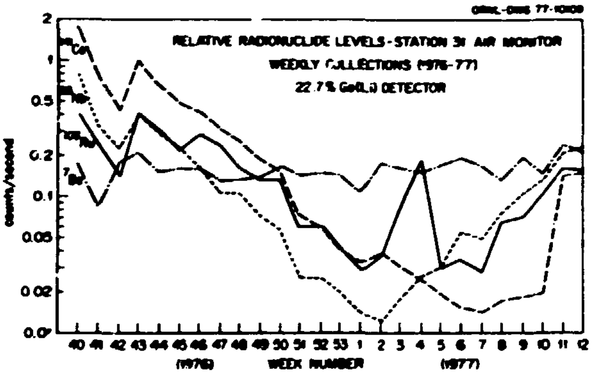


Fig. 5.1. Variation of relative fallout nuclide concentrations at a perimeter air monitor station during the fourth quarter of 1976 and the first quarter of 1977.

Emergency Sample Analysis

The emergency preparedness program of ORNL has acquired a new computing gamma-spectrometer system from Lawrence Livermore Laboratory. The spectrometer is a complete system for sodium-iodide gamma-ray spectroscopy for field use. It is intended to be used wherever a man can carry it. The system contains a 1024-channel integrated-circuit memory, divisible into four 256-channel groups. It can operate as a 1024-channel system with solid-state detectors.

---

[1] J. S. Eldridge, T. W. Oakes, and M. E. Pruitt, "Environmental Surveillance for Radionuclide Contamination Utilizing High-Resolution Gamma-Ray Spectrometry," *Proceedings of the Eleventh Annual Conference on Trace Substances in Environmental Health, University of Missouri, June 6-9, 1977* (in press).

[2] Industrial Safety and Applied Health Physics Division.

The memory quadrants can be added, subtracted, overlapped, or moved from one section to another. The spectral display is presented on a 3- × 5-cm cathode-ray tube. There are two movable and one fixed-channel markers for ease in summation and calibration techniques. In addition to the analyzer, amplifier, power supply, computer circuits, and detector, the system contains a Polaroid SX70 display camera, telephone audio coupler, and an alternating-current charging cord.

The major application of the spectrometer will be in unexpected or emergency situations involving radioactivity. The instrument will also be used in a residential dosimetry program in selected Oak Ridge dwellings in which gamma-ray spectral determinations will be performed in conjunction with thermoluminescent dosimeter measurements for overall radiation-dose assessments.

The spectrometer has been applied to field measurements at one of the old waste disposal trenches at ORNL. It was possible to demonstrate the presence of ^{137}Cs and ^{60}Co in the foliage of trees growing on the site. The field measurements demonstrated a need for implementation of the "hard copy" or telemeter readout to completely document data collected in the field. This is deemed necessary for emergency use and in the post-accident investigation phase. (*J. S. Eldridge, M. E. Pruitt*)

Monitoring of Radioactivity from Chinese Nuclear Device

Atmospheric testing of a nuclear device by the Chinese on September 26, 1976, caused extensive fallout in the eastern United States about one week after the detonation. Fallout was detected in aerosol samples at ORNL, beginning on October 4. Because of extensive publicity and public concern about this fallout, we were requested to provide a fast-response method for monitoring milk samples for ^{131}I at levels of several picocuries per liter. The standard anion exchange concentration method followed by specific radioiodine analysis is routinely used at ORNL, but the low-level facility does not have the capacity for extensive screening analyses.

Our approach to the analysis problem was direct: we determined the minimum detectable concentration in a high-geometry configuration with the low-level germanium spectrometer system, using untreated milk samples. We found the Marinelli beaker geometry containing 900 ml to have a photopeak counting efficiency of 1.7% for the 364-keV gamma rays of ^{131}I. This efficiency, coupled with the favorably low background in our facility, permitted detection of ^{131}I at levels of 20 pCi liter and quantitative estimation at levels of 40 pCi liter, with counting periods as low as 1000 sec. No treatment of the sample was required.

With this screening method, we surveyed milk from two herds of cows in East Tennessee on a daily basis during the period of maximum fallout. Results of the October 1976 studies are shown in Table 5.3. Iodine-131 levels in herd M decreased to less than 50 pCi liter, beginning on October 12. Levels in herd H increased to 110 and 60 pCi liter on October 17 and 18 before dropping below the detectable levels.

Table 5.3. Iodine-131 in East Tennessee milk in October 1976

Date	Iodine-131 (pCi liter)	
	Herd M	Herd H
October 8	85	*a*
October 9	50	130
October 10	95	110
October 11	70	80
October 12 15	<5	<5
October 17	<5	110
October 18	<5	60

[a] No sample.

Following an atmospheric test of a nuclear device on September 17, 1977, we were asked to reactivate our surveillance procedures. Fallout was detected in rainwater and aerosol samples during the latter days of the month. Iodine-131 levels exceeded our detection limits in milk samples collected on September 27. Results of this study are shown in Table 5.4.

Table 5.4. Iodine-131 in East Tennessee milk in September and October 1977

Date	Iodine-131 (pCi liter)	
	Herd M	Herd H
September 27	30	50
September 28	75	90
September 29	95	130
September 30	65	150
October 1	60	150
October 2	60	120
October 3	55	140
October 4	80	120

Iodine-132 (2.3-hr half-life) was detected in milk samples of September 28 and 29 (about 11 and 12 days after the test). Levels of the 2.3-hr ^{132}I are supported by the 78-hr ^{132}Te parent. About 8% of ^{132}Te would remain after a 12-day decay period. (*J. S. Eldridge, T. W. Oakes,*[3] *J. E. Turner*[3])

Environmental Impact Work

We collaborate with the Environmental Impact Section of the Energy Division in the assessment of the chemical and radiological impacts of proposed facilities and operations that involve possible radioactive releases. Items of concern in this period were potential hazards from in-situ leaching of uranium, preparation of uranium fuels, and radionuclides in consumer products. An extensive survey of published literature and documents prepared by license applicants was made with respect to in-situ leaching ("solution mining"). Extensive recommendations are being prepared for research on in-situ leaching to be supported by the Nuclear Regulatory Commission. Sites in South Texas were visited, and information was obtained from operating companies and public health officials. Two visits have been made to the Bureau of Mines Research Center in Minneapolis. A local review of the field is in preparation. Three fuel-fabrication plants were visited, including one at Erwin, Tennessee. We contributed a substantial portion of the environmental statement for the Erwin plant. Internal reports were prepared on some of the trips. Contributions were made to a plan for a possible generic treatment of consumer products containing radionuclides. Other assistance included information on radiological impact of geothermal plants, nuclear data on some radionuclides, and reviews of local and outside documents. (*S. A. Reynolds*)

New Low-Level Laboratory Facilities

New facilities for low-level radiochemical work are being prepared to handle an increased sample load and to centralize operations in one area as well as to provide for research and development. The overall facilities will consist of three chemistry laboratories and a counting room. Thorough studies of background levels and special utility accommodations were made prior to completion of plans to move to the new facilities.

The arrangement of the three chemistry laboratories in the new facilities will permit screening and routing of work to minimize cross contamination and to allow maximum efficiency in sample preparation. Portions of the laboratories will be designated for special types of analyses, and as much space as possible will be allocated for large projects to be accommodated without in-line delays.

Improvements and consolidation of counting instruments will be realized in the new facilities. Expansion of an existing Nuclear Data 3300 multichannel analyzer to include alpha and gamma detectors will improve throughput in sample counting. One counting area will be maintained for the monitoring and screening of incoming samples and samples in process. All the low-level counting systems including alpha, beta, and gamma spectroscopy will be centrally located for maximum efficiency and reliability. Once in the new quarters, the low-level radiochemistry group can offer its customers more diverse services and shorter turn-around time. (*T. G. Scott, M. E. Pruitt*)

INTERMEDIATE-LEVEL RADIOCHEMISTRY GROUP

Sample Analysis Program

The Intermediate-Level Radiochemical Analysis group assists several divisions in providing radiochemical data for their various programs. During the past year, most of this assistance was given to the Chemical Technology Division (50%), Operations Division (10%), Health and Safety Research and Industrial Safety and Applied Health Physics divisions (10%), Environmental Sciences Division (5%), and Solid State Division (5%). We also provide radiochemical services in support of decontamination studies of coated reactor-component specimens. Some low-level gamma spectrometry is currently done by the group but will be transferred to the low-level radiochemistry group in the near future. During the past year, approximately 25,000 sample analyses were made. Gamma-spectrometry results comprise more than half of reported results. Liquid-scintillation counting for tritium and carbon-14 accounted for about 20% of our work. The remaining work consisted of general radiochemical analyses for reactor programs, fuel reprocessing development, and isotope analysis.

During the past year a new Nuclear Data 6620 multichannel analyzer-computer system and a Packard liquid-scintillation counter (sample capacity: 150) have been put in service. These two systems have greatly reduced turn-around time for gamma-spectrometry and liquid-scintillation beta assays. We

---

[3] Health and Safety Research Division.

have restructured the sample logging and filing system to increase efficiency in handling and recording data. Further improvement will be possible in the next few months when a data-management terminal is installed in the laboratory and the division's data-management system is implemented within the group. (*H. A. Parker, L. M. Jenkins, T. G. Harmon*).

Installation of Nuclear Data 6620 Multichannel Analyzer

In December of 1976 the Nuclear and Radiochemical Analysis Section purchased a Nuclear Data (ND) 6620 analyzer system, which was installed in the Intermediate-Level Radiochemical Analysis Laboratory, Building 3019, and has been used to acquire and process gamma-spectrometry data.

The ND 6620 is the first multiuser, multitask data acquisition and processing system offered commercially. It contains two of Digital Equipment Corporation's 16-bit LSI-11 microcomputers. One microcomputer provides system control, and the other provides independent display and acquisition of data. Microprocessors designed by Nuclear Data are used in data-storage peripherals for high-speed data processing. The operating system software, MIDAS, manages the resources of all computer-based data acquisition and processing and enables direct communication between the user and the ND 6620 system. Using simple commands, multiple users can independently access memory or disk files, run programs, operate I/O devices, or write new FORTRAN or basic software. The software package enables the user to perform data acquisition and display, data manipulation, data transfer, energy calibration, automatic peak search with multiplet resolution, detector efficiency calibration, nuclide identification, and minimum detectable activity calculations, and to generate reports. Included with the system are a Perteck dual hard-disk drive, a Perteck 9-track magnetic-tape unit, four ND 570 analog-to-digital converters, an ND 568 gated analog router, and a Centroixer 306 line printer.

The ND 6620 system is continuing to be developed, improved, and actively supported by the Nuclear Data Corp. Some initial hardware and software problems were resolved during the first several months of operation. The ND 6620 has processed all germanium gamma spectrometry since about June 1. The analyzer checked well in comparison with the ND 3300 and MONSTR program previously in use. Three staff members are familiar with its operation, and two technicians can process samples both manually and automatically. We have had initial success in writing our own FORTRAN programs for use on the ND 6620 and are anticipating more extensive use of this capability The IBM 360 can now be used as a backup to the system for data reduction and provides plotting features as well.

We have acquired solid experience in operating the ND 6620. In the future, we hope to extend its capacity through the addition of three Ge(Li) detectors, two terminals, 32K memory, and three sample changers. The ND 6620 will be the backbone of our gamma spectrometry capability in the Intermediate-Level Radiochemical Analysis Laboratory. (*L. M. Jenkins, J. F. Emery*)

Data Management for Intermediate-Level Radiochemical Analysis

The division's sample transaction system (STS) is a computer system developed by the Computer Sciences Division to replace manual sample accounting and reporting. The STS features interactive data entry and information retrieval. The STS automatically generates sample inventory reports and sends computer-printed reports to the customer. Historical information is periodically transferred to magnetic tape and microfiche cards.

In the past year we have worked to adapt this system to the special needs and problems associated with radiochemical analysis and spectrometry. Reports can now be generated in tabular form as desired. Any analysis request, such as "gamma scan," can be expanded to allow the reporting of any number of radionuclides found in the sample. Sample inventory, or BACKLOG, reports are generated daily. The BACKLOG lists all work not yet completed and includes the customer's name and charge code, the date the work was received, and the number and type of analyses requested. It also lists the total analyses pending as well as the total analyses reported since the last BACKLOG. Thus the flow of work through the laboratory is easily monitored.

To take full advantage of the interactive nature of the STS, access of ORNL's DEC System 10 via computer-terminal input is necessary. We have been sharing a terminal located at Building 2026, which is outside of our security perimeter. A hard-line hook-up to the computer with visual and hard-copy readout will be installed during the next year. At that time we hope to fully implement the STS in the Intermediate-Level Laboratory. (*L. M. Jenkins*)

Quality Assurance

As an analytical chemistry laboratory, we have a commitment to provide precise, accurate analytical results. The assurance of high quality requires that we use tested and well documented methods, that we maintain an active training program for personnel, and that instrumentation and equipment be current and in good working order.

