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ANALYTICAL CHEMISTRY DIVISION

ANNUAL PROGRESS REPORT

Period Ending November 30, 1976

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ANALYTICAL CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

For Period Ending November 30, 1976

W. D. Shults, Director

W. S. Lyon, Editor

Activities and Research Results Compilers

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for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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Introduction and Summary

W. D. Shults

The Analytical Chemistry Division of Oak Ridge National Laboratory is a large and diversified analytical chemical organization. As such, it serves a multitude of functions for a clientele that resides both within and outside of the Laboratory. 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 Laboratory and ERDA 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 ERDA. The program constituted approximately 11% of the FY 1976 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, Laboratory, and ERDA 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 1976.

3. **Analytical Service and Assistance.** The Division performs chemical and physiochemical 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 largely comes from other divisions and programs within the Laboratory; however, a significant fraction originates outside of ORNL. Outside work of an analytical service-assistance nature often involves the use of Division talent and or facilities that are particularly strong, unusual, or even unique. This effort accounted for approximately 55% of the budget during FY 1976.

4. **Consultation, Collaboration, and Special Projects.** This work is distinguished from the analytical service-assistance function mentioned above by the nature of interaction between this Division and its clientele. Typically, work that falls in this category is 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 customer, to instructing others in the use of analytical equipment plus the interpretation of data, and to participating as analytical members of technical task forces. Activities range from special measurements or tests to program development and 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 9% of the FY 1976 budget.

The Analytical Chemistry Division is organized into four major sections, each of which may carry out any type of work falling in the four categories mentioned above. Chapters 1 through 4 of this report describe progress and accomplishments made within

the four divisional sections during the period December 1, 1975, through November 30, 1976. Some of these are highlighted in the following paragraphs.

Advanced Methodology Section (Chap. 1). Spectroscopy has continued to be prominent in the Analytical Instrumentation Group activities. J. P. Young has been the analytical member of a team that has been studying resonance ionization spectroscopy under G. S. Hurst's leadership in the Health Physics Division. Much progress has been made in this supersensitive technique for detecting atomic vapors: as little as a few atoms of cesium have been detected at present. "One-atom detection" is one goal of the work; however, we are interested in various analytical applications of this laser-based technique. We have developed a project in laser-excited optoacoustic spectrometry and have acquired equipment and initiated experiments in this area. During this reporting period the Tektronics rapid-scan spectrometry (RSS) system was acquired for a host of studies that involve multispectral data accumulation. Interfacing and programming for the RSS system have been accomplished. Significant progress has also been made in our studies of high-powered microwave excitation sources; however, the sensitivity of the system is not as great as we had hoped. One objective of this work is to provide an element-selective detector for liquid chromatography (LC), in keeping with our general interest in improved chromatographic detectors. We have completed studies of an electrochemical LC detector and have continued to use and improve our dielectric-constant detector. Particularly exciting have been the studies of an arc-excited optical-emission detector for gas chromatographic use, which has proved to have excellent sensitivity as well as good selectivity in many situations. Its use in o .sional programs is already under way.

The "fundamental-parameters" approach to x-ray fluorescence analysis has been shown to be feasible for certain types of samples and has been put to use within the Division. Significant improvements in our electron spectrometer system have been made, and we have begun to construct a new electrostatic spectrometer. The development of a position-sensitive detector system is an inherent part of this project.

The demand for the rather specialized kinds of measurements that are made in this section has increased. This is particularly true in the case of scanning electron microscopy, neutron activation analysis, low-level gamma spectrometry, and delayed neutron counting. The last technique has undergone a renaissance because of its utility in the National Uranium Resources Evaluation Program. UCC-ND is responsible for the midwestern portion of the United States in this massive effort.

Our research in transuranium-element chemistry and analysis, in pattern recognition techniques, in the application of microelectronics circuitry, and in methodology for determining species (e.g., sulfate and organoarsenicals) has continued. The incorporation of a recently announced commercial calculator-controller module into our microelectronics research program is under consideration.

Mass and Emission Spectrometry Section (Chap. 2). During this reporting period we completed construction of the two-stage mass spectrometer system for the International Atomic Energy Agency. The instrument has been installed in the Seibersdorf Analytical Laboratory near Vienna and has met all specifications. This instrument plus the "resin-bead technique" that was developed at ORNL earlier will be used for safeguards analyses by IAEA. H. McKown is on leave of absence from the section for a two-year assignment at the Seibersdorf Laboratory. Work with the resin-bead technique has continued and can now be used to determine fission product zirconium and to study ^{239}Pu at levels below that accessible by conventional counting techniques.

W. H. Christie and D. H. Smith have continued to study and use the ion microprobe mass analyzer (IMMA) with real success. They are participating in the National Bureau of Standards interlaboratory program aimed at quantifying IMMA data. Results to date indicate that better results are obtained through the use of empirical sensitivity factors than with the CARISMA computer program. Christie and Smith have also collaborated closely with others at ORNL in answering important questions about the relationship between surface composition (treatment) and tritium permeation and about thermocouple failure in reactor-burst experiments.

The MS-50 GC-MS and its companion DS-50 computer system have been placed in operation during this reporting period. We have constructed and installed a special gas inlet system for this ultrahigh-resolution organic mass spectrometer, and have continued to learn more about the total system capabilities. We also acquired and placed in operation a Du Pont 490B GC-MS system at ORNL. This instrument incorporates a Perkin-Elmer 3920 GC unit comparable to the GC units that are used in much of our organic analysis work. The Du Pont system is intended to provide routine GC-MS

information for firm structural identification purposes to the staffs of several ORNL divisions. Several members of the Division have studied various aspects of HTGR operations from the organic chemistry point of view to improve understanding of fuel preparation procedures and to determine the potential release of hazardous compounds. An extensive compilation of the mass spectra of nitrosamines was completed and published during this period.

We have acquired and begun to evaluate an inductively coupled plasma excitation source for emission spectrometry. The use of gelatin-free film for spark-source mass spectrometry (SSMS) is also under study. Our "dry-spike" technique for conducting isotope-dilution (ID) SSMS analyses has been used effectively, and IDSSMS procedures for several new elements have been developed. A second computer-based photoplate reader system has been put into operation to expedite the heavy SSMS workload. This section performed analyses for 18 ORNL divisions and reported a total of more than 80,000 results during this period.

Analytical Services Section (Chap. 3). A major accomplishment in this section during this period has been the implementation of a computer-based data management system (DMS). This system was designed by Analytical Chemistry Division and Computer Sciences Division personnel to improve the cost effectiveness in time-costs data management and the efficiency and accuracy with which we process and report analytical data. The DMS is designed to operate via the ORNL DEC system 10 computer. We have acquired and installed terminals to the DEC-10 in the General Analyses Laboratory and in the Environmental and Radiochemical Analyses Laboratory. Time and cost data are already being processed by the DMS on a trial basis. Many subprograms have been written to perform analytical computations and to handle the total problem of processing analytical results.

The Molten-Salt Reactor Experiment at ORNL was terminated in mid-1976. We were able to close out the experimentation for which we were responsible (loop monitoring and in-line monitoring research) in an orderly fashion. Other work in the Reactor Projects Group has progressed. The organic mass spectrometric study of fuel preparation procedures has been mentioned. We have also continued to study and optimize methods for measuring defective fuel particles and to improve methods for heavy-metal assay. F. F. Dyer has continued his gamma-spectrometric studies of the fission product distribution in fuel elements from the Peach Bottom Reactor.

The Analytical Services Section also carried out a wide variety of analyses in support of various ORNL programs during this report period. These are summarized in Chap. 5. New procedures and equipment were used to meet sample loads. The section acquired a new Perkin-Elmer model 240 elemental analyzer, a P-E model 3920B gas chromatograph, a P-E model 460 atomic absorption system, a liquid scintillation counter, and an automatic sampler for the graphite furnace atomic absorption system. Additionally, we relocated most of the low-level alpha analysis work into a remotely situated laboratory and have made final plans to move the ND-3300 spectrometer there to facilitate multiple detector operation. This move will be possible because a new ND-6600 system will soon be available for gamma spectrometric work. Nonanalytical technical services of various types are also provided by this section, for example, the synthesis-preparation of special research compounds, the cleaning of mercury, and the testing of nuclear coatings. The demand for these last tests has increased significantly, primarily because we have the only testing laboratory capable of conducting all of the recently updated specified tests. During the present reporting period we improved facilities for performing the design-basis accident test and air irradiations.

Bio-Organic Analysis Section (Chap. 4). The work of the Bio-Organic Analysis Section has continued to be programmatic in nature, with notable growth in the area of synthetic fuels technology. Multicomponent methodology continues to be a prime concern because of its obvious benefit to all of the section's programs. Methods for polynuclear aromatic hydrocarbons, phenolics, and polyglycols have been developed and or improved significantly. Separations studies have also continued, and striking results have been obtained through the use of Sephadex LH-20 gel. This latter separation scheme offers a valuable preparative-scale technique that may be of real benefit to new programs in which characterized research materials are prepared for others. Studies of techniques for analyzing organic materials in aqueous discharges from energy-related technologies have also continued.

The traditional posture of this section has been one that reflects a keen interest in health (and environmental) programs and the role that chemistry can play. Accordingly, the section has worked closely with various members of the Biology Division, the

Environmental Sciences Division, and the Industrial Hygiene Department. Especially noteworthy has been the collaboration with J. L. Epler in the Biology Division, in which our chemical fractionation-characterization techniques and his mutagenicity screening (the Ames test) have been used for rapid examination of fossil-derived materials. We have studied in some detail the sampling and analysis of airborne organic materials present in the work environment around certain nuclear fuel preparation facilities at ORNL. An important finding is that total particulate matter (taken on glass-fiber filters) is not an accurate means for collecting and detecting polynuclear aromatic hydrocarbons less than four rings in size. In a joint venture with the Environmental Sciences Division, we designed, built, tested, and now operate a microcosm for exposing vegetation to synthetic gaseous effluents resembling those from coal conversion processes.

The development of unique or specialized instrumentation has been a necessary function of this section for some time. During this period a smoke exposure machine, model II (SEM-II), was designed and constructed for the Council of Tobacco Research, and a monitoring system was devised specifically for use with the SEM-II (to protect against excessive dosage to experimental animals due to machine malfunction). Work of this nature and quality has led to an increasing number of requests for assistance in designing and monitoring large-scale animal exposure experiments conducted by contractors at other institutions.

This section has continued to perform many types of chemical anaiyses on tobacco smokes and smoke condensates in support of National Cancer Institute programs, and to conduct numerous special projects on request.

Chapters 5 and 6 contain information that reflects upon the Division as a unit. Changes in the quality assurance and safety programs are mentioned in Chap. 5, along with a tabulation of analyses rendered. Publications, oral presentations, professional activities of the staff, educational programs, seminars, etc., are cited in Chap. 6. In general, the levels of these activities are comparable to those of the preceding year. Approximately 100 articles and reports have been published, and approximately 100 talks have been given during this reporting period. One shift in emphasis is worthy of mention here. We have become increasingly involved in workshops and topical meetings of various types, and hence we have contributed significantly to a large number of proceedings. Accordingly, this type of publication has been listed separately. Educational programs, via faculty and student guests plus in-house training, have also continued at levels comparable to previous years.