During the past year, several activities were initiated to assure that high-quality data are being reported by the Intermediate-Level Radiochemical Analysis Laboratory. The acquisition of the Nuclear Data 6620 Analyzer, featuring on-line data reduction, has decreased turn-around time for gamma spectrometry and improved reliability. Two Ge(Li) detectors, used for gamma spectrometry, were recalibrated, using NBS Mixed Radionuclide Standards. Upon completion of those calibrations, internal consistency between detection methods was assured by sample comparison between three independent measurement methods. Response factors for gross alpha, beta, and gamma detectors are being reevaluated. In addition to these calibration activities, the laboratory participated in an internal ORNL Quality Assurance audit. The major recommendation of the audit team that we improve all facets of documentation is being implemented.

In the coming year we plan to improve the quality assurance program through increased documentation and a more rigorous, routine QA schedule. (*L. M. Jenkins*)

NEUTRON ACTIVATION ANALYSIS

Sample Analysis Program

The NAA group provided a large number of special sample analyses for ORNL and UCC-ND programs. This year over 7500 determinations were made on 3040 samples. Uranium determination by neutron irradiation and delayed neutron counting comprised the largest single type of analysis; 2460 determinations were made for uranium over the past year. Multielement analyses resulted in more than 2000 determinations. Sample types consisted of the following: metals (Al, U, Nb, Cu), inorganic compounds (Al_2O_3, CuI, FeS, MgO, Ra salts), biological materials (fish, mouse tissue, hair), vegetable ashes, coal, charcoal, sediments, soils, water, and gasoline. The NAA work load at the Oak Ridge Research Reactor has been partially reduced this year because of a limited reactor schedule. An increase in reactor operating time in the coming months is expected and will result in a larger volume of sample analysis work. In addition, more extensive use of the Bulk Shielding Reactor and the High Flux Isotopes Reactor will be implemented in the future to permit a larger sample analysis load. (*J. F. Emery, K. J. Northcutt*)

Special Projects

The Department of Energy (DOE) is engaged in the measurement of uranium and other trace elements in bodies of water and sediments around the country via the NURE program. We determine uranium in sediment samples for a part of the NURE program by counting the delayed neutrons following fission. Thermal neutron irradiation fissions only ^{235}U; therefore, ^{232}Th does not interfere in the uranium determination. About 1800 sediments were analyzed for uranium, using this technique. Eleven of these samples were also analyzed for other trace elements. Because the technique is ideally suited for automation and the pneumatic tube is already under computer control, a new easily automated delayed-neutron moderator counter assembly has been designed, fabricated, and installed. It is about four times more efficient (17%), and the limit of detection for natural uranium is 4×10^{-9} g. DOE is currently considering the possible determination of other trace elements by neutron activation analysis. Expected sample loads of 20,000 or more per year might require automated counting equipment. Four systems with automated sample changers are planned. The decision to implement these plans is pending.

We have been involved with personnel from the Neutron Physics Division in a project to improve the accuracy and precision of the measurement of decay heat from radioactive fission products after reactor shutdown. Time periods from shutdown to 10,000 sec are being studied. The heat produced during such periods is a primary determinant of reactor core shutdown cooling requirements. Three methods are used (*1*) a *thermal calorimetric measurement*, (*2*) a total-absorption scintillation detector, and (*3*) a scintillation spectromter to measure the beta and gamma spectra. A decay heat curve with an overall error of 3 to 5% is expected. At ORNL, our involvement is in the study of ^{235}U, ^{239}Pu-^{241}Pu, and possibly ^{233}U by use of beta- and gamma-ray spectrometry. The experimental work on ^{235}U and ^{239}Pu is complete. A report on ^{235}U has been issued,[4] and a report on ^{239}Pu

---

[4] J. K. Dickens, J. F. Emery, T. A. Love, J. W. McConnell, K. J. Northcutt, R. W. Peele, and H. Weaver, *Fission-Product Energy Release for Times Following Thermal Neutron Fission of ^{235}U Between 2 and 14000 Seconds*, ORNL/NUREG-14, October 1977.

is in preparation. The irradiations for ^{241}Pu are planned for December 1977.

Hair samples from 11 Chinese residents of Hong Kong were obtained to study trace-element concentrations and a possible relationship to environmental exposures. The hair samples were cleaned and irradiated according to the procedure of Dr. Yu. S. Ryabukhin (IAEA RL 41H, January 1977). Trace-element concentrations were determined by absolute neutron activation analysis. A paper is being prepared for publication with L. S. Chuang (Chinese University of Hong Kong) describing this work. (*J. F. Emery, K. J. Northcutt, L. C. Bate*)

6. Quality Assurance, Safety, and Tabulation of Analyses

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

QUALITY ASSURANCE

Since July 1976, each group in the Analytical Chemistry Division has continued to report its Quality Assurance programs and results semiannually. In addition to the semiannual report, the Analytical Services Section has continued its control program with monthly internal reports and with quarterly summaries of the statistical data.

Table 6.1 shows the quality level for each of the service laboratories and compares the results with those from the previous year. Lists of the different control programs and the number of results reported for each program are given in Table 6.2. During the past year, there has been a 15% decrease in the number of control determinations reported and in the number of control programs.

SAFETY

During the past year the Analytical Chemistry Division had nine first-aid cases, seven of which were caused by cuts, acid burns, or falls. The remaining two were the result of an electrical shock and a finger cut on a truck door. The quarterly safety and housekeeping inspections reveal a noticeable improvement in the appearance of the laboratories and an increased effort to eliminate safety hazards.

Safety meetings included presentations by H. Green of the Shift Supervisor's Office on "Emergency Procedures," Dr. H. B. Ruley on "Medical Hazards of High Voltage," and Dr. H. B. Hurt on "Alchohol and Health."

SUMMARY OF ANALYSES RENDERED

Table 6.3 contains a tabulation of analyses performed by the various laboratories and/or groups within the division during this reporting period. Analyses performed as part of Analytical Chemistry Division programs are *not* included in this tabulation.

Table 6.1. Distribution by laboratory of control tests for October 1976–September 1977

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1976	1977
Environmental Analysis	591	8	96.41	98.65
Radioactive Materials	558	75	95.69	86.56
General Analysis	903	58	95.46	93.58
Totals	2052	141	95.79	93.13

[a] Control results within 2S limits.

BLANK PAGE

Table 6.2. Distribution of control results (by method) for October 1976–September 1977

Method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption	Cadmium	2	8	
	Calcium	2	69	
	Chromium	1	19	
	Copper	2	11	
	Iron	1	55	
	Lead	2	1	
	Lithium	1	7	
	Magnesium	2	50	
	Molybdenum	1	1	
	Nickel	1	63	
	Potassium	1	14	
	Sodium	1	23	
	Zinc	2	10	331
Colorimetric	Molybdenum	2	14	
	Nitrogen	2	185	
	Phosphorus	1	66	
	Sulfate	2	155	
	Thorium	2	80	
	Uranium	2	200	
	Zirconium	1	11	711
Coulometric	Uranium	1	40	40
Flame emission	Potassium	1	33	
	Sodium	1	67	100
Fluorometric	Uranium	2	264	264
Gravimetric	Carbon	1	68	68
Infrared absorption	Carbon	1	60	60
Volumetric	Acid	3	127	
	Nitrate	1	69	
	Sulfur	1	14	
	Thorium	2	36	
	Uranium	2	232	478
Total		47		2052

Table 6.3. Summary of analytical work

Organization	Number of results reported by							
	Elemental Spectrometry	Mass Spectrometry Service Laboratory	General Analysis Laboratory	Environmental Analysis Laboratory	Radioactive Materials Analysis Laboratory	Physicochemical Laboratory	Nuclear and Radiochemical Analysis	Total
ORNL divisions								
Analytical Chemistry	3,048	598	1,934	14	29	20	13	5,656
Biology	40				5		300	345
Chemical Technology	16,457	14,688	18,588	1,554	23,088	4,781	6,130	85,286
Chemistry	2,277	897	2,390	1	61	1,482	329	7,437
Energy	30			5				35
Engineering Technology	1,370	80	1,661	13		60	188	3,372
Environmental Sciences	653			29,667	287	91	4,201	34,899
Fusion Energy	50							50
Health	624							624
Health Physics[a]	340	66	186	189		41	5,522	6,344
Inspection Engineering				70				70
Instrumentation and Controls	10	20			9			39
Metals and Ceramics	15,680	70	8,561		655	1,717	529	27,212
Neutron Physics	228			2		20		250
Operations	937	804	1,531	309	5,996		5,651	15,228
Physics	84	42			18			144
Plant and Equipment	219	170						389
Solid State	1,479		191		51		94	1,815
Other								
Protective Coating Testing					1,530			1,530
NURE[b]							2,427	2,427
K-25	2,709	50			80			2,839
Y-12	1,900	400	39	27	31			2,397
Paducah							15	15
Los Alamos Scientific Laboratory		36			6			42
Miscellaneous	14,100	1,882	309		6	241	229	16,767
Total	62,235	19,803	35,390	31,851	31,852	8,453	25,628	215,212

[a] Now Health and Safety Research and Industrial Safety and Applied Health Physics divisions.

[b] National Uranium Resources 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:

E. C. Dunlop, Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware,

V. A. Fassel, Deputy Director, Ames Laboratory, DOE, Iowa State University, Ames,

A. F. Findeis, Program Director for Chemical Analysis, Division of Mathematical and Physical Sciences, National Science Foundation, Washington, D.C., and

A. G. Sharkey, Research Supervisor, Spectro-Physics, Pittsburgh Energy Research Center, DOE, Pittsburgh, Pennsylvania.

CONSULTANTS

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

M. T. Kelley (Adjunct Research Participant) advises the Advanced Methodology Section, with particular emphasis on computer applications.

G. Mamantov, University of Tennessee, was a consultant to the division until September 30, 1977, at which time he became a part-time employee. His areas of expertise are electrochemistry and spectrometry of various types.

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. **J. J. Kirkland**, E. I. du Pont de Nemours and Company, Wilmington, Delaware,

Dr. **L. Jones**, University of Georgia, Athens,

Dr. **J. S. Fritz**, Iowa State University, Ames,

Dr. **G. A. Huff**, Allied General Nuclear Sciences, Barnwell, South Carolina,

Dr. **E. Schönfeld**, NASA Johnson Space Center, Houston, Texas,

Dr. **S. R. Crouch**, Michigan State University, East Lansing,

Dr. **T. L. Theis**, University of Notre Dame, Notre Dame, Indiana,

Dr. **E. Yeung**, Iowa State University, Ames,

Dr. **J. Jordan**, Pennsylvania State University, University Park, and

Dr. **H. M. Fales**, National Institutes of Health, Bethesda, Maryland.

BLANK PAGE

PARTICIPATION IN ORNL IN-HOURS PROGRAM

The following divisional people completed courses during the 1977 winter term of the Continuing Education Program for Scientific and Technical Personnel:

C-200. Organic Chemistry Enricher: C. A. Pritchard.

M-600B. Practical Statistics: A. R. Crook.

S-201B. Grammar and Mechanics of Technical Writing: W. R. Laing, F. L. Layton, J. H. Moneyhun, A. J. Weinberger, and L. B. Yeatts.

S-202A. Design and Structure of Technical Writing: F. L. Ball, J. L. Botts, D. A. Costanzo, H. W. Dunn, and C. E. Higgins.

Below are the courses completed during the spring and summer 1977 terms:

C-201. Organic Chemistry Enricher: C. A. Pritchard.

M-320. Introduction to DISSPLA Computer Graphics Package: L. N. Klatt.

S-202B. Design and Structure of Technical Writing: W. R. Laing.

S-203. Technical Writing Workshop: C. E. Higgins.

R. W. Shaw was a guest instructor for **Laser Applications in Physical and Life Sciences** during the fall 1977 term.

The following people completed the **ORNL–Perry Oral Technical Presentation** course: J. A. Carter, W. H. Christie, J. H. Cooper, D. A. Costanzo, J. M. Dale, J. C. Franklin, L. D. Hulett, L. N. Klatt, W. R. Laing, R. R. Rickard, H. H. Ross, J. R. Stokely, R. L. Walker, and J. P. Young.

GREAT LAKES COLLEGES ASSOCIATION (GLCA) EDUCATION PROGRAM

This cooperative program is now in its eighth year. One student was assigned to the division during the fall 1977 semester: C. L. Talcott from Denison University in Granville, Ohio, to work with W. R. Laing on fluorescence of heavy metal complexes in solution.

SOUTHERN COLLEGES AND UNIVERSITIES UNION (SCUU) SCIENCE SEMESTER

One undergraduate student was assigned to the division as part of the SCUU cooperative program for the winter 1977 semester: E. C. Siebold from the University of the South, Sewanee, Tennessee, worked with B. R. Clark in organic analytical research.

IAEA FELLOWSHIP PROGRAM

F. Ohene-Aniapam, IAEA Fellow, Chemistry Department, Ghana Atomic Energy Commission, Ghana, Africa, was assigned to the division for 8 months starting in March 1977 to work with J. R. Stokely on radiochemistry functions such as uranium and thorium assays, activation analysis, and general radiochemistry techniques and to gain 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 to work with J. R. Stokely on radiochemistry functions, the determination of uranium and thorium by chemical techniques, activation analysis, and counting of uranium and thorium.

ORAU GRADUATE PARTICIPATION PROGRAM

V. E. Norvell, University of Tennessee, was assigned to the division in January 1977 for 12 months to work on his thesis research on the study of rapid-scan spectrometry in analytical methodology with H. H. Ross and L. N. Klatt.

ORAU FACULTY RESEARCH PROGRAM

Dr. N. A. Goeckner, Western Illinois University, was appointed as a faculty research participant in August 1977 to work for 11 months 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 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.

ORAU Summer Research Participant

Dr. Wilmer J. Stratton, Earlham College, Richmond, Indiana, continued his work from last year with H. H. Ross on new methods for trace metal analysis, using a microwave emission detector.

ORAU Summer Undergraduate Research Trainees

The division was host to three undergraduate research trainees:

A. H. Janowicz, The College of Wooster, Wooster, Ohio, worked with D. A. Lee on in-line monitoring of effluent off-gases from carbonization processes in HTGR fuel preparation by mass spectrometry.

S. M. Schultz, Saint Mary's College, Winona, Minnesota, worked with W. R. Laing on the analysis of gas and liquids resulting from coal liquefaction processes.

S. G. Zeldes, Centre College of Kentucky, Danville, Kentucky, worked with A. D. Horton on trapping and analyzing the gas phase of cigarette smoke, using Tenax GC.

Temporary Summer Graduate Student Employees

S. V. Johanningsmeier, DePauw University, Greencastle, Indiana, worked with J. E. Caton on the liquid chromatographic separation of nicotine and its metabolites.

E. C. Siebold, University of the South, Sewanee, Tennessee, worked with B. R. Clark in organic analytical research as part of the National Science Foundation Summer Program.

21ST ANNUAL ORNL CONFERENCE ON ANALYTICAL CHEMISTRY IN ENERGY TECHNOLOGY

The theme of this year's meeting, held at the Riverside Motor Lodge in Gatlinburg, October 4–6, was "Analytical Chemistry in Nuclear Fuel Reprocessing." Attendance was about 200. Six sessions occupied the full three days. Titles of the sessions were: Accountability and Safeguards (two sessions), Nondestructive Analysis (two sessions), Instrumental Analysis, and In-line and Effluent Analysis.

L. J. Brady was Chairman of the Conference Committee, W. S. Lyon was Technical Program Chairman, and A. L. Harrod was Treasurer and Exhibits Coordinator. Other committee members included L. T. Corbin, D. A. Costanzo, H. H. Ross, W. D. Shults, and R. L. Walker.

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.

Frances L. Ball

Secretary: Electron Microscopy Society of America

Representative from EMSA: Section Committee, AAAS Section on Physics (B)

J. A. Carter

Secretary: Subcommittee C5:05, Test Methods, Analytical Task Group, Committee C-26, ASTM

Session Chairman: 21st Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 4–6, 1977

J. E. Caton

Lecturer: ORAU Traveling Lecture Program

Consultant: National Cancer Institute

Instructor: ORNL Personnel Development Chemistry Course

W. H. Christie

Lecturer: ORAU Traveling Lecture Program
Secretary: Subcommittee E42.06, SIMS, Committee E-42 on Surface Analysis, ASTM

B. R. Clark

Chairman: Analytical Chemistry Division Seminar Committee

L. T. Corbin

Fellow: American Society for Testing and Materials
Member: Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM
Subcommittee E10:01, Fuel burnup
Subcommittee E10:02, Radiation-Induced Changes in Metallic Materials

Chairman: Committee C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM

Coordinator: Divisional Non-technical Recruiting
Quality Assurance Program
Energy Conservation Program

Division Representative:	Job Opportunity System Labor Relations
D. A. Costanzo	
Member:	Committees C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications; and C-26.05, Methods of Test, ASTM
Session Chairman:	21st Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., Oct. 4-6, 1977
J. M. Dale	
Member:	Committee E-42, Surface Analysis, ASTM
F. F. Dyer	
Lecturer:	ORAU Traveling Lecture Program
J. S. Eldridge	
Member:	Subcommittee No. 9, Radiological Environmental Surveillance Information Exchange of the Ad Hoc Committee on Upgrading the Quality and Usability of Environmental Radiation Data, Health Physics Society
C. Feldman	
Fellow:	American Society for Testing and Materials
Scientific Editor:	*Optics and Spectroscopy* (English translation of Russian journal, *Optika i Spektroskopiya*)
Member:	Committee E-2 on Emission Spectroscopy, ASTM; Subcommittees on Fundamental Methods, Editorial Practices, and Nomenclature
J. C. Franklin	
Member:	DOE Mass Spectrometer Technical Group
G. Goldberg	
Member:	Committee D-1, Paint, Varnish, Lacquer, and related projects, ASTM Subcommittee D-1.43, Coatings for Power Generation Facilities, ASTM Advisory Board of Utilities Nuclear Coating Work Committee (UNCWC)
Secretary:	Rewrite "Suggested Tests for Coatings for Nuclear and Power Generating Facilities," Subcommittee D01.43, ASTM
G. Goldstein	
Member:	Committee on Specifications and Criteria for Biochemical Compounds, NAS-NRC

Chairman: Subcommittee on Nucleotides and Related Compounds
Ad Hoc Committee on Radioactive and Isotopic Specifications of Labelled Compounds, IUB-IUPAC

M. R. Guerin

Consultant: National Cancer Institute

Invited Participant: DOD/DOE/EPA/NIOSH Workshop on Shale Oil, Wright-Patterson Air Force Base, Dayton, Ohio, July 19-20, 1977
US-Japan Cooperative Research Program, International Conference on Polycyclic Hydrocarbon Carcinogenesis: Chemistry, Biology, and Environment, New Orleans, La., Jan. 24-27, 1977
Special Study Section, Project Site Visit for Review of MIT proposals

C. E. Higgins

Coordinator: Analytical Chemistry Division Affirmative Action Program

R. W. Holmberg

Consultant: National Cancer Institute

Coordinator: Analytical Chemistry Division University Relations

A. D. Horton

Member: Committee E-19, Chromatography, ASTM
Subcommittee E-19.07, Indexing of Chromatographic Methods, ASTM

L. D. Hulett

Member: Editorial Board, *Journal of Electron Spectroscopy*
Committee E-42, Surface Analysis, ASTM

R. A. Jenkins

Consultant: National Cancer Institute

Invited Participant: Site Reviews for NCI and Enviro Control, Inc.

L. N. Klatt

Associate Editor: *Chemical Instrumentation*

Chairman-Elect: Analytical Group of East Tennessee Section, ACS

W. R. Laing

Chairman: Subcommittee C26.05, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications, ASTM

Coordinator: Divisional B.S./M.S. Recruiting

Division Representative: Coal Technology Program Steering Committee

L. L. Landau

Member:	Nominating Committee, Sigma Xi

W. S. Lyon

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 E10:01, Fuel Burnup Subcommittee E10:03, Tracer Applications and Activation Analysis Subcommittee E10:05, Dosimetry Organizing Committee, 6th International Conference on Modern Trends in Activation Analysis Isotopes and Radiation Division, ANS: Executive Committee; Program Chairman 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:	21st ORNL Conference on Analytical Chemistry in Energy Technology, Gatlinburg, Tenn., October 1977
Session Chairman:	Third International Conference on Nuclear Methods in Environmental and Energy Research, Columbia, Mo., October 1977

W. T. Rainey, Jr.

Member:	Committee VI, Biological Applications, ASMS Committee on Computers and Data Processing, ASMS Committee D-2, Task Group on Hydrocarbon Components of Synthetic Fuels from Coal, ASTM ORNL Landscape and Architectural Review Committee

S. A. Reynolds

Member:	Committee D-19, Water, ASTM Committee E-10, Nuclear Technology and Applications, ASTM Environmental Sciences Division, ANS Committee on Environmental Analytical Methodology, ACS 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

E. Ricci

Secretary: Isotope and Radiation Division, ANS

Chairman: Planning Committee, Isotopes and Radiation Division, ANS

Recipient: 1977 Radiation Industry Award, IRD-ANS

H. H. Ross

Member:
ORNL Graduate Student Selection Panel
ORNL Technology Utilization Committee
Editorial Advisory Board, *Journal of Radioanalytical Chemistry*
Education Committee, ORNL Credit Union

Invited Participant: ANACHEM Awards Symposium, Fourth Annual FACSS Meeting, Detroit, Mich., November 1977

W. D. Shults

Member:
ORNL In-Hours Continuing Education Committee
Fellowship Committee, Analytical Chemistry Division, ACS
Committee on Environmental Analytical Methodology, ACS

Editorial Board: *Analytical Chemistry*

D. H. Smith

Coordinator: Divisional Ph.D. Recruiting

J. R. Stokely

Member: Committee D-22, Methods of Sampling and Analysis of Atmospheres, ASTM

Consultant: National Cancer Institute

Instructor: Part-time, Roane State Community College, Harriman, Tenn., NSC-1010 "Survey of Physical Science," Winter Quarter 1977

J. P. Young

Member: "Actinide Partitioning Workshop" ERDA, New Orleans, La., Mar. 24, 1977

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

Book

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHER
Lyon, W. S.	Lyon, W. S. *Trace Element Measurement at the Coal-Fired Steam Plant*	CRC Press, Cleveland, Ohio, 1977

Contributions to Books

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Ferguson, N. M.	Lindberg, S. E.;* Turner, R. R.;* Ferguson, N. M.; Matt, D.* "Walker Branch Watershed Element Cycling Studies: Collection and Analysis of Wetfall for Trace Elements and Sulfate"	*Watershed Research in Eastern North America*, vol. 1, Smithsonian Press, Washington, D.C., 1977, p. 125-52
Lindberg, S. E.*	Lindberg, S. E.;* Turner, R. R.;* Ferguson, N. M.; Matt, D.* "Walker Branch Watershed Element Cycling Studies: Collection and Analysis of Wetfall for Trace Elements and Sulfate"	*Watershed Research in Eastern North America*, vol. 1, Smithsonian Press, Washington, D.C., 1977, p. 125-52
	Turner, R. R.;* Lindberg, S. E.;* Talbott, C. K. "Dynamics of Trace Element Export from a Deciduous Watershed, Walker Branch, Tennessee"	*Watershed Research in Eastern North America*, vol. 2, Smithsonian Press, Washington, D.C., 1977, p. 661-82
Matt, D.*	Lindberg, S. E.;* Turner, R. R.;* Ferguson, N. M; Matt, D.* "Walker Branch Watershed Element Cycling Studies: Collection and Analysis of Wetfall for Trace Elements and Sulfate"	*Watershed Research in Eastern North America*, vol. 1, Smithsonian Press, Washington, D.C., 1977, p. 125-52
Talbott, C. K.	Turner, R. R.;* Lindberg, S. E.;* Talbott, C. K. "Dynamics of Trace Element Export from a Deciduous Watershed, Walker Branch, Tennessee"	*Watershed Research in Eastern North America*, vol. 2, Smithsonian Press, Washington, D.C., 1977, p. 661-82
Turner, R. R.*	Lindberg, S. E.;* Turner, R. R.;* Ferguson, N. M.; Matt, D.* "Walker Branch Watershed Element Cycling Studies: Collection and Analysis of Wetfall for Trace Elements and Sulfate"	*Watershed Research in Eastern North America*, vol. 1, Smithsonian Press, Washington, D.C., 1977, p. 125-52
	Turner, R. R.;* Lindberg, S. E.;* Talbott, C. K. "Dynamics of Trace Element Export from a Deciduous Watershed, Walker Branch, Tennessee"	*Watershed Research in Eastern North America*, vol. 2, Smithsonian Press, Washington, D.C., 1977, p. 661-82