1. Advanced Methodology

W. S. Lyon, Head

The Analytical Instrumentation Group has enjoyed a most successful year as reflected by the continuing progress of both established programs and fledgling projects of a year ago. The interfacing of our rapid-scan spectrometer to the computer for fast data acquisition and processing is completed; the result is a powerful new capability in multiwavelength analysis that will be applied to a variety of optical excitation systems. Data collection with the optoacoustic spectrometer has also begun. Although the system response is not yet optimized, we have verified expected improvements by use of laser excitation rather than overarc-source systems. This instrument setup will provide the Division with an analytical initiative not previously available in any form. Last year a high-power microwave device was acquired to generate plasmas for the possible direct excitation of liquids; this difficult objective has been achieved. Several liquid systems are now being investigated with the intent of eventually coupling this unit to the rapid-scan spectrometer for multielement analysis. Our cooperative program with the Health Physics Division on resonance ionization spectroscopy has yielded data that strongly suggest the realization of one-atom detection. Possible analytical applications are being explored.

More seasoned projects in pattern recognition, atomic spectroscopy, liquid chromatography, transuranium analysis, and integrated-circuit instrumentation hold our continuing interest because of their projected use in solving a range of existing problems. Specific tasks in the areas of coal liquefaction and gasification have been identified, and some of these are under study. The main objective of our instrumentation effort remains the same—to maintain a research program that offers significant potential benefit to ERDA programs.

Work continues in improving and applying multielement analytical techniques. A general method for matrix correction of quantitative x-ray fluorescence (XRF) analysis data from alloys and similar samples was developed and successfully applied. We are making substantial changes in the electron spectroscopy for chemical analysis (ESCA) machine; these should result in much improved sensitivity and instrument stability. The x-ray diffraction system is also being upgraded. These changes are in response to an increased demand for physicochemical methods of analysis.

Neutron activation analysis continues to provide a large number of investigators with multielement analytical data. A sizable contribution to the work load is the determination of uranium in sediments for the Uranium Resource Evaluation Program for which the Union Carbide Corporation, Nuclear Division, is responsible. Our involvement in environmental monitoring and assay of radionuclides in the environment has grown, since we have greatly expanded collaborative efforts with the Environmental Sciences, Health Physics, and Chemical Technology Divisions.

The activities of the Advanced Methodology Section are thus seen to range from: (1) basic research and development, through (2) improvement and modification of existing techniques, to (3) the application of acquired expertise for problems of interest, not only to analytical chemists, but also to environmentalists, health physicists, and technologists engaged in energy research.

ANALYTICAL INSTRUMENTATION

H. H. Ross, Group Leader

Instrumentation-Computerization Research

Array detector for multiwavelength spectroscopy. In terms of the amount of information obtained during a single observation, spectroscopic techniques can be divided into single- and multiwavelength detection modes. Multiwavelength detection has been recognized for quite some time as the means for significantly improving the capabilities of analytical spectroscopy. Recently, semiconductor array detector systems have become available at moderate cost. These devices have the potential of providing a multiwavelength capability with the advantages of photographic plate and phototube array with few, if any, of their disadvantages. The objective of this program is to provide an advanced spectroscopic capability using semiconductor array detectors.

Previous work dealt with the screening of various solid-state devices.[1] This evaluation indicated that the entire area of semiconductor array detectors is undergoing extremely rapid technological change and that any program requiring development of the optical and electronic systems necessary to use these devices would not be viable until advances in the semiconductor industry begin to plateau. Thus, work was redirected toward applications development using a commercially available silicon vidicon-based rapid-scan spectrometer (RSS).

We acquired a Tektronix model J20 RSS and interfaced it to a PDP-8/I computer. It operates as a peripheral service through the interrupt system of the computer. Features incorporated into the interface include: (1) an external time base for the analog-to-digital converter, (2) logic that synchronizes the vidicon sweep, integration time, and the initiation of the experiment and data acquisition routines, (3) switch-selectable vidicon ramp hold times ranging from 20 msec to 5 sec, (4) vidicon target current amplification circuitry, and (5) the ability of the RSS to operate as a stand-alone unit. The hardware assemblage has been tested, and the proper operation has been verified.

Application of the complete system—RSS and computer—to various research problems utilizes FOCRSS, a tailored version of FOCAL as an interactive high-level programming language. FOCRSS includes additional commands and functions that facilitate operation of the RSS and processing of the spectral data. The writing of assembly language programs required to implement FOCRSS is under way.

The first application of this system will involve multiwavelength liquid-chromatographic detection. Assembly of the detector cell, radiant-energy source, and optical system required to illuminate the entrance slit of the RSS is complete. Demonstration of the unique capability that this mode of liquid-chromatographic detection can provide will begin shortly. Subsequent studies will involve multicomponent analyses based upon molecular fluorescence and various types of atomic spectroscopy. (*L. N. Klatt*)

Resonance ionization spectroscopy. The study of resonance ionization spectroscopy (RIS) has continued in collaboration with G. S. Hurst's group, Health Physics Division, and a description of the basic principles of RIS has been given.[2] In the RIS technique, atoms in a vapor are excited to ionization by absorption of precisely tuned energy sources of sufficient power so that the ionization is a saturated phenomenon. The electrons thus formed are detected by standard counting techniques. In previous work,[3] a proton plus a tuned laser beam were allowed to interact with helium atoms to cause ionization; present work involves the interaction of atomic vapors with tuned laser light. RIS signals have been obtained by several different routes from cesium vapor at room temperature or above. Photoionization has occurred either by 2-photon absorption or by two 1-photon absorptions through the $7p$ level. In the latter case, light from two different lasers was required, and the lasers had to be fired in both space and time coincidence. Photoionization has also occurred by single-photon absorption directly to an upper Rydberg state, followed by perhaps some type of collisional or associative ionization. Such ionization has been demonstrated by successively tuning through the $12p$ to $21p$ levels. Approximately 10^3 to 10^4 atoms of cesium has been detected by each of the above three techniques in a parallel-plate detector operated within the pressure range of several microns to an atmosphere of argon. A concentration of the order of 5×10^2 atoms/cc has been detected by the

1. Y. Talmi and V. E. Norvell, "Multielement Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 2.

2. J. R. Mueller, "Applications of Large-Scale Integrated Circuits," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 2.

3. J. P. Young, "Resonance Ionization Spectroscopy," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 31.

two first-named techniques in a proportional counter under an atmosphere of 50 to 200 torr of argon-methane counting gas. In a proportional counter, it is possible to detect a single electron; thus the RIS technique should be able to identify and determine single atoms. This is our goal. It is probable that we have detected a single atom of lithium by RIS in the proportional counter. Lithium photoionization involves a three-step photon absorption through the $2p$ and $3d$ states. Problems of chemistry, either ground-state or excited-state, have as yet prevented a definitive proof of few-atom detection for this element. Signals are observed for short periods of time, up to 30 min with a fresh sample, and then disappear. Perhaps the RIS process is a destructive process; or more likely, the polymerization of CH_4 in the counting gas, caused by continually occurring cosmic events in the counter, yields products which react with lithium vapor. Besides the problems of chemistry, there is a continuing problem of sufficient tunability and power of the laser-excitation sources and, in the case of dual lasers, the previously mentioned requirement of space and time coincidence (within 500 nsec). In general, the laser parameters are under reasonable control for the atomic species we wish to study, so an investigation of the varied chemical reactions of the vapor can be made. (*J. P. Young*)

Optoacoustic spectroscopy. In January 1976 a new program was initiated to investigate the analytical applications of optoacoustic spectroscopy (OAS), the newly rediscovered technique for acoustic detection of optical absorption.

The OAS phenomenon can be explained in the following simplified fashion. Light energy absorbed by matter is reemitted in the form of either light (fluorescence or phosphorescence) or heat (radiationless decay). It is the latter of those two options upon which OAS is based. The emitted thermal energy yields a gas pressure increase when the sample is situated in an enclosed cell. Because the intensity of the original light source is modulated, the resultant pressure increase is periodic with the same modulation frequency; that is, a sound wave is generated. Quantitative determination of the sample absorbance is then accomplished via a sensitive microphone in the OAS cell. The amplitude of the acoustic signal is proportional to

$$I(\omega)\hbar\omega P(\omega)F(\omega) ,$$

where $I(\omega)$ is the intensity of the light source at frequency ω, $\hbar\omega$ is the energy of the light photons, $P(\omega)$ is the probability that a photon of frequency ω is absorbed, and $F(\omega)$ is the fraction of absorbed photons that are converted into thermal energy.

The advantages of this technique are threefold: (1) absorption spectra can be obtained for samples such as powders, opaque solids, turbid liquids, and living tissue (in vivo); conventional spectroscopy would be impossible with such materials, either due to scattering or opacity; (2) OAS also provides a sensitivity advantage over conventional spectroscopy in that the observed signal is directly proportional to the amount of input light; (3) OAS can yield excited-state radiationless decay information absent from conventional spectroscopy. Until now, only radiative photophysical processes have been well characterized experimentally. It should be possible to study the "dark" processes as well.

At the outset of this project, we decided that the optimum approach to developing a useful spectrometer for OAS would be to use a tunable laser for excitation. Such a light source would provide high input intensity (and hence satisfactory OAS signal-to-noise ratio) and also high-resolution capability. The laser selected for use was a flash-lamp-pumped tunable dye laser. That system, a Chromatix CMX-4, provides up to 200 mW of average power over the 720- to 430-nm wavelength range and up to 12 mW over 365 to 265 nm. Because this laser is pulsed, the modulation requirement of OAS is automatically met. The laser arrived very recently; installation and checkout procedures have begun.

While awaiting the arrival of the laser, preliminary OAS experiments were completed. An OAS cell was designed and used for the observation of the OAS phenomenon for several solid samples. The cell was constructed from a windowed Pyrex cylinder fitted with a 90° prism for light input and a brass microphone adapter. The cell was designed with eventual laser excitation in mind. The unobstructed cell optical path minimizes background levels. Thus far, a continuous (dc) filament lamp has served for OAS excitation. Due to the low-output power available, the light from that source has not been dispersed, and only "white-light" observations have been possible. Modulation of the input light was accomplished with a mechanical chopper designed and constructed for this project.

For signal detection and treatment, a tuned amplifier has been designed and is under construction. In breadboarded form its performance is slightly better than a phase-sensitive lock-in amplifier previously tested. For example, for a white-light input of 25 nW the breadboard-tuned amplifier yielded a signal-to-noise ratio of 40, whereas a commercial lock-in

amplifier with a comparable time constant yielded a signal-to-noise ratio of 11. However, laser-generated OAS signals will be more sawtooth in nature (as opposed to sine wave), and the above comparison of tuned vs phase-sensitive detection schemes may not be valid. These data will therefore be redetermined. Since the above preliminary experiments have been satisfactorily completed, we are now in a position to use the new dye laser for OAS almost immediately. Unconventional absorption spectroscopy of a multitude of samples of ORNL interest will be possible and are planned. Sorbed monolayers on surfaces can be investigated; this can facilitate particulate, aerosol, and catalyst studies currently under way. An environmental monitor for certain trace gases and a wavelength-specific radiometer are both possible developments of this OAS study. (*R. W. Shaw*)

Microwave-excited plasma for analytical spectroscopy. The adaptation of a high-powered microwave generator (2.45 GHz, 2.5 kW) as an excitation source for emission spectroscopy is not yet complete, though most of the original experimental problems have been solved. The purchase and installation of a forward-reverse power meter has made it possible to optimize coupling between antenna and the position and geometry of the quartz plasma tube for the best impedance match. The plasma tube has been through a series of 11 modifications to maximize the elemental sensitivity and avoid deterioration of the optical window. In our present configuration, the liquid sample is converted to a wet aerosol in a pneumatic generator and injected into a low-pressure (60 cm Hg) argon plasma just downstream from the microwave antenna. Introduction of the sample in this manner somewhat reduces the absolute detection sensitivity but avoids the changing impedance, power transfer, and emission sensitivity observed when the sample is injected upstream and passes through the antenna.