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Haire, R. G.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Study of the Solid-State Phase Transformation of $^{249}\mathrm{BkBr}_3$ via Absorption Spectroscopic and X-ray Diffraction Techniques"	*Proc. 2nd Int. Conf. Electronic Structure of the Actinides, Wroclaw, Poland, Sept. 13–16, 1976,* J. Mulak, W. Suski, and R. Troć, eds., Ossolineum, 1977, p. 111–16
Hurst, G. S.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P.; Payne, M. G.;* Grossman, L. W.* "Selective Single Atom Detection in a 10^{19} Atom Background"	*Proc. 3rd Int. Conf. Laser Spectroscopy,* Springer Series in Optical Sciences, vol. 7, Laser Spectroscopy III, J. L. Hall and J. L. Carlsten, eds., Springer-Verlag, New York, 1977, p. 44
Kollie, T.*	Christie, W. H.; Kollie, T.* "An Ion Microprobe Investigation of the High Temperature Decalibration of Al_2O_3 – Insulated Pt-Rh Thermocouples"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics,* ASMS, Washington, D.C., 1977, p. 435
Nayfeh, M. H.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P.; Payne, M. G.;* Grossman, L. W.* "Selective Single Atom Detection in a 10^{19} Atom Background"	*Proc. 3rd Int. Conf. Laser Spectroscopy,* Springer Series in Optical Sciences, vol. 7, Laser Spectroscopy III, J. L. Hall and J. L. Carlsten, eds., Springer-Verlag, New York, 1977, p. 44
Payne, M. G.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P.; Payne, M. G.;* Grossman, L. W.* "Selective Single Atom Detection in a 10^{19} Atom Background"	*Proc. 3rd Int. Conf. Laser Spectroscopy,* Springer Series in Optical Sciences, vol. 7, Laser Spectroscopy III, J. L. Hall and J. L. Carlsten, eds., Springer-Verlag, New York, 1977, p. 44
Peterson, J. R.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Study of the Solid-State Phase Transformation of $^{249}\mathrm{BkBr}_3$ via Absorption Spectroscopic and X-ray Diffraction Techniques"	*Proc. 2nd Int. Conf. Electronic Structure of the Actinides, Wroclaw, Poland, Sept. 13–16, 1976.* J. Mulak, W. Suski, and R. Troć, eds., Ossolineum, 1977, p. 111–16
Reynolds, S. A.	Bondietti, E. A.;* Reynolds, S. A. "Field and Laboratory Observations on Plutonium Oxidation States"	*Proc. Actinide-Sediment Reactions Working Mtg. at Seattle, Wash.,* Battelle Pacific Northwest Laboratory, VBNWL-2117, Feb. 10–11, 1977, p. 505
Smith, D. H.	Smith, D. H.; Christie, W. H. "A Study of the Quantification of SIMS Data"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics,* ASMS, Washington, D.C., 1977, p. 309
Young, J. P.	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P.; Payne, M. G.;* Grossman, L. W.* "Selective Single Atom Detection in a 10^{19} Atom Background"	*Proc. 3rd Int. Conf. Laser Spectroscopy,* Springer Series in Optical Sciences, vol. 7, Laser Spectroscopy III, J. L. Hall and J. L. Carlsten, eds., Springer-Verlag, New York, 1977, p. 44
	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Study of the Solid-State Phase Transformation of $^{249}\mathrm{BkBr}_3$ via Absorption Spectroscopic and X-ray Diffraction Techniques"	*Proc. 2nd Int. Conf. Electronic Structure of the Actinides, Wroclaw, Poland, Sept. 13–16, 1976,* J. Mulak, W. Suski, and R. Troć, eds., Ossolineum, 1977, p. 111–16

Contributions to Proceedings

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Bondietti, E. A.*	Bondietti, E. A.;* Reynolds, S. A. "Field and Laboratory Observations on Plutonium Oxidation States"	*Proc. Actinide-Sediment Reactions Working Mtg. at Seattle, Wash.*, Battelle Pacific Northwest Laboratory, BNWL-2117, Richland, Wash., Feb. 10–11, 1977, p. 505
Carter, J. A.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics*, ASMS, Washington, D.C., 1977, p. 332
Christie, W. H.	Christie, W. H.; Kollie, T.* "An Ion Microprobe Investigation of the High Temperature Decalibration of Al_2O_3-Insulated Pt-Rh Thermocouples"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics*, ASMS, Washington, D.C., 1977, p. 435
	Smith, D. H.; Christie, W. H. "A Study of the Quantification of SIMS Data"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics*, ASMS, Washington, D.C., 1977, p. 309
Clark, B. R.	Clark, B. R.; Guerin, M. R. "Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes"	*Proc. Toxic Substances in the Air Environment Specialty Conf.*, Cambridge, Mass., Nov. 7–9, 1976
Donohue, D. L.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics*, ASMS, Washington, D.C., 1977, p. 332
Fellows, R. L.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Study of the Solid-State Phase Transformation of $^{249}BkBr_3$ via Absorption Spectroscopic and X-ray Diffraction Techniques"	*Proc. 2nd Int. Conf. Electronic Structure of the Actinides, Wroclaw, Poland, Sept. 13–16, 1976*, J. Mulak, W. Suski, and R. Troć, eds., Ossolineum, 1977, p. 111–16
Franklin, J. C.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Proc. 25th Ann. Conf. on Mass Spectrometry and Allied Topics*, ASMS, Washington D.C., 1977, p. 332
Griest, W. H.	Griest, W. H.; Guerin, M. R. "Influence of Tobacco Type on Smoke Composition"	*Proc. Recent Advances in Tobacco Science*, vol. 3, 31st Tobacco Chemists' Research Conf., Greensboro, N.C., Oct. 5–7, 1977, p. 121–44
Grossman, L. W.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P.; Payne, M. G.;* Grossman, L. W.* "Selective Single Atom Detection in a 10^{19} Atom Background"	*Proc. 3rd Int. Conf. Laser Spectroscopy*, Springer Series in Optical Sciences, vol. 7, Laser Spectroscopy III, J. L. Hall and J. L. Carlsten, eds., Springer-Verlag, New York, 1977, p. 44
Guerin, M. R.	Clark, B. R.; Guerin, M. R. "Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes"	*Proc. Toxic Substances in the Air Environment Specialty Conference*, Cambridge, Mass., Nov. 7–9, 1976
	Griest, W. H.; Guerin, M. R. "Influence of Tobacco Type on Smoke Composition"	*Recent Advances in Tobacco Science*, vol. 3, Proc. 31st Tobacco Chemists' Research Conf., Greensboro, N.C., Oct. 5–7, 1977, p. 121–44