Our present sensitivities lie in the range of 50 to 1 μg of solute per milliliter of sample, using a flow rate of 0.58 ml/min into the aerosol generator and 0.13 ml/min into the plasma. We are in the process of determining elemental sensitivities and evaluating the common-ion effect in multielement analysis. The effect of absolute pressure in the plasma tube and microwave power has been tabulated. The use of 1 kW of input power has been adopted as standard for sensitivity measurements, although sensitivity increases with increasing power.

In addition to using argon as a plasma support gas, plasmas have also been created in nitrogen, air, helium, oxygen, and hydrogen. Background spectra have been accumulated from 250 to 800 nm on all of these plasmas and elemental lines and band structures identified with a view toward their possible analytical application with real-sample systems. (*J. E. Strain, J. L. Knuckles*)

Helium arc detector for gas chromatography. Two general types of light sources have been proposed as multielement detectors for gas chromatography: the microwave discharge[4] and the helium arc.[5] The former has very good sensitivity and specificity (see discussion of the term "specificity" below), but involves relatively expensive and complex equipment and is sometimes subject to window-coating problems and variations of the size and intensity distribution pattern of the luminous discharge. The latter, in the form published,[5] encountered fairly serious window-coating problems, required the use of wide slits with the attendant spectral interference problems, and showed widely varying specificities.

It appeared that the window-coating problem could be eliminated by making certain changes in arc chamber design and that a discharge of excellent stability could be obtained at very little trouble or expense by using appropriate electrode materials and a newly available low-cost ($225) current-regulated power supply.

Ordinarily, the specificity of an optical emission detector is not entirely under the control of the operator. Good specificity exists if the element sought produces an intense signal at the wavelength observed *and* if other species that do not contain that element, but which may be eluted from the gas chromatograph at any time during the run, do not produce optical emission at the same wavelength. Any such emission (e.g., bands due to C_2, CH, N_2, NO, NH, CO, etc.) would constitute a false positive signal, thus lessening the specificity of the detector for the sought element in that sample mixture. It appeared obvious that any simple method of correcting the specific element signal for the underlying spectral background would greatly enhance the specificity of the detector.

Arc chamber design. The arc chamber used for the present detector is shown schematically in Fig. 1.1. The chamber body is made of 6-mm-OD Pyrex tubing, with a 1-in.-diam silica window cemented to

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4. M. G. Payne, G. S. Hurst, M. H. Nayfeh, J. P. Judish, C. H. Chen, E. B. Wagner, and J. P. Young, "Kinetics of $He(2^1S)$ Using Resonance Ionization Spectroscopy," *Phys. Rev. Lett.* 35, 1154 (1975).

5. A. J. McCormack, S. C. Tong, and W. D. Cook, *Anal. Chem.* 37, 1470 (1965).

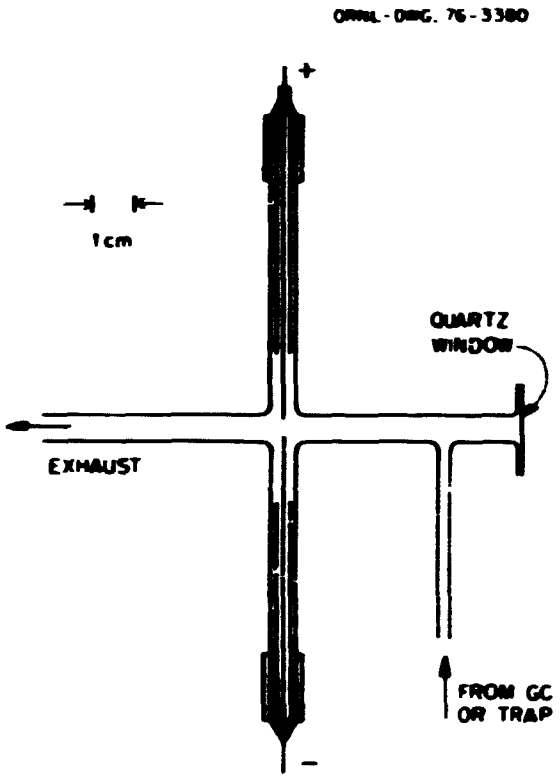

Fig. 1.1. Helium arc chamber.

this flange with epoxy adhesive. The electrodes, consisting of commercially available 0.060-in.-diam W 2% ThO_2 welding rods, are sheathed in glass and held in place by Silastic rubber sleeves. The electrode gap is 4 to 6 mm. The observation window remains clean because it is located considerably upstream from the gas inlet and arc. The inlet tube is connected to the gas chromatograph outlet with a No. 5 Pyrex O-ring flange fitting or other appropriate coupling. The inlet tube and the upstream arm of the arc chamber are heated, when necessary, by a heating cord, or by an appropriately designed oven. The extension leading to the window is not heated.

The carrier gas entering the chamber is normally helium at atmospheric pressure. The potential across the glow discharge between the above-mentioned electrodes in this atmosphere is ~400 V. To produce a stable discharge, the power supply should be current controlled and have an open-circuit voltage of ~600 V. These requirements are met by certain hollow-cathode power supplies. However, 600 V is not sufficient to ignite the discharge; this must be done by a weak external silent discharge produced by a Tesla coil (leak tester) with the power supply protected from the triggering pulse. An additional difficulty is posed because hollow-cathode sources with this output voltage are no longer available commercially as separate units. Both the self-ignition and the availability problems have been solved, however, by the recent appearance of a separately available current-regulated (40–50 mA) power supply[6] with an open-circuit voltage of 1100 V. This is high enough to reignite the discharge if quenched by a substantial, but transient, change in gas composition, for example, by the passage of a solvent peak through the detector.

A background correcting device should be flexible if it is to be usable with various types of spectrum profiles; that is, it should enable the operator to choose the wavelength at which he measures the background. After scanning the spectral range of interest, the operator can thus select a wavelength near the signal line at which the background intensity is the same as it is beneath the signal line. The apparatus available was a Jarrell-Ash Mark V 0.5-m Ebert monochromator, with an exit-beam deflecting mirror and side exit port. The easiest way to effect such a background correction appeared to be to split the exit beam by cutting the deflecting mirror in half horizontally. The upper half of the beam then continued to the normal (fixed) exit slit, while the lower half was deflected ~90° to a second (movable) exit slit mounted on the side exit port. Each channel had its own photomultiplier and amplifier; the background signal was subtracted from the (line + background) signal, and the corrected line intensity was fed to a strip-chart recorder. Operation of the background corrector was checked by simultaneously directing the light from an incandescent lamp and a low-pressure mercury lamp into the monochromator and adjusting the latter to pass a minor mercury line through the normal exit slit; the side exit slit was displaced from this wavelength by a few angstrom units. The observed intensity of the mercury line remained the same regardless of whether the incandescent lamp was on or off, thus indicating that the background correction was effective.

Preliminary measurements were made by attaching the helium arc chamber to the outlet of a Tracor MT-220 gas chromatograph containing a 6-ft × ¼-in. column of 4% OV-101 on Chromosorb GHP. The helium flow rate was 90 to 110 cc/min. Entrance and exit slits were 50 to 100 μm. The detection limits

6. R. S. Braman and A. Dynako, *Anal. Chem.* 40, 95 (1968).
7. Hollow-cathode power supply, model 555F-400, George W. Gates and Co., Inc., Franklin Square, New York.

Table 1.1. Limits of detection for various elements using the helium arc detector

Element observed	Compound used	Wavelength of line (nm)	Element detection limit	
			ng	ng/sec
F	Monochlorotrifluorobenzene	685.6	4.5	0.075
Cl	Monochlorotrifluorobenzene	725.7	45	0.75
CCl[a]	Monochlorotrifluorobenzene	277.8[b]	15	0.15
Br	Bromobenzene	734.9	45	0.75
I	Iodobenzene	206.2	4.5	0.075
C		193.1		
P	Tributylphosphate	213.6	6.4	0.1
S	Dibutyl sulfide	527.9	110	1.9
Al	Al trifluoroacetylacetonate	396.2	12	0.14
Cr	Cr acetylacetonate	425.4	1.4	0.024
Cu	Cu hexafluoroacetylacetonate	324.7	110	3.8

[a] Molecule
[b] Band

shown in Table 1.1 were measured by injecting an appropriate amount of the compound listed and comparing its peak height to the peak-to-peak noise of the chromatographic baseline. The detection limit given is the quantity corresponding to signal/noise = 2. The above-described background corrector was not yet available when these detection limits were measured. It is safe to assume, however, that in some cases, detection limits can be lowered by using wider slits and correcting for background, or by achieving better resolution of chromatographic peaks.

Other elements have been detected at comparable levels, but limits of detection have not yet been measured (e.g., Si at 251.6 and 288.1 nm, As at 228.8 nm, Co at 345.3 nm, Mn(II) at 403.1 nm, Ni at 341.5 nm, and V(III) at 437.9 nm).

Initial testing of the background corrector to maximize specificity of element detection is reported in Chap. 4. (*C. Feldman, D. A. Batistoni, R. A. Jenkins*)

Detectors. During the past year, a simple general-purpose electrochemical detector having both a small internal volume and high electrolytic efficiency was developed for liquid chromatography. Electrochemical detectors are becoming increasingly important in liquid chromatography because they are selective for electroactive substances and they exhibit inherently great sensitivity. Selectivity can be further enhanced by adjustment of the potential at the working electrode. For example, an electrical signal of 1 nA from the detector, which is easily measurable, corresponds to a flow of approximately 10 femtoequivalents/sec of electroactive material. The working electrode of the new detector consists of a vitreous carbon tube, 1 mm in inside diameter and 5 cm long, packed with carbon microspheres; 45- to 75-μm microspheres were prepared for us by the Metals and Ceramics Division by a technique used for preparation of nuclear reactor fuels involving carbonization of spherical cation exchange resin beads at controlled temperature in an inert atmosphere.[8] The microspheres are held in the tube by porous Teflon frits and Teflon Swagelok fittings. At the inlet end, the cell is connected to standard $\frac{1}{16}$-in. Teflon liquid-chromatography (LC) tubing, and the outlet end is connected to a $\frac{1}{4}$-in.-ID reservoir, which is large enough to allow insertion of platinum auxiliary S.C.E. reference electrodes. The assembled detector has an active volume of 20 to 25 μl. An ORNL coulometric titrator, model Q-4010, was used to control the potential of the working electrode and to measure and integrate the current flow. Electrolytic efficiency of the detector is 50 to 100%, depending on the solute concentration, conductivity, and flow rate; essentially 100% efficiency can be achieved under conditions normally used. Primary advantages of the detector include: (1) high electrolytic efficiency at low concentrations—limit of detection is at the nanogram level, flow rate dependence is small, and quantitative analysis by coulometric integration of peak areas is possible; (2) versatility—because materials of construction are solely Teflon and nonporous carbon, the detector is useful in all media, both

8. The use of a movable auxiliary exit slit was suggested by J. D. Defreese and H. V. Malmstadt, paper No. 286, FACSS meeting, Indianapolis, Indiana, November 1975.

aqueous and organic, over a wide potential range and in both oxidation and reduction modes; (3) a small internal volume compatible with high-efficiency LC separations. We intend to use this detector in a chromatographic system under development for the separation and determination of phenolic compounds. Because of relatively low molar absorptivities, the sensitivity of conventional ultraviolet LC detectors for phenolics is poor. A paper describing this work has been published.[9]

We previously reported that the dielectric constant may provide the basis for a universal LC detector and also proposed an electronic system that offered a solution to the energy dissipation problem encountered in high-dielectric-constant solvents.[10] Both of these suppositions have been shown to be valid. The detector has been characterized, and its potential usefulness as an LC monitor has been ascertained.