Articles

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Batistoni, D. A.*	Feldman, C.; Batistoni, D. A.* "Simple Spectroscopic Element Detector for Gas Chromatography"	*Anal. Chem.* 49, 2215 (1977)
Bemis, C. E.*	Bemis, C. E.;* Oliver, J. H.;* Eby, R. E.; Halperin, J.* "Thermal-Neutron Capture and Fission Cross Sections and Resonance Integrals for Curium-243"	*Nucl. Sci. Eng.* 63(4), 413 (1977)
Blank, M. L.*	Blank, M. L.;* Rainey, W. T., Jr.; Christie, W. H.; Piantadosi, C.;* Snyder, F.* "Mass Spectral Analysis of a Homologous Series of *S*- and *O*-Alkyl Glycerols"	*Chem. Phys. Lipids* 17, 201 (1976)
Bostick, D. A.	Bostick, D. A.; Talmi, Y.* "Application of the Microwave Emission Spectrometric System as a Silicon-Selective Detector"	*J. Chromatogr. Sci.* 15, 164–68 (1977)
Botts, J. L.	Walker, R. L.; Botts, J. L.; Carter, J. A.; Costanzo, D. A. "Mass Spectrometric Determination of Zirconium from a Resin Bead"	*Anal. Lett.* 10(4), 251–62 (1977)
Braun, T.*	Braun, T.;* Lyon, W. S.; Bujdoso, E.* "Literature Growth and Decay: An Activation Analysis Resume"	*Anal. Chem.* 49, 682A (1977)
Bujdoso, E.*	Braun, T.;* Lyon, W. S.; Bujdoso. E.* "Literature Growth and Decay: An Activation Analysis Resume"	*Anal. Chem.* 49, 682A (1977)
Canada, D. C.	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
Caputo, A. J.*	LaValle, D. E.; Costanzo, D. A.; Lackey, W. J.;* Caputo, A. J.* "The Determination of Defective Particle Fraction in HTGR Fuels"	*Nucl. Technol.* 33, 290–95 (1977)
Carpenter, J. A., Jr.*	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
Carr, P. W.*	Senn, D. R.;* Carr, P. W.;* Klatt, L. N. "Minimization of a Sodium Dithionite Derived Interference in Nitrate Reductase - Methyl Viologen Reactions"	*Anal. Biochem.* 75, 464 (1976)
Carter, J. A.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Anal. Lett.* 10(5), 371–79 (1977)
	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
	Walker, R. L.; Botts, J. L.; Carter, J. A.; Costanzo, D. A. "Mass Spectrometric Determination of Zirconium from a Resin Bead"	*Anal. Lett.* 10(4), 251–62 (1977)
	Carter, J. A.; Donohue, D. L.; Franklin, J. C. "Trace Metal Analysis in Coal by Multielement Isotope Dilution Spark Source Mass Spectrometry"	*Am. Chem. Soc., Div. Fuel Chem. Prepr.* 22(2), 60 (1977)
Caton, J. E.	Griesemer, R. A.;* Nettesheim, P.;* Martin, D. H.;* Caton, J. E. "Quantitative Exposure of Grafted Rat Tracheas to 7,12-Dimethylbenz[*a*]anthracene"	*Cancer Res.* 37, 1266–71 (1977)
	Nettesheim, P.;* Griesemer, R. A.;* Martin, D. H.;* Caton, J. E. "Induction of Prenoplastic and Neoplastic Lesions in Grafted Rat Tracheas Continuously Exposed to Benzo[*a*]pyrene"	*Cancer Res.* 37, 1272–78 (1977)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Christie, W. H.	Blank, M. L.;* Rainey, W. T., Jr.; Christie, W. H.; Piantadosi, C.;* Snyder, F.* "Mass Spectral Analysis of a Homologous Series of *S*- and *O*-Alkyl Glycerols"	*Chem. Phys. Lipids* 17, 201 (1976)
Clark, B. R.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Approaches to Chemical Class Fractionation of Fossil-Derived Materials"	*Am. Chem. Soc., Div. Pet. Chem. Prepr.* 22(2), 811 (1977)
	Clark, B. R.; Ho, C.-h.; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. A.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Jones, A. R.; Guerin, M. R.; Clark, B. R. "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale"	*Anal. Chem.* 49, 1766 (1977)
Costanzo, D. A.	LaValle, D. E.; Costanzo, D. A.; Lackey, W. J.;* Caputo, A. J.* "The Determination of Defective Particle Fraction in HTGR Fuels"	*Nucl. Technol.* 33, 290–95 (1977)
	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
	Walker, R. L.; Botts, J. L.; Carter, J. A.; Costanzo, D. A. "Mass Spectrometric Determination of Zirconium from a Resin Bead"	*Anal. Lett.* 10(4), 251–62 (1977)
Dale, J. M.	Hulett, L. D.; Dale, J. M.; Dunn, H. W.; Murty, P. S.* "Characterization of Corrosion Scale from Nuclear Reactors: Approaching the Whole Problem"	*Anal. Chem.* 48, 1160A (1976)
Donohue, D. L.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Anal. Lett.* 10(5), 371–79 (1977)
	Carter, J. A.; Donohue, D. L., Franklin, J. C. "Trace Metal Analysis in Coal by Multielement Isotope Dilution Spark Source Mass Spectrometry"	*Am. Chem. Soc., Div. Fuel Chem. Prepr.* 22(2), 60 (1977)
Dunn, H. W.	Hulett, L. D.; Dale, J. M.; Dunn, H. W.; Murty, P. S.* "Characterization of Corrosion Scale from Nuclear Reactors: Approaching the Whole Problem"	*Anal. Chem.* 48, 1160A (1976)
Eby, R. E.	Bemis, C. E.;* Oliver, J. H.;* Eby, R. E.; Halperin, J.* "Thermal-Neutron Capture and Fission Cross Sections and Resonance Integrals for Curium-243"	*Nucl. Sci. Eng.* 63(4), 413 (1977)
Epler, J. L.*	Clark, B. R.; Ho, C.-h.; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. A.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Rubin, I. B.; Guerin, M. R.; Hardigree, A. A.;* Epler, J. L.* "Fractionation of Synthetic Crude Oils from Coal for Biological Testing"	*Environ. Res.* 12, 358 (1976)
Feldman, C.	Feldman, C. "The Determination of Traces of Arsenic in Siliceous Materials"	*Anal. Chem.* 49, 825 (1977)
	Feldman, C.; Batistoni, D. A.* "Simple Spectroscopic Element Detector for Gas Chromatography"	*Anal. Chem.* 49, 2215 (1977)
Fellows, R. L.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Etude du Dimorphisme du Bromure de berkelium $^{249}BkBr_3$, par spectrometrie d'absorption et par diffraction des rayons X"	*Rev. Chim. Miner.* 14, 172 (1977)
Fitzgerald, V.*	Rock, C. O.;* Fitzgerald, V.;* Rainey, W. T., Jr.; Snyder, F.* Mass Spectral Identification of *T*-(*O*-Acyl) Hydroxy Fatty Acid Esters in the White Portion of the Rabbit Harderian Gland"	*Chem. Phys. Lipids* 17, 207 (1976)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Franklin, J. C.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	*Anal. Lett.* 10(5), 371-79 (1977)
	Carter, J. A.; Donohue, D. L.; Franklin, J. C. "Trace Metal Analysis in Coal by Multielement Isotope Dilution Spark Source Mass Spectrometry"	*Am. Chem. Soc., Div. Fuel Chem. Prepr.* 22(2), 60 (1977)
Goeckner, N. A.*	Griest, W. H.; Goeckner, N. A.* "Determination of Methyl Chrysenes in a Coal Liquefaction Product"	*Sci. Total Environ.* 8, 187-93 (1977)
Goldstein, G.	Goldstein, G. "Liquid Chromatographic Separation of Plant Phenolics Using Polyethylene Glycol Dimethacrylate Gel"	*J. Chromatogr.* 129, 466 (1976)
	Goldstein, G. "Separation of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography on Cross-Linked Polyvinylpyrrolidone"	*J. Chromatogr.* 129, 61 (1976)
Griesemer, R. A.	Griesemer, R. A.;* Nettesheim, P.;* Martin, D. H.;* Caton, J. E. "Quantitative Exposure of Grafted Rat Tracheas to 7,12-Dimethylbenz[*a*]anthracene"	*Cancer Res.* 37, 1266-71 (1977)
	Nettesheim, P.;* Griesemer, R. A.;* Martin, D. H.;* Caton, J. E. "Induction of Prenoplastic and Neoplastic Lesions in Grafted Rat Tracheas Continuously Exposed to Benzo[*a*]pyrene"	*Cancer Res.* 37, 1272-78 (1977)
Griest, W. H.	Griest, W. H.; Goeckner, N. A.* "Determination of Methyl Chrysenes in a Coal Liquefaction Product"	*Sci. Total Environ.* 8, 187-93 (1977)
	Ho, C.-h.; Griest, W. H.; Guerin, M. R. "Application of the Blind Assay to Biological Activity and Tobacco Smoke Terpenes"	*Anal. Chem.* 48, 2223 (1976)
Guerin, M. R.	Clark, E. R.; Ho, C.-h.; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. R.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Ho, C.-h.; Griest, W. H.; Guerin, M. R. "Application of the Blind Assay to Biological Activity and Tobacco Smoke Terpenes"	*Anal. Chem.* 48, 2223 (1976)
	Jones, A. R.; Guerin, M. R.; Clark, B. R. "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale"	*Anal. Chem.* 49, 1766 (1977)
	Rubin, I. B.; Guerin, M. R.; Hardigree, A. A.;* Epler, J. L.* "Fractionation of Synthetic Crude Oils from Coal for Biological Testing"	*Environ. Res.* 12, 358 (1976)
	Rubin, I. B.; Guerin, M. R. "Chemical Evaluation of the Beeswax Pellet Implantation Bioassay Model for Studies of Environmental Carcinogens"	*J. Natl. Cancer Inst.* 58, 641 (1977)
Haire, R. G.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Etude du Dimorphisme du Bromure de Berkelium $^{249}BkBr_3$ par spectrometrie d'absorption et par diffraction des rayons X"	*Rev. Chim. Miner.* 14, 172 (1977)
Halperin, J.*	Bemis, C. E.;* Oliver, J. H.;* Eby, R. E.; Halperin, J.* "Thermal-Neutron Capture and Fission Cross Sections and Resonance Integrals for Curium-243"	*Nucl. Sci. Eng.* 63(4), 413 (1977)
Hardigree, A. A.	Clark, B. R.; Ho, C.-h; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. A.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Rubin, I. B.; Guerin, M. R.; Hardigree, A. A.;* Epler, J. L.* "Fractionation of Synthetic Crude Oils from Coal For Biological Testing"	*Environ. Res.* 12, 358 (1976)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Ho, C.-h.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Approaches to Chemical Class Fractionation of Fossil-Derived Materials	*Am. Chem. Soc., Div. Pet. Chem. Prepr.* 22(2), 811 (1977)
	Clark, B. R.; Ho, C.-h.; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. A.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Ho, C.-h.; Griest, W. H.; Guerin, M. R. "Application of the Blind Assay to Biological Activity and Tobacco Smoke Terpenes"	*Anal. Chem.* 48, 2223 (1976)
Hulett, L. D.	Hulett, L. D.; Dale, J. M.; Dunn, H. W.; Murty, P. S.* "Characterization of Corrosion Scale from Nuclear Reactors: Approaching the Whole Problem"	*Anal. Chem.* 48, 1160A (1976)
Hurst, G. S.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P. "One-Atom Detection Using Ionization Spectroscopy"	*Phys. Rev.* 15, 2283 (1977)
	Nayfeh, M. H.;* Hurst, G. S.;* Payne, M. G.;* Young, J. P. "Collisional Line Broadening Using Laser Excitation and Ionization"	*Phys. Rev. Lett.* 39, 604 (1977)
	Young, J. P.; Hurst, G. S.;* Nayfeh, M. H.* "Specific Detection of Single Atoms by Resonance Ionization Spectroscopy"	*J. Appl. Phys. Lett.* 30, 229 (1977)
Issigonis, M. J.	Kesler, S. E.;* Sutter, J. F.;* Issigonis, M. J.;* Jones, L. M.;* Walker, R. L. "Evolution of Porphyry Copper Mineralization in an Oceanic Island Arc: Panama"	*Econ. Geol.* 72, 1142–53 (1977)
Jones, A. R.	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Approaches to Chemical Class Fractionation of Fossil-Derived Materials"	*Am. Chem. Soc., Div. Pet. Chem. Prepr.* 22(2), 811 (1977)
	Jones, A. R.; Guerin, M. R.; Clark, B. R. "Preparative-Scale Liquid Chromatographic Fractionation of Crude Oils Derived from Coal and Shale"	*Anal. Chem.* 49, 1766 (1977)
Jones, L. M.*	Kesler, S. E.;* Sutter, J. F.;* Issigonis, M. J.;* Jones, L. M.;* Walker, R. L. "Evolution of Porphyry Copper Mineralization in an Oceanic Island Arc: Panama"	*Econ. Geol.* 72, 1142–53 (1977)
	Kesler, S. E.;* Sutter, J. F.;* Jones, L. M.;* Walker, R. L. "Early Cretaceous Basement Rocks in Hispaniola"	*Geol.* 5, 245 (1976)
	Whitney, J. A.;* Jones, L. M.;* Walker, R. L. "Age and Origin of the Stone Mountain Granite"	*Geol. Soc. Am. Bull.* 87, 1067 (1976)
Kesler, S. E.*	Kesler, S. E.;* Sutter, J. F.;* Issigonis, M. J.;* Jones, L. M.;* Walker, R. L. "Evolution of Porphyry Copper Mineralization in an Oceanic Island Arc: Panama"	*Econ. Geol.* 72, 1142–53 (1977)
	Kesler, S. E.;* Sutter, J. F.;* Jones, L. M.;* Walker, R. L. "Early Cretaceous Basement Rocks in Hispaniola"	*Geol.* 5, 245 (1976)
Klatt, L. N.	Klatt, L. N. "A Universal Detector for Liquid Chromatography Based upon Dielectric Constant"	*Anal. Chem.* 48, 1845 (1976)
	Senn, D. R.;* Carr, P. W.;* Klatt, L. N. "Minimization of a Sodium Dithionite Derived Interference in Nitrate Reductase–Methyl Viologen Reactions"	*Anal. Biochem.* 75, 464 (1976)
Lackey, W. J.*	LaValle, D. E.; Costanzo, D. A.; Lackey, W. J.;* Caputo, A. J.* "The Determination of Defective Particle Fraction in HTGR Fuels"	*Nucl. Technol.* 33, 290–95 (1977)
LaValle, D. E.	LaValle, D. E.; Costanzo, D. A.; Lackey, W. J.;* Caputo, A. J.* "The Determination of Defective Particle Fraction in HTGR Fuels"	*Nucl. Technol.* 33, 290–95 (1977)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Lee, D. A.	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
Lyon, W. S.	Braun, T.,* Lyon, W. S.; Bujdoso, E.* "Literature Growth and Decay: An Activation Analysis Resume"	*Anal. Chem.* 49, 682A (1977)
	Lyon, W. S. "Scholars Through Space"	*Radiochem. Radioanal. Lett.* 26, 161 (1976)
	Lyon, W. S. "Solutions at the Science Society Interface"	*Radiochem. Radioanal. Lett.* 28, 1 (1977)
	Lyon, W. S. "Small Report from the Shotgun Uranium Hunt"	*Radiochem. Radioanal. Lett.* 29, 223 (1977)
	Lyon, W. S. "Oil from Coal via Old Papers"	*Radiochem. Radioanal. Lett.* 30, 325 (1977)
Maddox, W. L.	Maddox, W. L.; Mamantov, G.* "Analysis of Cigarette Smoke by Fourier Transform Infrared Spectroscopy"	*Anal. Chem.* 49, 331 (1977)
Mamantov, G.*	Maddox, W. L.; Mamantov, G.* "Analysis of Cigarette Smoke by Fourier Transform Infrared Spectroscopy"	*Anal. Chem.* 49, 331 (1977)
	Manning, D. L.; Mamantov, G.* "Electrochemical Studies of Oxide Ions and Related Species in Molten Fluorides"	*J. Electrochem. Soc.* 124, 480 (1977)
Manning, D. L.	Manning, D. L.; Mamantov, G.* "Electrochemical Studies of Oxide Ions and Related Species in Molten Fluorides"	*J. Electrochem. Soc.* 124, 480 (1977)
Martin, D. H.*	Griesemer, R. A.;* Nettesheim, P.;* Martin, D. H.;* Caton, J. E. "Quantitative Exposure of Grafted Rat Tracheas to 7,12-Dimethylbenz[*a*]anthracene"	*Cancer Res.* 37, 1266–71 (1977)
	Nettesheim, P.;* Griesemer, R. A.;* Martin, D. H.;* Caton, J. E. "Induction of Preneoplastic and Neoplastic Lesions in Grafted Rat Tracheas Continuously Exposed to Benzo[*a*]pyrene"	*Cancer Res.* 37, 1272–78 (1977)
Murty, P. S.*	Hulett, L. D.; Dale, J. M.; Dunn, H. W.; Murty, P. S.* "Characterization of Corrosion Scale from Nuclear Reactors: Approaching the Whole Problem"	*Anal. Chem.* 48, 116[illegible]A (1976)
Nayfeh, M. H.*	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P. "One-Atom Detection Using Ionization Spectroscopy"	*Phys. Rev.* 15, 2283 (1977)
	Nayfeh, M. H.;* Hurst, G. S.;* Payne, M. G.;* Young, J. P. "Collisional Line Broadening Using Laser Excitation and Ionization"	*Phys. Rev. Lett.* 39, 604 (1977)
	Young, J. P.; Hurst, G. S.;* Nayfeh, M. H.* "Specific Detection of Single Atoms by Resonance Ionization Spectroscopy"	*J. Appl. Phys. Lett.* 30, 229 (1977)
Nettesheim, P.*	Griesemer, R. A.;* Nettesheim, P.;* Martin, D. H.;* Caton, J. E. "Quantitative Exposure of Grafted Rat Tracheas to 7,12-Dimethylbenz[*a*]anthracene"	*Cancer Res.* 37, 1266–71 (1977)
	Nettesheim, P.;* Griesemer, R. A.;* Martin, D. H.;* Caton, J. E. "Induction of Preneoplastic and Neoplastic Lesions in Grafted Rat Tracheas Continuously Exposed to Benzo[*a*]pyrene"	*Cancer Res.* 37, 1272–78 (1977)
Oliver, J. H.*	Bemis, C. E.;* Oliver, J. H.;* Eby, R. E.; Halperin, J.* "Thermal-Neutron Capture and Fission Cross Sections and Resonance Integrals for Curium-243"	*Nucl. Sci. Eng.* 63(4), 413 (1977)
Payne, M. G.*	Nayfeh, M. H.;* Hurst, G. S.;* Payne, M. G.;* Young, J. P. "Collisional Line Broadening Using Laser Excitation and Ionization"	*Phys. Rev. Lett.* 39, 604 (1977)
Peterson, J. R.*	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Etude du Dimorphisme du Bromure de berkelium $^{249}BkBr_3$, par spectrometrie d'absorption et par diffraction des rayons X"	*Rev. Chim. Miner.* 14, 172 (1977)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Piantadosi, C.	Blank, M. L.;* Rainey, W. T., Jr.; Christie, W. H.; Piantadosi, C.;* Snyder, F.* "Mass Spectral Analysis of a Homologous Series of *S*- and *O*-Alkyl Glycerols"	*Chem. Phys. Lipids* 17, 201 (1976)
Rainey, W. T., Jr.	Blank, M. L.;* Rainey, W. T., Jr.; Christie, W. H.; Piantadosi, C.;* Snyder, F.* "Mass Spectral Analysis of a Homologous Series of *S*- and *O*-Alkyl Glycerols"	*Chem. Phys. Lipids* 17, 201 (1976)
	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr., Canada, D.C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
	Rock, C. O.;* Fitzgerald, V.;* Rainey, W. T., Jr.; Snyder, F.* "Mass Spectral Identification of *T*-(*O*-Acyl) Hydroxy Fatty Acid Esters in the White Portion of the Rabbit Harderian Gland"	*Chem. Phys. Lipids* 17, 207 (1976)
Rock, C. O.*	Rock, C. O.,* Fitzgerald, V.;* Rainey, W. T., Jr.; Snyder, F.* "Mass Spectral Identification of *T*-(*O*-Acyl)- Hydroxy Fatty Acid Esters in the White Portion of the Rabbit Harderian Gland"	*Chem. Phys. Lipids* 17, 207 (1976)
Rubin, I. B.	Clark, B. R., Ho, C.-h.; Rubin, I. B.; Guerin, M. R.; Epler, J. L.;* Hardigree, A. A.* "Testing for Health Hazards in Coal Liquids"	*Chem. Eng. Prog. Tech. Manual* 3, 37 (1977)
	Rubin, I. B.; Guerin, M. R.; Hardigree, A. A.;* Epler, J. L.* "Fractionation of Synthetic Crude Oils from Coal for Biological Testing"	*Environ. Res.* 12, 358 (1976)
	Rubin, I. B., Guerin, M. R. "Chemical Evaluation of the Beeswax Pellet Implantation Bioassay Model for Studies of Environmental Carcinogens"	*J. Natl. Cancer Inst.* 58, 641 (1977)
Senn, D. R.*	Senn, D. R.;* Carr, P. W.;* Klatt, L. N. "Minimization of a Sodium Dithionite Derived Interference in Nitrate Reductase–Methyl Viologen Reactions"	*Anal. Biochem.* 75, 464 (1976)
Snyder, F.*	Blank, M. L.;* Rainey, W. T., Jr.; Christie, W. H. Piantadosi, C.;* Snyder, F.* "Mass Spectral Analysis of a Homologous Series of *S*- and *O*-Alkyl Glycerols"	*Chem. Phys. Lipids* 17, 201 (1976)
	Rock, C. O.;* Fitzgerald, V.;* Rainey, W. T., Jr.; Snyder, F.* "Mass Spectral Identification of *T*-(*O*-Acyl) Hydroxy Fatty Acid Esters in the White Portion of the Rabbit Harderian Gland"	*Chem. Phys. Lipids* 17, 207 (1976)
Stinton, D. P.	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A., Jr.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from High-Temperature Gas-Cooled Reactor Fuel Particle Preparation Processes by Mass Spectrometry"	*Nucl. Technol.* 34(1), 89–97 (1977)
Sutter, J. F.*	Kesler, S. E.;* Sutter, J. F.;* Issigonis, M. J.;* Jones, L. M.;* Walker, R. L. "Evolution of Porphyry Copper Mineralization in an Oceanic Island Arc: Panama"	*Econ. Geol.* 72, 1142–53 (1977)
	Kesler, S. E.;* Sutter, J. F.,* Jones, L. M.;* Walker, R. L. "Early Cretaceous Basement Rocks in Hispaniola"	*Geol.* 5, 245 (1976)
Talmi, Y.*	Bostick, D. A.; Talmi, Y.* "Application of the Microwave Emission Spectrometric System as a Silicon-Selective Detector"	*J. Chromatogr. Sci.* 15, 164–68 (1977)
Walker, R. L.	Kesler, S. E.;* Sutter, J. F.;* Issigonis, M. J.;* Jones, L. M.;* Walker, R. L. "Evolution of Porphyry Copper Mineralization in an Oceanic Island Arc: Panama"	*Econ. Geol.* 72, 1142–53 (1977)
	Kesler, S. E.;* Sutter, J. F.;* Jones, L. M.;* Walker, R. L. "Early Cretaceous Basement Rocks in Hispaniola"	*Geol.* 5, 245 (1976)
	Walker, R. L.; Botts, J. L.; Carter, J. A.; Costanzo, D. A. "Mass Spectrometric Determination of Zirconium from a Resin Bead"	*Anal. Lett.* 10(4), 251–62 (1977)
	Whitney, J. A.;* Jones, L. M.;* Walker, R. L. "Age and Origin of the Stone Mountain Granite"	*Geol. Soc. Am. Bull.* 87, 1067 (1976)