General operating characteristics of the detector were determined with solvents of dielectric constant ranging from 1.88 (hexane) to 78 (water); the operating frequency varied from 4.88 to 0.83 MHz respectively. Noise was independent of dielectric constant, averaging 48 Hz (rms), and is limited by residual temperature changes within the detector cell. Drift as measured with hexane was 3.5 ± 1.8 Hz/min; qualitative observations with other solvents indicate that it was frequency independent. A small dependence of the frequency shift upon solvent flow rate was observed, but when considered in terms of the precision of modern LC pumps, it was an insignificant factor. Initial tests of the detector in actual chromatographic applications employed low-dielectric-constant solvents. Separations of *o*-dichlorobenzene from nitrobenzene on silica were monitored; excellent precision and linearity were observed. Because the dipole-dipole interactions between solvent and solute with low dielectric constants are relatively small, the dielectric constants of the individual components are additive on a volume-fraction basis. One can therefore express a detection limit applicable to these systems in terms of a change in dielectric constant. Analysis of response data for naphthalene dissolved in benzene, using three times the rms noise level to define the detection limit, yielded a value of $0.0002\Delta\epsilon$ for the detection limit.

Previous designs of dielectric-constant detectors have been inoperable with high-dielectric-constant solvents.[10,11] Figure 1.2 shows a separation of chloroform from 1-chlorobutane with permanently bonded octadecyl silane (ODS) using a 40 to 60% (v/v) isopropanol-water mixture as eluant. The solvent peak corresponds to a negative frequency shift and is the result of water being displaced from the stationary phase by the less polar solutes; the solute peaks are positive frequency shifts. Clearly, the present instrument can be used with high-dielectric-constant solvents.

Linearity and reproducibility of the detector-chromatographic system in high-dielectric-constant solvents were excellent. Analysis of data for peak height vs solute volume for the separation shown in Fig. 1.2 yielded detection limits of 0.04 μl of chloroform and 0.05 μl of 1-chlorobutane. Due to the large dipole-dipole interaction in high-dielectric-constant solvents, these detection limits, expressed as a quantity of solute, cannot be converted to a change in dielectric constant, which is the fundamental manner of reporting detection limits for this detector.

This development effort has demonstrated that the dielectric constant can be the basis of a universal LC monitor. Recent refinements in the electronic system have improved the detection limit by a factor of 2 from those measured during initial evaluation and make this detector concept competitive with other universal monitors. The instrument is being used on a routine basis in the characterization of fossil-derived oils; see Chap. 4. (*L. V. Klatt, G. Goldstein, D. A. Thomas*)

"Stainless steel" analyzer for LMFBR fuel program. The LMFBR fuel recycle program is generating a large number of samples that require an analysis for stainless steel by our General Analytical Laboratories. The samples are sized portions of a cut-fuel-rod assembly. In the current studies, alumina is used to simulate the spent fuel in the rods. A nondestructive procedure for determining the stainless steel content of these cut-fuel-rod assemblies was developed; it involves observing the frequency shift of an oscillator upon insertion of the sample into the core of the frequency-determining inductor of the oscillator. Samples with iron contents ranging from 0.5 to 4.3% can be measured. The response was not linearly related to the percentage of iron, but use of a second- or third-degree polynomial for the calibra-

9. G. W. Weber, R. L. Bratty, and V. J. Tennery, *Properties of Carbonized and Converted Uranium-Loaded Weak Acid Resins*, ORNL-5201 (1976).

10. G. Goldstein and D. A. Thomas, "A Simple, General-Purpose Electro-Chemical Detector For Liquid Chromatography," submitted to *Analytical Letters*.

11. L. V. Klatt, "Liquid Chromatography," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 4.

12. R. Vespalec and K. Hana, *J. Chromatogr.* 65, 53 (1972).

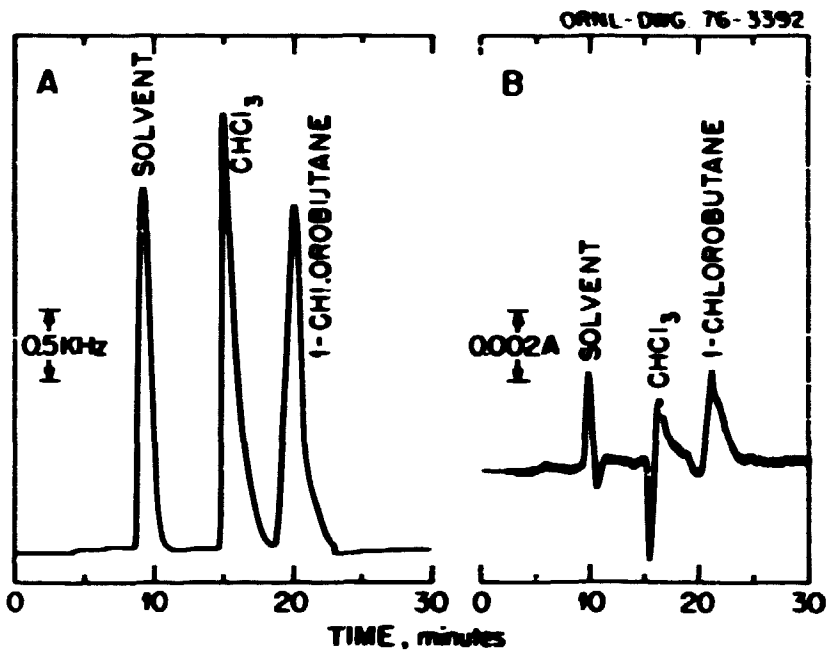

Fig. 1.2. Separation of chloroform and 1-chlorobutane on a 4.6-mm × 25-cm Partisil ODS column with 40–60% isopropanol-water mixture as eluant. Flow rate, 0.36 ml/min. (A) 100 μl chloroform and 100 μl 1-chlorobutane diluted to 10 ml with isopropanol-water eluant; 50 μl injected; dielectric constant monitor. (B) 150 μl chloroform and 150 μl 1-chlorobutane diluted to 10 ml with isopropanol-water eluant; 50 μl injected; uv monitor with air in reference beam.

tion curve yielded good results; correlation of this method with the chemical analysis was excellent. A prototype instrument was evaluated by the General Analytical Laboratories; the instrument performed satisfactorily. Approximately 75% of the samples received from this program can be analyzed by this method. The remaining portion requires alternate procedures because of either insufficient material or too large a particle size that results in nonrepresentative sampling. Sample throughput is 10 to 15 per hour. (*L. V. Klatt*)

Applications of microelectronic circuitry. In 1975 we initiated a program to investigate the analytical instrumentation applications of large-scale integrated circuits. At that time we recognized that the major problem in using a minicomputer as an analytical instrument (i.e., configured by software) was the extensive design required for the computer-instrument interface. Each interface must be closely tied to the architecture and language of the computer. Thus, even minor changes in instrument operation occasionally require extensive changes in the interface and in the system programming. A complete change in instrument concept entails a virtually new design effort. This is a regrettable situation, since the computer is ideally suited for both data collection and processing and interactive instrument control. It is clear that the forte of computer application is in the dedicated mode rather than in the attempt to adapt it to continuously changing, short-term instrumentation needs. Unfortunately, analytical needs *are* continuously changing and often are short term. Our usual response to these needs is unit design and fabrication rather than the time-consuming computerization via software.

To overcome these design difficulties, we conceived the idea of developing a new type of computer-controller for instrumentation application. The key feature of this device is that it can be quickly configured via software into a wide variety of instrumentation formats. This is accomplished by combining a "calculator" type of programming language with a software-defined, highly flexible input-output interface system. The result is that computer-type data collection and instrument control can be realized in a fraction of the time generally required. The complete system specification has been detailed.[13]

This year we have continued the system design and fabrication program. The work has primarily been that of defining system logic, translating this logic

[13] W. F. Fifield, *Anal. Chem.* 47, 1983 (1975).

into an electronic component array, and, finally, fabricating the array. A majority of the subsystems have been completed, but integration of these systems into a working unit (including testing and debugging) remains a formidable task.

Commercial devices have now become available that embody many of the programming and controlling concepts that we originally envisioned. We plan to evaluate one or more of these units in terms of our instrumentation requirements. Should the devices prove sufficiently promising, we will incorporate them into this project as a means of saving both time and fabrication costs.

The originality of this work was recognized by invited participation in a joint Japan-U.S. seminar titled "Computer Assisted Chemical Research Design" held in Washington, D.C., under the auspices of the National Science Foundation and the Japan Society for the Promotion of Science. (*T. R. Mueller*)

Pattern recognition. We have continued our study of pattern-recognition mathematical techniques for handling complex analytical problems, in cooperation with the Computer Sciences Division. High-resolution gas chromatographic (GC) profiles consisting of ~150 peaks produced in the Tobacco Smoke Program are used to generate the data sets. Goals of the project are: (1) to determine which of the GC peaks are most directly related to the biological activity of the cigarettes and (2) to predict a biological effect, given only the gas-phase profile.

Three highly sophisticated pattern recognition computer codes are now operational on the ORNL large computer systems. These are RECOG (written originally by C. F. Bender of Lawrence Livermore Laboratory), DENDRO (original version by E. Hall of the University of Southern California), and ARTHUR (written originally by D. L. Duewer, J. R. Koskinen, and B. R. Kowalski of the University of Washington, Seattle).

The analysis of series I cigarettes (provided by the National Cancer Institute) is now performed on a data set of 87 GC peaks. These peaks have been selected by a semiautomatic indexing procedure that runs interactively on the ORNL DEC system 10 computer. The 87 peaks are consistent from one chromatogram to another and can be chosen with confidence. Using a "leave-one-out" algorithm, biological activities have been predicted for the series I set with an average error of 5.6%. The simple correlation coefficient (P_i experimental vs P_i predicted) is 0.97, where P_i is the adjusted percentage survival of the experimental animals at the 540th day of the biological evaluation.

The cluster analysis program, DENDRO, has been of special importance in classification of the series I cigarettes through reduction of an 87-dimensional space to a two-dimensional space; two-dimensional displays are more readily visualized and comprehended by humans. The cigarettes are classified into clusters "good," "bad," and "in-between." Significantly, GC runs on the same cigarette show closest clustering.

We have completed initial work on the computer processing and analysis of selected members of series II and series C (commercial) cigarettes. The pattern-recognition results show good agreement in ranking of the series II cigarettes according to biological activity, but the absolute values of the activities do not agree well with experimental numbers. Predicted values were calculated using the linear, least-squares model developed for series I cigarettes. The discrepancy between experimental and predicted biological activities may be due to different experimental conditions (different GC columns, different times for biological experiments, and different nature of the cigarettes). We plan to investigate further, using a training set from series II cigarettes.

This application of pattern recognition to chemical-biological problems was assisted in part by a "seed money" grant from ORNL to the Computer Sciences Division. (*R. W. Stelzner*)

Chemical Research and Development

Separation systems. Investigations of the characteristics of polyvinylpyrrolidone (PVP) as a stationary phase for liquid chromatography have indicated that binding of solutes to PVP can be based on several mechanisms. These include nonpolar interactions (adsorption), hydrogen bonding between proton-donating groups in a solute and the carbonyl oxygen on the lactam ring of PVP, partition of the solute between the eluent and a liquid phase adsorbed on PVP, and, under appropriate conditions, weakly basic anion exchanger behavior of PVP. Consequently, it appears that PVP ought to provide a very versatile, general-purpose stationary phase for chromatographic separations and that its full potential as an analytical tool has yet to be realized. Chromatographic studies have been made of various classes of aromatic organic compounds, including many which have been identified as primary

structures in coal[13] or are potentially hazardous pollutants released in coal conversion processes. Results are presented in Table I.2. With isopropanol as eluent, retention on PVP evidently depends both on the number of aromatic rings [adsorption mechanism, as in the polynuclear aromatic hydrocarbon (PAH) series] and on the availability of protons for hydrogen bonding (phenols, amines). Heteroatoms appear to have only a small effect. Excellent separations between classes of compounds and of compounds within classes are possible.

Last year a liquid chromatographic method for the separation of PAH's, using PVP as the stationary phase and isopropanol as the eluent, was described; it is now in press.[14] PAH's in several types of synthetic oils from coal conversion processes have been partially resolved by this method, however, these materials are far too complex for successful analysis by a single technique. We are taking advantage of the simplicity, low cost, and high capacity of PVP columns to scale up to the semipreparative range (1.25 × 40 cm column) for preliminary separations of these very complex materials. Collected fractions will then be further analyzed by other high-resolution techniques. In the present scheme, 250-mg oil samples are fractionated into seven groups representing, in general, (1) monoaromatics, (2) diaromatics, (3) triaromatics, (4) pericondensed four-ring structures, (5) catacondensed four-ring structures, (6) pericondensed five-ring structures, and (7) other five-ring structures and large-ring systems. Representative chromatographic fractions have been provided to G. Mamantov and E. L. Wehry (University of Tennessee) for examination by Fourier transform infrared and fluorescence spectroscopy, using matrix isolation. A paper describing these tests will be presented.[15]

A new cross-linked polymer, prepared by copolymerization of polyethylene glycol dimethacrylate and ethylene glycol dimethacrylate, has recently been reported[16] as a stationary phase for aqueous gel permeation chromatography (GPC). Compared with conventional dextran and acrylamide stationary phases for GPC, this polymer is physically stronger, more stable to acidic and basic hydrolyses, and more resistant to microorganisms. Because of our interest in improved methods for the separation of very complex mixtures of organic compounds, we have investigated some of the properties of this gel. A 1 × 90 cm column was packed by simple sedimentation, and 0.1 *M* acetic acid in 1:1 isopropanol–water was used as eluent at a flow rate of 20 ml/hr and a temperature of 62°. Elution volumes of compounds with free, polar functional groups (carboxylic acids, phenols) were greater than the total column volume, and they are retained on the gel and separated by adsorption effects or hydrogen bonding. Phenolic acids having more than one free phenolic group were strongly, sometimes irreversibly, retained. However, in tests with flavonoid compounds having esterified phenolic groups, many were eluted within the included volume of the column, and molecular sieving may be an important part of the separation mechanism. In general, it appears that polyethylene glycol gels may be a useful tool for gel chromatography of complex materials. A report of this work will be published.[17] (*G. Goldstein*)

Determination of arsenic and the methylarsines. Studies were completed on the vapor-phase HF-HNO_3 method for determining traces of arsenic in

Table I.2. Liquid chromatography of aromatic compounds on cross-linked polyvinylpyrrolidone[a]

Compound	k'[b]	Compound	k'[b]
PAH's		S-Heterocycles	
Benzene	0.41	Thiophene	0.48
Naphthalene	0.55	Benzothiophene	0.74
Phenanthrene	1.15	Dibenzothiophene	1.00
Fluoranthene	1.52	Phenols	
N-Heterocycles		Phenol	1.62
Pyridine	0.21	*o*-Cresol	1.55
Quinoline	0.31	*m*-Cresol	1.38
Acridine	0.47	*p*-Cresol	1.37
Indole	2.09	2,6-Xylenol	1.21
Carbazole	3.56	Amines	
O-Heterocycles		Aniline	1.30
Fluorenone	0.69	*N*-Methylaniline	0.85
Anthraquinone	0.68	*N*,*N*-Dimethylaniline	0.42
Dibenzofuran	0.77	Diphenylamine	1.88
Xanthone	0.51	α-Naphthylamine	2.99

[a] Eluent, isopropanol; temperature, 62°.
[b] Capacity factor, $(V_e - V_o)/V_o$.

14. R. Hayatsu, R. G. Scott, L. P. Moore, and M. H. Studier, "Aromatic Units in Coal," *Nature (London)* 257, 378 (1975).
15. G. Goldstein, "Separation of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography on Cross-Linked Polyvinylpyrrolidone," *Journal of Chromatography*, in press.
16. G. Mamantov, E. L. Wehry, R. R. Kemmerer, F. R. Hutton, R. C. Stroupe, and G. Goldstein, "Characterization of Mixtures of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography and Matrix Isolation Spectroscopy," Symposium on Analytical Chemistry on Tar Sands and Oil Shale, American Chemical Society Meeting, March 21–25, 1977, New Orleans, La.
17. D. Randau, H. Bayer, and W. Schnell, "Chromatographic Use of the Polyethylene Glycol Dimethacrylate E M Gel PGM 2000 Under Normal and Elevated Pressure," *J. Chromatogr.* 57, 77 (1971).
18. G. Goldstein, "Liquid Chromatographic Separation of Plant Phenolics Using Polyethylene Glycol Dimethacrylate Gel," *Journal of Chromatography*, in press.

siliceous materials.[19] It was found that 2-g samples of rocks containing very resistant minerals such as quartz, magnetite, ilmenite, etc., could be dissolved completely if their particle size was ≤150 μm. It was also found that if arsenic is present in the HF-HNO_3 mixture, some of it (25 to 40%) is transferred to the sample if the arsenic is trivalent, but not if it is pentavalent. Both AsF_3 and AsF_5 are quite volatile; the fact that As^{+5} does not volatilize indicates that AsF_5 is not formed, presumably because of the substantial concentration of water (~40%) in the acid mixture. The HF-HNO_3 mixture is therefore treated with $KMnO_4$ before use to oxidize any As^{+3} which might be present, thus preventing contamination of the sample. A paper on this procedure has been submitted to *Analytical Chemistry*.

If the relative amounts of inorganic arsenic and methylarsonic and cacodylic acids in a mixed solution are to be determined by measuring the relative amounts of the corresponding arsines produced by reduction, the pH behavior and interaction of the various chemical reactions must be known. A study was therefore made of the effect of solution pH on the amount of the appropriate arsine produced by the reaction of various arsenic compounds with 1% $NaBH_4$ solution. A given number of gram-atoms of As and AsO_4^{-3} produced the maximum amount of AsH_3 at the lowest initial pH (0.25) (1 *N* H_2SO_4); as the initial pH rose to 3.5 [1% $(COOH)_2$], the yield of AsH_3 decreased fourfold. When the arsenic was present as a methylated acid, a low-starting pH caused the reaction to produce 10 to 15% AsH_3, as well as the expected methylated arsine. When the initial reduction medium was 1% $(COOH)_2$, the amount of AsH_3, CH_3AsH_2, and $(CH_3)_2AsH$ produced was linearly dependent on the amount of arsenious, methylarsonic, and cacodylic acid, respectively, regardless of the proportions of the components. As would be expected from the above-described behavior of the methylated compounds in 1 *N* H_2SO_4, this linearity was not found in mixtures prepared in 1 *N* H_2SO_4. Thus, 1 *N* H_2SO_4 is a better starting medium if only inorganic arsenic is present, but the analysis of mixtures of inorganic and organic arsenic compounds should be carried out in 1% $(COOH)_2$. No work has yet been done on $(CH_3)_3As$ because of the difficulty and danger involved in producing accurate calibration curves. Since accurately prepared mixtures of $(CH_3)_3As$ and helium are now available commercially, however, an attempt will be made to analyze for this species.

In using the present arsine evolution-accumulation-arc emission detector procedure, the gas mixture swept out of the sample solution must be free of water vapor before entering the cold trap. In determining inorganic arsenic, $Mg(ClO_4)_2$ was used as the desiccant, since it does not absorb AsH_3. It does absorb CH_3AsH_2 and $(CH_3)_2AsH$, however, and thus cannot be used as a desiccant in the corresponding analyses. Trials showed that concentrated H_2SO_4 might be useful for this purpose, since it did not absorb any of the arsines. It is not possible to use H_2SO_4 in a bubbling tower, since pressure changes occurring during the analytical cycle displace the H_2SO_4. A desiccator was therefore constructed in which the gas stream passes over, rather than through, the H_2SO_4. This desiccator has performed satisfactorily in all cases.

The cold trap found to give the best resolution of the three arsines, with satisfactory sensitivity, was a U-shaped section of 6-mm-OD Pyrex tubing (cooled area 2 in. high, 1 in. wide) filled with 0.3-mm glass beads. The arsine peaks obtained from a mixture of 0.5 ng of As as AsO_4^{-3}, 0.5 ng as $CH_3AsO(OH)_2$, and 1.5 ng as $(CH_3)_2As(O)OH$ were easily measured and completely resolved.

In early experiments the CH_3AsH_2 and $(CH_3)_2AsH$ peaks were superimposed on a broad, irregular peak caused by an unknown reaction product. This material did not appear to contain arsenic, but caused interference by generating optical band emission at the arsenic and adjacent wavelengths. This interference was eliminated by inserting a trap containing granulated NaOH between the desiccant and the cold trap.

Another broad peak was observed to occur after the $(CH_3)_2AsH$ had been released from the cold trap (i.e., near room temperature). Although this peak did not interfere with the present determinations, we considered it desirable to eliminate the peak in the event that the technique was applied to less-volatile arsines. We found that either aeration or partial evacuation of the cold trap between analyses eliminated the second broad peak. To further purge the cold trap between analyses, the radiation from a quartz-iodine heat lamp is directed onto the trap for

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19. J. R. Peterson, R. J. Fellows, J. P. Young, and R. G. Haire, "Study of the Solid-State Phase Transformation of $^{249}BkBr_3$ Via Absorption Spectroscopic and X-Ray Diffraction Techniques," Proceedings of the 2nd International Conference on the Electronic Structure of the Actinides, Wroclaw, Poland, September 13-16, 1976, in press.