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED IN
Whitney, J. A.*	Whitney, J. A.;* Jones, L. M.;* Walker, R. L. "Age and Origin of the Stone Mountain Granite"	*Geol. Soc. Am. Bull.* 87, 1067 (1976)
Young, J. P.	Hurst, G. S.;* Nayfeh, M. H.;* Young, J. P. "One-Atom Detection Using Ionization Spectroscopy"	*Phys. Rev.* 15, 2283 (1977)
	Nayfeh, M. H.;* Hurst, G. S.;* Payne, M. G.;* Young, J. P. "Collisional Line Broadening Using Laser Excitation and Ionization"	*Phys. Rev. Lett.* 39, 604 (1977)
	Peterson, J. R.;* Fellows, R. L.;* Young, J. P.; Haire, R. G.* "Etude du Dimorphisme du Bromure de berkelium ^{249}BkBr$_3$ par spectrometrie d'absorption et par diffraction des rayons X"	*Rev. Chim. Miner.* 14, 172 (1977)
	Young, J. P.; Hurst, G. S.;* Nayfeh, M. H.* "Specific Detection of Single Atoms by Resonance Ionization Spectroscopy"	*J. Appl. Phys. Lett.* 30, 229 (1977)

Thesis

AUTHOR	AUTHOR(S) AND TITLE	PUBLISHED AS
Crosmun, S. T.	Crosmun, S. T. "Part I: Application of Pulse Polarography and Pulse Anodic Stripping to the Determination of Selected Heavy Metals in Natural Waters. Part II: Application of Controlled Potential Coulometric Techniques to the Determination of Uranium"	Ph.D. thesis, University of Tennessee, Knoxville (1977)

REPORTS

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Bradley, D. J.*	Leitnaker, J. M.;* Franklin, J. C.; Potter, G. A.;* Bradley, D. J.;* Laing, W. R. "The Composition of ETA Carbide in Hastelloy N After Aging 10,000 Hours at 815°C	ORNL-5340 (1977)
Canada, D. C.	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)
Carpenter, J. A.*	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)
Carter, J. A.	Carter, J. A. "Analytical Chemistry Division Research and Development Summary for January 1977: Mass and Emission Spectrometry Section"	ORNL/CF-77/23 (Feb. 1, 1977)
	Carter, J. A. "Analytical Chemistry Division Research and Development Summary for May 1977: Mass and Emission *Spectrometry Section*"	ORNL/CF-77/308 (June 1, 1977)
	Carter, J. A. "Analytical Chemistry Division Research and Development Summary for September 1977: Mass and Emission Spectrometry Section"	ORNL/CF-77/414 (Oct. 1, 1977)
	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)
Christie, W. H.	Rainey, W. T., Jr.; Christie, W. H.; Pritchard, C. A.; Lijinsky, W.* "Mass Spectra of *N*-Nitroso Compounds"	ORNL/TM-5500 (September 1977)
	Smith, D. H.; Christie, W. H. "Investigation of Quantification of SIMS Data: Analysis of NBS Glass and Iron Standards"	ORNL/TM-5728 (June 1977)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Corbin, L. T.	Corbin, L. T. "Analytical Chemistry Division Research and Development Summary for November 1976: Analytical Services Section"	ORNL/CF-76/430 (Dec. 1, 1976)
	Corbin, L. T. "Analytical Chemistry Division Research and Development Summary for March 1977: Analytical Services Section"	ORNL/CF-77/181 (Apr. 1, 1977)
	Corbin, L. T. "Analytical Chemistry Division Monthly Report for July 1977: Analytical Services Section"	ORNL/CF-77/372 (Aug. 1, 1977)
	Corbin, L. T. "Quality Assurance Report, Analytical Chemistry Division, July Through December 1976"	ORNL/CF-76/454 (Jan. 1, 1977)
	Corbin, L. T. "Quality Assurance Report, Analytical Chemistry Division, January Through June 1977"	ORNL/CF-77/336 (July 1, 1977)
Costanzo, D. A.	Lee, D. A., Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr., Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)
Dickens, J. K.*	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121 (July 1977)
Emery, J. F.	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121 (July 1977)
Franklin, J. C.	Leitnaker, J. M.;* Franklin, J. C.; Potter, G. A.;* Bradley, D. J.;* Laing, W. R. "The Composition of ETA Carbide in Hastelloy N After Aging 10,000 Hours at 815°C"	ORNL-5340 (1977)
Freestone, R. M.*	Dickens, J. K.;* Emery, J. F. Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121
Griest, W. H.	Griest, W. H.; Quincy, R. B.; Guerin, M. R. "Selected Constituents in the Smoke of Domestic Low Tar Cigarettes"	ORNL/TM-6144 (November 1977)
Guerin, M. R.	Griest, W. H.; Quincy, R. B.; Guerin, M. R. "Selected Constituents in the Smoke of Domestic Low Tar Cigarettes"	ORNL/TM-6144 (November 1977)
	Guerin, M. R. "Analytical Chemistry Division Research and Development Summary for February 1977: Bio/Organic Analysis Section"	ORNL/CF-77/74 (Mar. 1, 1977)
	Guerin, M. R. "Analytical Chemistry Division Research and Development Summary for June 1977: Bio/Organic Analysis Section"	ORNL/CF-77/344 (July 1, 1977)
	Guerin, M. R. "Analytical Chemistry Division Research and Development Summary for October 1977: Bio/Organic Analysis Section"	ORNL/CF-77/468 (Nov. 1, 1977)
Judd, M. S.*	Judd, M. S.;* Van Cleve, J. E., Jr.;* Rainey, W. T., Jr. "Recovery of Perchloroethylene Scrubbing Medium Generated in the Refabrication of High-Temperature Gas-Cooled Reactor Fuel"	ORNL/TM-5620 (November 1976)
Laing, W. R.	Leitnaker, J. M.;* Franklin, J. C.; Potter, G. A.;* Bradley, D. J.;* Laing, W. R. "The Composition of ETA Carbide in Hastelloy N After Aging 10,000 Hours at 815°C"	ORNL-5340 (1977)
Lee, D. A.	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)

AUTHOR	AUTHOR(S) AND TITLE	REPORT NO. AND DATE
Leitnaker, J. M.*	Leitnaker, J. M.;* Franklin, J. C.; Potter, G. A.;* Bradley D. J.;* Laing, W. R. "The Composition of ETA Carbide in Hastelloy N After Aging 10,000 Hours at 815°C"	ORNL-5340 (1977)
Lijinsky, W.	Rainey, W. T., Jr.; Christie, W. H.; Pritchard, C. A.; Lijinsky, W.* "Mass spectra of *N*-Nitroso Compounds"	ORNL/TM-5500 (September 1977)
Love, T. A.*	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ONRL/NUREG/TM-121 (July 1977)
Lyon, W. S.	Lyon, W. S. "Analytical Chemistry Division Research and Development Summary for December 1976: Analytical Methodology Section"	ORNL/CF-76/451 (Dec. 17, 1976)
	Lyon, W. S. "Analytical Chemistry Division Research and Development Summary – August 1977"	ORNL/CF-77/392 (1977)
	Lyon, W. S. "Analytical Chemistry Division Research and Development Summary – April 1977"	ORNL/CF-77/289 (1977)
McConnell, J. W.*	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121 (July 1977)
Northcutt, K. J.	Dickens, J. K;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121 (July 1977)
Peele, R. W.*	Dickens, J. K.;* Emery, J. F.; Freestone, R. M.;* Love, T. A.;* McConnell, J. W.;* Northcutt, K. J.; Peele, R. W.* "Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1977"	ORNL/NUREG/TM-121 (July 1977)
Potter, G. A.*	Leitnaker, J. M.;* Franklin, J. C.; Potter, G. A.;* Bradley, D. J.;* Laing, W. R. "The Composition of ETA Carbide in Hastelloy N After Aging 10,000 Hours at 815°C	ORNL-5340 (1977)
Pritchard, C. A.	Rainey, W. T., Jr.; Christie, W. H.; Pritchard, C. A.; Lijinsky, W.* "Mass Spectra of *N*-Nitroso Compounds"	ORNL/TM-5500 (September 1977)
	Walker, R. L.; Pritchard, C. A. "Report of Foreign Travel to Seibersdorf and Vienna, Austria"	ORNL/FTR-289 (1977)
Quincy, R. B.	Griest, W. H.; Quincy, R. B.; Guerin, M. R. "Selected Constituents in the Smoke of Domestic Low Tar Cigarettes"	ORNL/TM-6144 (November 1977)
Rainey, W. T., Jr.	Judd, M. S.;* Van Cleve, J. E., Jr.;* Rainey, W. T., Jr. "Recovery of Perchloroethylene Scrubbing Medium Generated in the Refabrication of High-Temperature Gas-Cooled Reactor Fuel"	ORNL/TM-5620 (November 1976)
	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)
	Rainey, W. T., Jr.; Christie, W. H.; Pritchard, C. A.; Lijinsky, W.* "Mass Spectra of *N*-Nitroso Compounds"	ORNL/TM-5500 (September 1977)
Smith, D. H.	Smith, D. H.; Christie, W. H. "Investigation of Quantification of SIMS Data: Analysis of NBS Glass and Iron Standards"	ORNL/TM-5728 (June 1977)
Stinton, D. P.*	Lee, D. A.; Costanzo, D. A.; Stinton, D. P.;* Carpenter, J. A.;* Rainey, W. T., Jr.; Canada, D. C.; Carter, J. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL/TM-5579 (1976)

AUTHOR	AUTHOR(S) AND TITLE*	REPORT NO. AND DATE
Stokely, J. R.	Stokely, J. R. "Analytical Chemistry Division Summary Report: Nuclear and Radiochemical Analysis Section"	ORNL/CF-77/488 (1977)
Van Cleve, J. E., Jr.*	Judd, M. S.;* Van Cleve, J. E., Jr.;* Rainey, W. T., Jr. "Recovery of Perchloroethylene Scrubbing Medium Generated in the Refabrication of High-Temperature Gas-Cooled Reactor Fuel"	ORNL/TM-5620 (November 1976)
Walker, R. L.	Walker, R. L., Pritchard, C. A. "Report of Foreign Travel to Seibersdorf and Vienna, Austria"	ORNL/FTR-289 (1977)

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.

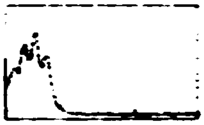
At Meetings of Professional Societies, Conferences, and the Like

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Canada, D. C.	Canada, D. C.; Rainey, W. T., Jr. "Mass Spectrometry R&D for Organic Analysis"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 - Apr. 1, 1977
Carpenter, J. A., Jr.*	Carpenter, J. A., Jr.;* Lee, D. A. "Kinetics and Mechanisms of the Carbonization of Uranium-Loaded Weak Acid Resin HTGR Fuel Microspheres"	79th Annual Meeting of American Ceramic Society, Chicago, Ill., Apr. 27, 1977
Carter, J. A.	Carter, J. A., Donohue, D. L.; Franklin, J. C. "Trace Metal Analyses in Coal by Multielement Isotope Dilution Spark Source Mass Spectrometry"	American Chemical Society Meeting, Chicago, Ill., August 1977
	Carter, J. A., Walker, R. L. "Preparation and Isotopic Analysis of U and Pu for Safeguards"	21st Annual Gatlinburg Conference, Gatlinburg, Tenn., Oct. 4 - 6, 1977
Caton, J. E.	Caton, J. E. "Immunotechnology in Analytical Chemistry"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 - Apr. 1, 1977
	Caton, J. E. "Use of Immunobiological Reagents in Analytical Chemistry"	ORAU Traveling Lecture Series, Grambling State University, Grambling, La., and University of Alabama, University, Ala., Apr. 14 - 15, 1977
	Caton, J. E. "Cigarette Smoke Inhalation Dosimetry"	Invited lecture, ORAU Monthly Seminar, Oak Ridge, Tenn., Apr. 26, 1977

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Christie, W. H.	Christie, W. H. "The Ion Microprobe Mass Analyzer – A New Technique for Surface Analysis"	ORAU Traveling Lecture Series, Atlanta University, Atlanta, Ga., Feb. 18, 1977
	Christie, W. H.; Kollie, T. G.* "An Ion Microprobe Investigation of the High Temperature Decalibration of AL203-Insulated Pt-Rh Thermocouples"	25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 29 - June 3, 1977
	Christie, W. H.; Smith, D. H.; Eby, R. E. "Research, Development and Applications in Ion Microprobe Mass Analysis"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Clark, B. R.	Clark, B. R.; Guerin, M. R. "Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Processes"	Air Pollution Control Association Conference on Toxic Substances in the Air Environment, Cambridge, Mass., Nov. 8–9, 1976
	Clark, B. R.; Guerin, M. R. "Chemical Characterization of Organic Constituents in Oil Shale Materials"	2nd ERDA Meeting and Workshop on Oil Shale Environmental Research, Richland, Wash., Nov. 1–2, 1977
	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Approaches to Chemical Class Analyses of Fossil Derived Materials"	American Chemical Society Meeting, New Orleans, La., Mar. 27–Apr. 1, 1977
	Clark, B. R.; Ho, C.-h.; Jones, A. R. "Approaches to Chemical Class Fractionation of Fossil Derived Materials"	Symposium on Analytical Chemistry of Tar Sands and Oil Shale, American Chemical Society Meeting, New Orleans, La. Mar. 20, 1977
	Clark, B. R.; Kubota, H.; Griest, W. H. "Polynuclear Aromatic Isolates from Fossil Fuels Materials"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Dale, J. M.	Dale, J. M.; Hulett, L. D. "The Effect of Firing on Co-Mo Supported Catalysts; Comparison of the Results of an ESCA Study with Those of Other Methods"	29th Annual Southeast Regional Meeting of the American Chemical Society, Tampa, Fla., Nov. 9–11, 1977
Donohue, D. L.	Donohue, D. L.; Carter, J. A.; Franklin, J. C. "Separated Isotopes as Internal Standards in Spark Source Mass Spectrometry"	25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 29 - June 3, 1977
Dyer, F. F.	Dyer, F. F. "Activation Analysis in Criminalistics – A Look at the Past and a Peek at the Future with Emphasis on the Human Hair Problem"	Seminar - University of Florida, Department of Nuclear Engineering Sciences, Gainesville, Fla., Feb. 17, 1977
	Dyer, F. F.; Wichner, R. P.;* Malinauskas, A. P.* "A Study of Radionuclides in the Peach Bottom HTGR Primary Circuit During Core 2 Operation"	American Nuclear Society 19th Annual Meeting, New York, June 12–17, 1977
Eldridge, J. S.	Eldridge, J. S.; Lyon, W. S.; Oakes, T. W.* "Planning for Unplanned Releases"	Symposium on the Monitoring of Radioactive Airborne and Liquid Releases from Nuclear Facilities, Portoroz, Yugoslavia, Sept. 5–9, 1977
	Eldridge, J. S.; Oakes, T. W.;* Turner, J. E.* "A Rapid Method for the Determination of Iodine-131 Concentration in Milk Due to Fallout"	Health Physics Society Annual Meeting, Atlanta, Ga., July 3–8, 1977
	Eldridge, J. S.; Oakes, T. W.;* Pruitt, M. E. "Radioactive Pollutant Determinations Using Gamma-Ray Spectroscopy"	1977 American Industrial Hygiene Conference, New Orleans, La., May 22–27, 1977

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Feldman, C.	Feldman, C.; Jenkins, R. A.; Batistoni, D. A.;* Horton, A. D. "Arc Emission Detector for Gas Chromatographic Analysis"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Fellows, R. L.*	Fellows, R. L.;* Peterson, J. R.;* Young, J. P.; Haire, R. G.* "Transcurium Element Oxyhalides – Their Synthesis and and Stud	173rd American Chemical Society, New Orleans, La., Mar. 20–25, 1977
	Fellows, R. L.;* Peterson, J. R.;* Young, J. P.; Haire, R. G.* "The First Preparation of an Einsteinium(II) Compound, $EsCl_2$"	13th Rare Earth Research Conference, Ogleby Park, Wheeling, W. Va., Oct. 16–20, 1977
Franklin, J. C.	Franklin, J. C.; Donohue, D. L. "Multielement Analysis by Spark Source Mass Spectrometry"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Fuller, E. L.*	Fuller, E. L.;* Hulett, L. D.; Dale, J. M. "Chemical and Physical Characterization of a Cobalt-Molybdate Catalyst"	9th American Chemical Society Central Regional Meeting, Charleston, W. Va., Oct. 12–14, 1977
Goldberg, G.	Goldberg, G. "Testing of Coatings for the Nuclear Industry"	173rd American Chemical Society Meeting, Division of Organic Coatings and Plastics Chemistry, New Orleans, La., Mar. 20–25, 1977
Goldstein, G.	Goldstein, G.; Mamantov, G.;* Wehry, E. L.;* Kemmerer, R. R.;* Hinton, E. R.;* Stroupe, R. C.* "Characterization of Mixtures of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography and Matrix Isolation Spectroscopy"	American Chemical Society Meeting, New Orleans, La., Mar. 27–Apr. 1, 1977
	Goldstein, G.; Mamantov, G.;* Wehry, E. L.;* Kemmerer, R. R.;* Hinton, E. R.;* Stroupe, R. C.* "Characterization of Synthetic Fuels by Liquid Chromatography and Matrix Isolation Spectroscopy"	Pittsburgh Conference, Cleveland, Ohio, Mar. 1–4, 1977
Griest, W. H.	Griest, W. H. "Polyaromatic Hydrocarbons"	HTGR Fuel Development Program Seminar, ORNL, Oak Ridge, Tenn., Mar. 16, 1977
	Griest, W. H.; Guerin, M. R. "Influence of Tobacco Type on Smoke Composition"	31st Tobacco Chemists' Research Conference, Greensboro, N.C., Oct. 5–7, 1977
	Griest, W. H.; Kubota, H.; Eatherly, W. P.* "Characterization of PAH-Containing Fugitive Emissions from a Graphite Production Operation"	ORNL Workshop on Exposure to Polynuclear Aromatic Hydrocarbons in Coal Conversion, ORNL, Oak Ridge, Tenn., Mar. 9–11, 1977
Guerin, M. R.	Guerin, M. R. "Polynuclear Aromatic Hydrocarbons Associated with Synfuels Technologies"	U.S.-Japan Cooperative Cancer Research Program Conference, New Orleans, La., Jan. 23–26, 1977
	Guerin, M. R. "Energy Sources of Polycyclic Aromatic Hydrocarbons"	Conference on Polycyclic Hydrocarbon Carcinogenesis, New Orleans, La., January 1977
	Guerin, M. R.; Epler, J. L.;* Clark, B. R.; Griest, W. H. "Polycyclic Aromatic Hydrocarbon Character of Synthetic Crudes"	2nd International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle Columbus Laboratories, Columbus, Ohio, Sept. 28–30, 1977