60 sec after the trap has come to room temperature. (*C. Feldman*)

Soluble sulfate in atmospheric particulates. A continued effort is under way to develop and evaluate a new analytical methodology for the determination of water-soluble sulfate present in atmospheric particulates collected on filters. The initial investigations involved a preliminary survey of several proposed methods for sulfate analysis. The remaining time was then used to study and optimize the sensitivity and selectivity of the method deemed most promising. The turbidimetric analysis of sulfate based on the CAD (4-amino-4'-chlorobiphenyl) reagent was surveyed first, using the miniature centrifugal fast analyzer (CFA). Poor reproducibility within replicates was encountered and was attributed to the instability of the CAD colloid in a centrifugal field. Although the addition of a polymer stabilizer did not enhance the reproducibility, a standard deviation of 1.7 ppm sulfate was achieved for a linear range of detection for 2 to 16 ppm sulfate if a deflocculant was present in the reaction mixture. Because the CAD reagent also reacted with such anions as sulfite and phosphate at similar ion concentrations, other methods for sulfate analysis were sought.

Two methods based on enzymatic reactions were investigated in an effort to establish a more selective technique for sulfate. The first procedure required the quantitative chemical reduction of sulfate to sulfite. The subsequent enzymatic reaction of sulfite with sulfite oxidase produces H_2O_2, which can be detected by one of the several existing spectrophotometric procedures. The feasibility of this enzymatic method is dependent upon the ability to chemically reduce sulfate, and, therefore, a study of several reducing agents was initiated. Various reducing columns, including a Jones reductor, Devarda's alloy, and Cd-Cu alloy, were investigated as possible reducing agents because they were most adaptable to the enzymatic reaction. However, no reduction of sulfate was observed under a variety of experimental conditions. Sodium borohydride was also tested as a reducing agent. Introduction of a $NaBH_4$ pellet reduced sulfate to sulfite and sulfide. Further studies in this direction did not appear advantageous because oxidation states other than sulfite were produced and because any remaining $NaBH_4$ would have to be removed prior to the enzymatic reaction.

The second enzymatic method surveyed was based on a three-enzyme "sulfate transferring system." In the proposed reaction scheme, sulfate concentration is proportional to the decrease in absorbance of a phenol as the phenol is sulfated via the transferring enzymes. Several attempts were made to isolate the enzymes in our laboratory because two of the three enzymes are not available commercially. No active preparation of the enzymes was obtained, owing to enzyme instability. A strain of *Salmonella typhimurium* mutant is being used that possesses two of the three required enzymes and completes the reaction scheme by reducing the transferred sulfate to free sulfite. Studies are under way to perform sulfate analysis by microbiologically reducing the anion to sulfite and then determining the liberated sulfite by the West-Gaeke colorimetric reaction.

A major portion of the project has involved the development of a direct kinetic sulfate assay carried out in cooperation with the Chemical Technology Division. In this procedure, sulfate ion catalyzes the depolymerization of zirconyl (Zr) polymer in acidic solution. Free zirconium ion then reacts with methylthymol blue (MTB) indicator to give a colored complex. The kinetic reaction is photometrically monitored at 586 nm, using the miniature CFA. The rate of formation of the Zr-MTB complex is proportional to sulfate concentration over the range 0 to 25 ppm. Kinetic data are typically accumulated over a 17-min reaction time at 30-sec intervals. A computer routine has been written to search for the linear portion of the reaction data and to calculate the maximum rate for the sample. The precision in the determination of the reaction rate, using the linear search routine, is 1 to 2%, or 0.2 to 0.3 ppm SO_4^{2-}. The detection limit is approximately 0.3 ppm. Run-to-run reproducibility and day-to-day reproducibility in sample analysis is ±0.2 ppm SO_4^{2-}. Several divalent cations have been found to interfere in the Zr-MTB technique. However, these have been removed by treating the aqueous sample batchwise with Amberlite IR-120 ion exchange resin (sodium form) prior to analysis. Fluoride, phosphate, and arsenate produce a positive interference in sulfate analysis, even at trace levels. Interference of these anions up to the 2-ppm concentration level (exceeding the upper limit of these species found in aerosol and surface water samples) can be eliminated by the addition of a 25-ppm Al(III) mask. Precipitation with excess magnesium oxide has been used for the removal of anion interferences present at concentrations greater than 2 ppm.

A correlation study between the Zr-MTB technique and a reference method was performed using rainwater samples provided by the Environmental Sciences Division. The reference method was performed independently by the Environmental

Analyses Laboratory, Analytical Chemistry Division, using the Technicon AutoAnalyzer. The correspondence between the two methods, determined by least-squares regression analysis, was found to be

(ppm SO_4^{2-}, Zr-MIB) = 1.01 × (ppm SO_4^{2-}, Technicon) − 0.15 ± 0.4 ppm SO_4^{2-},

correlation coefficient = 0.998.

Further studies in the analysis of water-soluble sulfates will include the completion of the Zr-MIB procedure, a more extensive evaluation of microbiological reduction of sulfate, and an investigation of a gas-chromatographic technique for sulfate determination (*D. Brune*).

Spectrophotometric studies at the Transuranium Research Laboratory. In cooperation with J. R. Peterson and R. L. Fellows, University of Tennessee (Knoxville), and R. G. Haire, Chemistry Division, a number of compound syntheses, characterizations and identifications, and chemical reactions were followed by spectrophotometric and x-ray diffraction techniques for microgram quantities of solid-state transuranium compounds. Such studies were primarily carried out with halides and oxyhalides of Bk, Cf, and Es and were aimed at generating knowledge about the behavior of compounds of the heaviest elements that can be obtained in microgram amounts. Such studies provide systematic and basic chemical information about the actinide series of the elements, give data for future use in the identification of synthesized elements beyond element 104, and indicate the effect of extremely high radiation fields on chemical stability and reactivity of these elements. Our ability to follow chemical reactions, or check stability, of actinide halides is the result of the unique nature of our experimental setup. Samples are obtained in sealed, thin-walled SiO_2 capillaries of suitable length for either x-ray diffraction or microspectral study. The capillary is sealed off under high vacuum or a reduced pressure of some appropriate gas, depending upon whether we desire to promote a subsequent chemical reaction when the capillary is heated.

Further studies of the reaction of H_2 with Bk, Cf, and Es halides seem to confirm the hypothesis that the attempted H_2 reduction of these halides in SiO_2 containers leads to the formation of trivalent oxyhalides. In the case of $CfBr_3$, some $CfBr_2$ is formed, but only as a transient species. With other actinide halides, little or no evidence is observed for the presence of a divalent species, but the respective trivalent oxyhalide is observed. It appears that an indirect indication for reduction of these actinide halides is the formation of oxyhalides. Conversely, preliminary data indicate that halides that are not reducible with H_2 do not yield oxyhalides on prolonged heating with H_2.

Further study of the emission (radioluminescence) spectra of einsteinium halides has confirmed an earlier hypothesis that such emissions are impurity excited and apparently not a fundamental property of pure Es(III). The emission appears to be independent of the impurity dopant and therefore represents energy transfer of einsteinium. It is known that Ca or Eu ions can cause the radioluminescence; the in-growth of Bk or Cf does not cause the emission. As more einsteinium becomes available, further studies of this phenomenon will be made.

An inferred solid-state phase transformation of $BkBr_3$ has been confirmed by both spectral and x-ray diffraction techniques. The results of this study were published.[20] The phase transformation is readily followed by observing increases in the intensities of Bk(III) *f-f* transitions when the crystal structure changes from the high-temperature, monoclinic form (AlCl$_3$ type) to the lower-temperature, orthorhombic structure ($PuBr_3$ type). The changes in the absorption spectra result from a modification of the metal ion's coordination symmetry that occurs when the crystal structure is altered from 6- to 8-coordinate. After we compared the x-ray and spectroscopic results, it was obvious that the absorption measurements were more sensitive, provided a more rapid analysis, and were not dependent upon the long-range order required for x-ray diffraction. By following the absorption intensity changes, it was also possible to study the kinetics of the phase transformation. It is believed that this is the first study where absorption changes have been used to follow a dimorphic modification of a compound or the kinetics of such a phase transition.

In carrying out the above investigations, a number of miscellaneous ancillary spectral studies were necessary, and several useful spectral results became obvious. In the phase-change studies of $BkBr_3$, it was observed that the Cf(III) daughter underwent the same coordination change as did the parent. This means that $CfBr_3$ was found as a daughter impurity in a heretofore unknown 8-coordinate form. In a study of the H_2 reduction of $BkBr_3$, preliminary results suggest that daughter $CfBr_3$ (unlike parent Bk) is

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20. C. Feldman, "Determination of Arsenic," *Anal. Chem. Div. Annu. Prog. Rep.* Nov. 30, 1975, ORNL-5100, p. 6.

more readily reduced to a reasonably pure $CfBr_3$ in the $BkBr_3$ matrix. Under the conditions of this study, the $BkBr_3$ did not react with H_2. There are several implications in these results that have application to solid-state storage of actinide compounds; further tests will be carried out. (*J. P. Young*)

PHYSICOCHEMICAL ANALYSES

X-ray fluorescence (XRF) instrumentation and quantitative analyses. Probably our most significant achievement this past year in XRF analysis is the development of a general method for matrix correction of quantitative analysis data from alloys and certain other types of samples. This method does not require the use of standards whose compositions closely resemble those of the unknown. Only "pure-element" standards for obtaining peak shapes to be used in deconvoluting spectra of mixtures are necessary. In the past, if one were going to analyze Cr-Fe-Ni-Mo alloys, for example, it was necessary to compare unknown Inconels with standard Inconels, unknown stainless steels with their corresponding standards, etc. Often, standards of suitable composition were not available. These difficulties have been eliminated.

Matrix corrections to x-ray fluorescence data must be made because the fluorescence intensity from a given element depends on the amount of absorption by other elements in the sample; simultaneously, some elements that absorb the fluorescence radiation of others have their own fluorescence enhanced. Sparks[21] of the Metals and Ceramics Division has developed a procedure that uses fundamental constants (cross sections and mass absorption coefficients) to correct for absorption and enhancement effects. Schematically, one can describe the procedure in terms of the following two equations.

$$C(N) = \frac{\text{fluorescence intensity from specimen}}{\text{fluorescence intensity from pure standard}} \times f\left(\begin{array}{c}\text{mass absorption coefficients of specimen;}\\ \text{cross sections of elements present}\end{array}\right). \quad (1)$$

$$\left(\begin{array}{c}\text{mass absorption}\\ \text{coefficients of}\\ \text{specimen}\end{array}\right) = f[C(1), C(2), \ldots, C(N)]. \quad (2)$$

where $C(1), C(2), \ldots, C(N)$ denote concentrations of the elements in the sample; the f quantities denote "functions of" factors. Equations such as the above cannot be solved in closed form. The method of successive approximations, using a minicomputer, works very well, however. The first step is to estimate the concentrations, $C(N)$, for each of the elements present by substituting their respective fluorescence intensity ratios into Eq. (1). The f quantity for Eq. (1) is first evaluated by using an estimate for the mass absorption coefficients of the specimen. The various cross sections needed are available from the literature. The second step is to make a more accurate estimate of the mass absorption coefficients of the specimen, using Eq. (2) and the $C(N)$ estimates from Eq. (1). The improved estimates of the mass absorption coefficients are substituted back into Eq. (1) for more refined calculations of the $C(N)$ values; these are then resubstituted into Eq. (2), etc. After about three iterations of this type, the $C(N)$ values converge such that they do not change further by more than 1%. A 12-element matrix can be corrected in less than 5 min on a PDP-11. Ten standards of stainless steels, Inconels, and Hastelloys have been analyzed; typical results are shown in Table 1.3.

A few brasses have been analyzed, but agreement with listed concentration values was poor. We think the listed values were incorrect, and better quality standards have been ordered. We have also applied the method to some W-Re-Os alloys (85 to 95% tungsten, varying rhenium and osmium) that had been cast in the Metals and Ceramics Division. We had no other analytical data for comparison, but results agreed well with the weight ratios used in the casting procedure. Cobalt-molybdenum-aluminum

Table 1.3. XRF analysis of some standard samples (wt %)

	Cr	Mn	Fe	Ni	Cu	Nb	Mo	Ti	Co
Stainless steel									
Certified	20.70	0.93	42.08	28.72	3.18	0.89	2.40		
XRF	20.58	1.05	43.08	28.84	3.44	0.76	2.22		
Inconel									
Certified	14.96	0.76	7.84	72.89	0.05	0.93		2.54	
XRF	14.98	0.43	7.09	74.26	0.07	0.59		2.55	
NBS Waspalloy									
Certified	18.88	0.34	2.2	56.1			4.50	3.09	13.0
XRF	18.98	0.31	2.15	57.2			4.06	2.52	14.8

21. C. J. Sparks, "Quantitative X-Ray Fluorescence Analysis Using Fundamental Parameters," *Advances in X-Ray Analysis*, vol. 19, ed. W. W. Gould et al., Plenum, New York, 1975.

oxides have also been successfully analyzed; this is discussed further in Chap. 2.

The quantitative analysis method that we have developed can be easily applied to any homogenous mixture for which *all* elements can be determined by XRF. Heavy-element alloys such as stainless steels, for which heavy elements account for 98% of the composition, are especially convenient. We are not yet ready to apply the method to biological and environmental matrices, however, because XRF cannot provide data on light elements such as carbon, hydrogen, and oxygen. To calculate mass absorption coefficients with Eq. (2), we must account for all of the elements. For light-element matrices, other methods of determining mass absorption coefficients must be used. Recently, Cox et al.[22] have reported the successful use of Compton scatter measurements for this purpose, and we will explore this technique in the coming year.

In previous annual reports we described the advantage of monochromated Ag $K\alpha$ radiation for exciting fluorescence. We have now incorporated a barrel monochromator into our system, which greatly increases intensities and reduces the time required for analyses. Detection limits are less than 10 ppm for elements having fluorescence energies (either K or L peaks) between 5 and 10 keV (atomic Nos. 24–32 and 60–74). Lowest detection limits, less than 1 p.p.m. are for elements having fluorescence energies in the 10- to 15-keV range (atomic Nos. 33–39 and 75–95). (*L. D. Hulett, H. W. Dunn*)

Photoelectron spectroscopy instrumentation. Advances in three areas related to instrumentation are being made. We are upgrading the performance of our magnetic spectrometer, building a new electrostatic spectrometer, and designing and fabricating a position-sensitive detector for simultaneous multienergetic electron detection.

The operation of the magnetic electron spectrometer has continuously been fraught with difficulties, most of which have been a result of the vacuum system. We have been aware for some time that surfaces etched by ion sputtering in this instrument undergo a process whereby material from the gas phase is deposited on the cleaned surface. This begins immediately after etching and results in a continuing degradation of peak heights and areas until the surface comes into equilibrium with the components of the gas phase. It can be shown that at a pressure of only 10^{-8} torr, which our old vacuum system had difficulty maintaining, there are sufficient gas atoms striking the surface every second to form one monolayer. With a sticking coefficient of 1, which is normally the case, a cleaned surface is very quickly covered by the adsorbed gas. In an attempt to study our capabilities for performing quantitative analysis on alloy surfaces, we found that the peak areas not only decreased rapidly after ion sputtering, but that those for different elements decreased at different rates. This made it virtually impossible to acquire data that could be reproduced with any degree of certainty. A pressure of 10^{-9} torr is desirable, and we hope that our new system will be able to maintain a pressure of at least 10^{-8} torr. For the new system, we have acquired a new 6-in. oil-diffusion pump with a matching roughing pump and a liquid-nitrogen cryotrap. We have fabricated a redesigned source chamber that will be compatible with 6-in. pump connections for adequate pumping speeds and have reduced the total pump-out volume. This new system should also increase the length of time that a clean surface can be maintained on the anode of our x-ray source. In the past, the anode surface became rapidly contaminated, which resulted in a simultaneous order of magnitude decrease in x-ray intensity after a few days of operation. Anode replacement was a major operation. The design of the new source chamber allows the x-ray components to be removed more easily. We have also purchased a new x-ray filament power supply with low drift characteristics that should provide more stable short-term photon intensity and improve the short-term counting statistics. Another inherent problem with the magnetic instrument is that it was originally designed as a beta spectrometer for high-energy electrons. At the lowest current range mode of operation the full-scale spectrometer coil current is 12.5 A, which will focus an electron with a kinetic energy of 50 keV. With an aluminum anode, our maximum measurement is for an energy of about 1.5 keV, which requires a current of 2 A. We are therefore operating on the low end of the current range and are unable to take advantage of the full resolution of the current step settings. We are considering the possibility of adding a lower current power supply that will provide full-scale current control within our present useful operating range.

For some time we have needed an electrostatic photoelectron spectrometer; E. C. Dunlop of our advisory committee suggested that we build such an instrument, using ORNL facilities, and we are

22. H. L. Cox, Jr., and P. S. Ong, "Sample Mass Determination Using Compton and Total Scattered Excitation Radiation for Energy Dispersive X-Ray Fluorescent Analysis of Trace Elements in Soft Tissue Specimens," *Journal of Medical Physics*, in press.

constructing a double-focusing electrostatic instrument with spherical field symmetry. The electrostatic field in this instrument is generated between two concentric spherical-sector aluminum electrodes with a 20-cm mean radius for the electron path. The sector angle is 145° in the horizontal section and 60° in the vertical section. A more detailed description of the instrument and the theory of its performance have been discussed by Siegbahn.[23] We have purchased a programmable power supply which will be used to accelerate or decelerate the electrons to a predetermined kinetic energy before they enter the analyzer. This will allow the selection of a constant resolution which will greatly simplify the data acquisition from the position-sensitive detector being designed. The first use of this instrument will be for testing the position-sensitive detector. The position-sensitive detector for simultaneous multienergetic electron detection consists of three components: an electron multiplier, a light-pipe array, and a solid-state line scanner. The electron multiplier (Chevron channel electron multiplier) has two tandem plates, each composed of two-dimensional arrays of parallel channels 25 μm in diameter and 31 μm center to center which can resolve events greater than 0.2 mm apart. A gain of 10^7 can be obtained. For each event a burst of electrons from the plates strikes a phosphor screen which creates a light pulse. The light pulse is channeled through the light-pipe array to the solid-state line scanner (Reticon), which stores the signal for subsequent readout. The light pipe is an array of alternating parallel transparent plates and opaque spacers. The Reticon consists of a row of silicon photodiodes, each with an associated storage capacitor to integrate the photocurrent and a multiplex switch for periodic readout via an integrated shift register scanning circuit. The Reticon has 1024 diodes on 25-μm centers, which provides a resolution exceeding that of the electron multiplier. We have checked out the Reticon response to several light-pipe configurations. At present we have selected a design that incorporates 20-mil transparent plates and 30-mil opaque spacers for a total of 20 channels across the face of the Reticon. The larger spacer is necessary to eliminate cross-talk between channels as a result of light diffraction at the light-pipe–Reticon interface. The first trial of the electron multiplier–light-pipe–Reticon combination will be made in the electrostatic spectrometer when it is completed. (*J. M. Dale, L. D. Hulett*)

Characterization of cobalt-molybdate catalysts. The electron and x-ray physics methods described in this section are, for the most part, nondestructive of the sample. When they are applied in a coordinated fashion to an individual sample or series of samples generated by a particular study, a highly detailed characterization of the samples can usually be constructed. We can determine the composition of the sample in terms of elements and compounds, using x-ray fluorescence, electron spectroscopy for chemical analyses (ESCA), electron diffraction, and x-ray diffraction. We can determine the shape and size of the specimen and the distribution of elements and compounds within it by using scanning and transmission electron microscopy. One of our main efforts this past year has been the application of our methods to a study of a coal hydrodesulfurization catalyst, cobalt-molybdenum supported on aluminum oxide. This study has been done partly in collaboration with E. L. Fuller, P. A. Agron, and R. A. Strehlow of the Chemistry Division. H. L. Richards of the Y-12 Development Division worked with us also in measuring photoelectron spectra. The effect of firing temperature on Co-Mo catalyst was studied. Six samples of catalyst fired in air at 300, 500, 700, 800, 900, and 1000° C have been characterized.

X-ray fluorescence has been found to be a quick and reliable method for determining bulk concentrations of cobalt and molybdenum in supported catalysts. We used the method of fundamental constants described above for matrix correction. XRF determinations on a large number of individual catalyst pellets showed that the cobalt concentration was approximately that specified by the manufacturer of the catalyst, but the molybdenum was significantly lower. Results from neutron activation analysis agreed very well with our measurements. XRF results indicated that the bulk concentration of cobalt and molybdenum did not change significantly with firing temperature. Many of the pellets showed brown spots on their fracture surfaces; XRF showed that these were isolated inclusions of iron, presumably Fe_2O_3.

Optical microscopy showed that for those samples fired at 900 and 1000° C, there were gross changes in phase. Purple and pink crystallites could be seen dispersed in a white-gray matrix; x-ray diffraction studies are being conducted to identify these phases. The samples fired below 900° C did not show the purple and pink phases, but one could see variations

23. K. Siegbahn, C. Hordling, and A. Fahlman, *Electron Spectroscopy for Chemical Analysis*, AFML-TR-68-189, Wright Patterson Air Force Base, Ohio.

in their overall color with the unaided eye. Samples fired at 700 and 800° C showed the most intense blue colors.

Scanning electron microscopy was used to study morphology and cobalt and molybdenum concentration profiles at the surfaces of the catalyst pellets. Pellets fired at 800° C and higher showed an increase in crystallite size. Also, there appears to be a concentration gradient in cobalt and molybdenum at the surface of pellets fired above 800° C.