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Haire, R. G.*	Haire, R. G.;* Young, J. P., Peterson, J. R.,* Fellows, R. L.* "Absorption Spectrophotometric and X-ray Diffraction Evidence for Mixed-Valence Compounds in Anhydrous Halides of Lanthanide-Actinide (Cf, Es) Mixtures"	13th Rare Earth Research Conference, Oglebay Park, Wheeling, W. Va., Oct. 16–20, 1977
Holmberg, R. W.	Holmberg, R. W.; Yeatts, L. B. "Particle Size Determinations for Inhalation Bioassay"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 – Apr. 1, 1977
Hulett, L. D.	Hulett, L. D. "Scanning Electron Microscopy"	Invited lecture, ORAU Special Training Division Programs, Oak Ridge, Tenn., Jan. 19 and July 26, 1977
	Hulett, L. D.; Dale, J. M.; Dunn, H. W., Ball, F. L. "Electron and X-ray Physics Methods and Their Applications to Energy-Related Problems"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 – Apr. 1, 1977
Hurst, G. H.*	Hurst, G. H.;* Nayfeh, M. H.;* Young, J. P. "A Laser *Technique for the Detection of Single Atoms*"	Invited Seminar, Los Alamos *Scientific Laboratory*, Albuquerque, N.M., Apr. 20, 1977
Jenkins, R. A.	Jenkins, R. A. "Inhalation Bioassay Monitoring"	Tobacco Working Group Meeting, Bethesda, Md., Mar. 16, 1977
	Jenkins, R. A. "Arc Emission Detector for Gas Chromatographic Analysis"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 Apr. 1, 1977
	Jenkins, R. A. "Inhalation Bioassay Monitoring"	Tobacco Working Group Meeting, Bethesda, Md., Mar. 16, 1977
	Jenkins, R. A. "Inhalation Bioassay Methods for Tobacco Smoke"	Invited lecture, ORAU Monthly Seminar, Oak Ridge, Tenn., Apr. 26, 1977
Jones, A. R.	Jones, A. R. "Gel Chromatographic Class Fractionation of Organic Mixtures"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 Apr. 1, 1977
	Jones, A. R. "A Preparative-Scale Fractionation of Fuels Derived from Coal and Shale"	CONFAB '77, Saratoga, Wyo., July 26 29, 1977
Klatt, L. N.	Klatt, L. N. "Multicomponent Detection in Liquid Chromatography"	Great Lakes Regional American Chemical Society Meeting, Stevens Point, Wis., June 6 8, 1977
	Klatt, L. N. "Rapid Scan Spectrometry Applied to Chemical Analysis"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 Apr. 1, 1977
	Klatt, L. N. "Simultaneous Multiwavelength Detection in Liquid Chromatography"	National American Chemical Society Meeting, New Orleans, La. Mar. 20 25, 1977
Kubota, H.	Kubota, H. "Quantitative Routine Analysis for BaP in Tobacco Condensate and Coal Processing Samples"	11th Great Lakes Regional American Chemical Society Meeting, Stevens Point, Wis., June 6 8, 1977
Laing, W. R.	Laing, W. R.; Stanton, J. S.* "Interactive Computer System for Improved Data Management"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30 Apr. 1, 1977



AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
Lee, D. A.	Lee, D. A. "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes by Mass Spectrometry"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Lyon, W. S.	Lyon, W. S. "Detection of Uranium in Sediments by Neutron Activation at Oak Ridge"	NURE-NSSR Technical Coordinating Committee Meeting, Technical Exchange Session, LASL, Los Alamos, N.M., Feb. 2–3, 1977
	Lyon, W. S. "Nuclear Methods in Coal Combustion Research"	3rd International Conference on Nuclear Methods in Environmental and Energy Research, University of Missouri, Columbia, Mo., Oct. 10–12, 1977
	Lyon, W. S. "Presentation of Hevesy Award"	3rd International Conference on Nuclear Methods in Environmental and Energy Research, University of Missouri, Columbia, Mo., Oct. 10–12, 1977
Moneyhun, J. H.	Moneyhun, J. H.; Higgins, C. E.; Stokley, J. R. "Evaluation of the Process and Instruments Corporations' Smoke Exposure Machine (SEM II)"	31st Tobacco Chemists' Research Conference, Greensboro, N.C., Oct. 5–7, 1977
Nayfeh, M. H.*	Nayfeh, M. H.;* Hurst, G. S.;* Young, J. P. "Collisional Broadening of Cs Resonance Lines by Ar, Using Two-Photon Ionization"	International Conference on Multiphoton Processes, University of Rochester, Rochester, N.Y., June 6–9, 1977
Oakes, T. W.*	Oakes, T. W.;* Eldridge, J. S.; Pruitt, M. E. "Environmental Surveillance for Radionuclide Contamination Utilizing High-Resolution Gamma-Ray Spectroscopy"	11th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, Mo., June 7–9, 1977
	Oakes, T. W.;* Shank, K. E.;* Eldridge, J. S. "Quality Assurance Applied to an Environmental Surveillance Program"	4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, La., Nov. 6–11, 1977
Raman, S.*	Raman, S.;* Gentry, R. V.;* Sparks, C. J. Jr.;* Christie, W. H.; Krause, M. O.;* Ricci, E.; Gossett, G. A.; Bates, J. B.* "New Results from Studies on Radioactive Giant Halos"	International Conference on Nuclear Structure, Tokyo, Japan, Sept. 5–10, 1977
Reynolds, S. A.	Reynolds, S. A. "Some Experiences in Alpha Spectrometry"	23rd Annual Bioassay Conference, Moran, Wyo., Sept. 15–16, 1977
	Reynolds, S. A. "The Chemistry of Solution Mining"	ORNL-NRC Seminar, Oak Ridge, Tenn., Feb. 4, 1977
Ricci, E.	Ricci, E.; Sparks, C. J., Jr.;* Raman, S.;* Krause, M. O.;* Gentry, R. V.* "X-Ray Fluorescence with Synchrotron Radiation"	26th Annual Denver Conference on Applications of X-ray Analysis, University of Denver, Denver, Colo., Aug. 3–5, 1977
Rickard, R. R.	Rickard, R. R. "Radiochemistry in Support of Fuel Reprocessing Studies and Environmental Monitoring"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Rodgers, B. R.*	Rodgers, B. R.;* Ball, F. L.; Dunn, H. W.; Eager, M. H.* "Identification and Separation of Micron-Sized Inorganic Particles from Coal Liquids"	AAAS Meeting, Denver, Colo., Feb. 22, 1977
Ross, H. H.	Ross, H. H. "Science Management: What I Didn't Learn in School"	Anachem Awards Symposium, FACSS IV, Detroit, Mich., Nov. 7–11, 1977

AUTHOR	AUTHOR(S) AND TITLE	PRESENTED AT
	Ross, H. H.; Lyon, W. S.; Carter, J. A.; Canada, D. C.; Dale, J. M.; Feldman, C.; Franklin, J. C.; Hulett, L. D.; Klatt, L. N.; Rainey, W. T., Jr.; Shaw, R. W.; Young, J. P. "Advanced Chemical Measurements Technology and Analytical Spectroscopy"	2nd Fuel Chemistry Research Meeting, ERDA, Office of Chemical Sciences, Washington, D.C., May 26–27, 1977
Rubin, I. B.	Rubin, I. B.; Holmberg, R. W. "ORNL Synfuels Program Poster Session"	American Industrial Hygiene Conference, New Orleans, La., May 26–27, 1977
Shaw, R. W.	Shaw, R. W. "Analytical Applications of Optoacoustic Spectroscopy"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
	Shaw, R. W. "Optoacoustic Spectroscopy with a Pulsed Dye Laser"	American Chemical Society National Meeting, Chicago, Ill., Aug. 28–Sept. 2, 1977
Smith, D. H.	Smith, D. H.; Christie, W. H. "A Study of Quantification of SIMS Data"	25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 29–June 3, 1977
Strain, J. E.	Strain, J. E. "Determination of Oxygen in Reactive Materials by 14-MeV Neutron Activation Analysis"	Annual Meeting of the American Nuclear Society, New York, June 12–15, 1977
Walker, R. L.	Walker, R. L. "Two-Stage Thermal Emission Mass Spectrometry and Resin Bead Methodology"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
Wichner, R. P.*	Wichner, R. P.;* Dyer, F. F.; Malinauskas, A. P.* "Distribution of Cesium and Other Fission Products in Peach Bottom HTGR Fuel Elements"	American Nuclear Society Annual Meeting, New York, June 12–17, 1977
Young, J. P.	Young, J. P. "Resonance Ionization Spectroscopy and the Detection of Single Atoms"	Chemistry Seminar, The Pennsylvania State University, University Park, Pa., Sept. 22, 1977
	Young, J. P.; Hurst, G. S.;* Nayfeh, M. H.* "Laser Spectroscopy and the Specific Detection of Single Atoms"	Annual May Conference, Society for Applied Spectroscopy and Applied Topics Section of the American Chemical Society, John Carrol University, Cleveland, Ohio, May 25, 1977
	Young, J. P.; Hurst, G. S.* "Specific Detection of Single Atoms by Resonance Ionization Spectroscopy"	Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 30–Apr. 1, 1977
	Young, J. P.; Hurst, G. S.;* Nayfeh, M. H.* "Specific Detection of Single Atoms by Resonance Ionization Spectroscopy"	173rd American Chemical Society National Meeting, New Orleans, La., Mar. 19–25, 1977
Young, R. T.*	Young, R. T.;* White C. W.;* Clark, G. J.;* Narayan, J.;* Westbrook, R. D.;* Christie, W. H. "Boron Implanted Silicon Solar Cells"	International Conference on Solar Cells, Luxemburg, Germany, Sept. 27–30, 1977

Analytical Chemistry Division Seminars at ORNL

SPEAKER(s)	TITLE	DATE
Kirkland, J. J. E. I. du Pont de Nemours and Company Wilmington, Del.	"Influence of Sampling and Extra-Column Effects in High-Performance Liquid Chromatography"	Jan. 12, 1977
Jones, L. University of Georgia Athens	"Isotope Composition of Naturally Occurring Strontium as a Geochemical Tracer"	Feb. 7, 1977
Young, J. P. ORNL	"Resonance Ionization Spectroscopy and the Specific Detection of Single Atoms"	Feb. 23, 1977
Fritz, J. S. Iowa State University Ames	"Determination of Trace Amounts of Organic Contaminants in Water"	Mar. 15, 1977
Huff, G. A. Allied General Nuclear Sciences Barnwell, S.C.	"The Allied General Nuclear Services Analytical Chemistry Facility"	Apr. 21, 1977
Schönfeld, E. NASA Johnson Space Center Houston, Tex.	"Preliminary Results and Photographic Summary of Viking Missions to Mars"	May 5, 1977
Bayne, C. K. Computer Sciences Division UCC-ND	"Optimization of Chemical Systems with Simplex Design"	June 22, 1977
Crouch, S. R. Michigan State University East Lansing	"Automated Stopped-Flow Mixing Systems for Rapid Chemical Analysis"	June 23, 1977
Theis, T. L. University of Notre Dame Notre Dame, Ind.	"Studies of the Sorbtive Characteristics of Heavy Metals in Fly Ash–Soil Environments"	Sept. 20, 1977
Kopp, M. ORNL	"Position-Sensitive Proportional Counters Solve Many Complex Measurement Problems Easily"	Sept. 23, 1977
Yeung, E. Iowa State University Ames	"New Laser Techniques for Chemical Analysis"	Oct. 28, 1977
Jordan, J. Pennsylvania State University University Park	"Enthalpimetric Analysis and Immunological Thermochemistry"	Nov. 8, 1977
Fales, H. M. National Institute of Health Bethesda, Md.	"Chemical Ionization Mass Spectrometry Applications"	Nov. 29, 1977

PATENTS

AUTHOR	AUTHOR(S) AND TITLE	PATENT NO. AND DATE ISSUED
Moore, F. L.	Moore, F. L. "Removal of Zinc or Cadnium and Cyanide from Cyanide Electroplating Wastes"	U.S. Patent No. 4,026,790, May 31, 1977

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodical																	
	Anal. Chem.	*Anal. Lett.*	*Asbestos Rep.*	ASTM book chap.	*ASTM Methods*	*Chem. Instrum.*	*Environ. Sci. Technol.*	*Int. J. Appl. Radiat. Isot.*	*J. Am. Chem. Soc.*	*J. Electrochem. Soc.*	*J. Electron Spectrosc.*	*J. Polym. Sci.*	*J. Radioanal. Chem.*	*Science*	ORNL reports	Proceeding papers	Proposals	Total
Ball, F. L.																3		3
Bostick, D. A.	2																1	3
Carter, J. A.														1				1
Clark, B. R.																	1	1
Emery, J. F.	1																	1
Feldman, C.	4																2	6
Franklin, J. C.																	1	1
Griest, W. H.	1																2	3
Guerin, M. R.																	6	6
Holmberg, R. W.																	3	3
Hulett, L. D.	1		1	1					1	1	2	7	1		1	3	2	21
Klatt, L. N.	3					3											1	7
Lyon, W. S.	4	1					3						15				3	26
Manning, D. L.	2																	2
Mueller, T. R.																	1	1
Rainey, W. T.																1		1
Reynolds, S. A.					9								1		1		1	12
Ross, H. H.								2					13				2	17
Shaw, R. W.																	3	3
Shults, W. D.	1																2	3
Young, J. P.	1																1	2
Total	20	1	1	1	9	3	3	2	1	1	2	7	30	1	2	7	32	123

ANALYTICAL CHEMISTRY DIVISION

[illegible]