ESCA studies of the catalyst pellets showed a significant decrease in cobalt concentration at the surface for those pellets fired at 900 and 1000° C. This correlates with the color bleaching effect seen at these temperatures and indicates that the cobalt diffuses away from the surface at the higher temperatures. At the lower temperatures the surface cobalt concentration was in good agreement with the bulk concentration found by XRF and neutron activation analysis. At all firing temperatures the surface molybdenum concentration was about twice that found in the bulk. This is somewhat suspect, however, since we have found higher-than-expected surface molybdenum concentrations in other materials. Appreciable concentrations of Ti, Ca, Si, Na, and Cl were also found in the surface. Another interesting result of the quantitative aspects of this work is that the average atomic ratio of Al:O in the Al_2O_3 substrate was found to be 2:3.1. This is further indication that ESCA can be developed as a quantitative tool, and we plan to pursue a detailed study in this area. The binding energies of the prominent peaks for both cobalt and molybdenum agreed to within 0.1 eV in the pellets fired at the different temperatures. However, as the temperature increased, there was peak broadening, which indicated that other chemical states were appearing. The prominent peak for cobalt agrees with that reported in the literature for CoO in octahedral symmetry. This work is not complete and further study is planned. (*L. D. Hulett, J. M. Dale, J. Tarter*)

Studies of particulates for EPA. As part of our task to develop and apply advanced concepts in analytical spectroscopy to problems in energy research, we entered an interagency agreement with EPA to identify compounds on and in particulate pollutants from mobile and stationary sources and atmospheric suspensions. The Aerosol Research Group at EPA was interested in the form of sulfur, nitrogen, and carbon found on particulates collected with eight-stage aluminum cascade impactors. The Emissions Testing and Characterization Section at EPA was interested in the elements contained on fly ash from (1) a coal-fired power plant which burned city refuse, (2) iron dust from a smelter bag house, and (3) exhaust emissions from light-duty vehicles fitted with catalytic converters.

Photoelectron spectroscopy (ESCA) techniques were used to determine the chemical form and the elemental surface concentrations of these samples to a depth of 10 to 50 atomic layers. X-ray fluoresence methods were used to complement the ESCA results by identifying the elements present in the substrates when this was of interest.

There were no unusual chemical forms found for the elements present in the surfaces of the particles from the impactor plates, the fly ash, or the iron dust. Carbon was present on all of the samples as either hydrocarbon or as adsorbed CO_2, and oxygen was present as oxide or adsorbed O_2. Other constituents present included chloride, sulfate, Ca^{2+}, adsorbed N_2, Pb^{2+}, and SiO_2. Although iron was the main constituent of the iron dust particles, as verified by XRF, it was not detected by ESCA. We have noticed this phenomenon with other types of samples, indicating that iron oxide has a tendency to cover itself with adsorbed material.

Two automobile exhaust emission specimens on fluorocarbon filters were taken from an AMC Hornet equipped with a platinum hydrocarbon oxidation catalyst and a nickel NO_x reduction catalyst. It is known that sulfur in gasoline affects the nickel catalyst and that high nickel emissions can occur. XRF showed the presence of Ni, Fe, Cr, and Pb in the first sample and only Ni in the second sample. In the first sample, ESCA revealed the presence of Ni, N, S, and Pt. Fluorine and fluorinated hydrocarbons from the filter were also detected. Sulfur was present as SO_4^{2-}, which is understandable since emissions of H_2SO_4 are known to occur. The filters had been neutralized with ammonium hydroxide after sampling, which accounts for the presence of nitrogen as NH_4^+. Platinum was present as the metal and nickel as Ni_2O_3. It is interesting to note that platinum was not detected by XRF, which is normally very sensitive for this element. Our explanation is that the platinum was present only in the outer atomic surface layer at a total overall concentration below the limits of XRF detectability. The ESCA spectra did not show the presence of nickel in the second sample; again this demonstrates the adsorption of material by transition-metal oxides.

One of the major questions to be answered in this work was whether carcinogenic nickel subsulfide was one of the products in the engine exhaust. The ESCA

spectra did not show a sulfide, and the nickel binding energy was higher than would be expected for a nickel sulfide. We concluded, therefore, that this species was either not originally present or was destroyed by the filter treatment. (*J. M. Dale, L. D. Hulett, P. S. Murty*)

Scanning electron microscopy. Our scanning electron microscopy work encompasses a number of cooperative research projects with investigators in other divisions as well as examination of special samples. The three examples below are representative of the types of studies in which we are involved.

Scaling in a geothermal system. In cooperation with E. G. Bohlmann of the Chemistry Division, we are investigating the scaling of test specimens in a dynamic geothermal test system. The specimens are exposed to a solution consisting of 800 ppm SiO_2 in 0.1 *M* $NaC_2H_3O_2$, pH 6.0, with a temperature gradient of 110 to 45°.

Samples from at least ten regions of a reaction system constructed of Pyrex tubing with stainless and carbon steel strips inserted at several locations within the system have been studied by scanning electron microscopy. Visual examination of specimens from the first experiment revealed a brown streak, several millimeters in diameter, on the bottom surface of some sections of tubing, along with some random spotting on the tube. An attempt was made to examine these specific areas. In all cases the deposits examined from the high-temperature (110°) region of the reaction system were composed of particles of silica averaging 25 μ in diameter, with smaller particles appearing to grow out from the large particles; faceting was observed on many particles. The particles were primarily silicon with a trace of iron. It was also observed that the deposit which formed in the cool (45°) region of the system was made up of silica particles with an average diameter of 0.2 μ. No gradual change in particle size was observed. Identical results were obtained on the metal strips examined. It was also noted that the deposit composed of 25-μ particles was very adherent to the tubing, while the 0.2-μ deposit could be brushed from it.

A second experiment was carried out with a more accurate temperature control in an attempt to explain the mechanism of the growth of the deposit. The temperature was increased to 175°; the solution consisted of 800 ppm SiO_2 in 0.1 *M* $NaC_2H_3O_2$ and 1 *M* NaCl, pH 6.0. We have examined the valve stem and valve seat which plugged early in the run. The scale on the valve stem was different from the one examined in the first experiment, probably due to the presence of NaCl. The scale tended to flake off the metal and appeared much rougher; that is, there were more hills and valleys observed than in the previous one. The scale was made up of Na, Si, and Cl. Some titanium was picked up from the underlying surface. Twelve samples of tubing along with some 15 metal samples have been received and are being examined.

Leaf studies. In cooperation with D. Shriner of the Environmental Sciences Division, we are examining hickory and chestnut-oak leaves by scanning microscopy. It was first necessary to determine the best method of "fixing" the leaves to preserve their wax structure. We agreed that the best method was to "fix" the leaves in OsO_4 vapor for 5 to 10 min, dehydrate through a graded series of alcohols, and store the sample in 100% C_2H_5OH prior to coating with carbon and/or gold-palladium. The structure of the wax was then examined on a number of leaves after their exposure to water at varying pH. Other leaf samples were prepared as above and studied for the presence of particles of fly ash. The leaves were taken from many trees located at varying distances and heights from a nearby steam plant; some leaves were washed in an attempt to determine if the fly ash could be removed by washing or rain; no appreciable amount of fly ash appeared to be removed by washing. At least 40 samples have been examined, and the results are being evaluated by the Environmental Sciences Division.

Particles in liquefied coal. Two samples of particles present in coal samples were received for examination of shape, size, and identification by elemental analysis. We are attempting to prepare these samples by spreading a thin film of the oily sample onto distilled water, picking up a portion of the resulting film on aluminum foil, drying, and coating with carbon prior to examining in the microscope. This technique has been successfully used in preparing similar samples for transmission microscopy. The particles isolated by this technique range in size from 0.6 to 10 μ. Some of the particles are copper compounds, while others contain Si, S, K, and Fe compounds. This work is continuing; our results along with work of B. R. Rodgers in the Chemical Technology Division will be presented at the AAAS meeting in Denver in February 1977. (*F. L. Ball*)

X-ray diffraction. For inorganic solid specimens, x-ray diffraction is probably the most-used technique for compound identification. One of the more interesting applications this year has been in the work of C. E. Bamberger, D. M. Richardson, and M. A. Bredig of the ORNL Chemistry Division. They are studying energy storage systems involving thermo-

chemical decomposition of water into hydrogen and oxygen. They propose a cycle using barium and chromium compounds.[24] The first step of the cycle is to generate hydrogen by reacting chromium sesquioxide with barium hydroxide.

$$Cr_2O_3\ (solid) + 4Ba(OH)_2\ (liquid) \xrightarrow{\sim 900^\circ C} 2BaCrO_4\ (solid) + 3H_2O\ (gas) + H_2\ (gas). \quad (3)$$

The second step is to generate oxygen from barium chromate:

$$BaCrO_4\ (solid) + Ba(OH)_2\ (liquid) \xrightarrow{\sim 1000^\circ C} \tfrac{1}{2}Ba_3(CrO_4)_2\ (solid) + H_2O\ (gas) + \tfrac{1}{2}O_2\ (gas). \quad (4)$$

The third step is to regenerate the chromium sesquioxide, barium chromate, and barium hydroxide:

$$2Ba_3(CrO_4)_2\ (solid) + 8H_2O \xrightarrow{\sim 100^\circ C} Cr_2O_3\ (solid) + 2BaCrO_4\ (solid) + 5Ba(OH)_2\ (dissolved). \quad (5)$$

X-ray diffraction was used to identify reaction products in the above cycle.

We are modifying one of our older x-ray diffraction systems to improve sensitivity and accuracy. Pyrolytic graphite crystal monochromators will be mounted on a GE goniometer to sharpen the degree of monochromation of the x radiation before and after diffraction by the specimens. This will improve the resolution of the diffracted peaks and greatly reduce the background. Much weaker diffracted peaks will be detectable, and measured lattice parameters will be more accurate. We estimate that in biological and environmental specimens we will be able to detect as little as 0.1% by weight of heavy-element crystalline material. The older detection electronics will be replaced with a low-noise solid-state system. A programmer to control the goniometer and detector has been ordered. (*H. W. Dunn*)

National Uranium Resources Evaluation Program. A national program is under way to survey and locate areas favorable for uranium prospecting. UCC-ND is responsible for the survey in the midwestern states. Part of our participation in the program is to determine uranium in sediment samples by the delayed-neutron counting method. The procedure is to irradiate samples in the ORR pneumatic tube for 60 sec, allow them to decay for 16 sec to remove ^{24}Na ($t_{1/2}$ = 4.1 sec), and then count the delayed neutrons produced by fission products for 80 sec. Since March we have analyzed 1779 samples and controls. In addition, we have run over 300 calibration standards and quality-control checks of our own. The NURE project control samples are submitted for analysis as if they were regular samples. These controls are carried through the entire sample preparation and analysis procedure and therefore reflect the quality control of the entire program. This is summarized in Chap. 5.

The uranium concentration in the sediments ranges from 1 to 20 ppm; however, most are about 2 to 3 ppm; the limit of detection for natural uranium is 0.02 ppm. A new neutron moderator and detector assembly is under construction which will improve detection efficiency for neutrons and also lower the system background. With those changes, an overall improvement of a factor of 10 is expected. (*J. F. Emery, K. J. Northcutt*)

Applied neutron activation analysis. Neutron activation analysis has been applied to a wide variety of samples, ranging from environmental materials to neutron flux monitors. Some of these materials are biologicals, coal, fly ash, air filters, rescues, plastics, quartz, resins, monozites, soot, Al, Ni, Be, Au, Pb, CsI, and MgO. The biological, coal, fly-ash, and air-filter samples were submitted for multielement analysis. In addition, assays of isotope products ^{57}Co, ^{58}Co, ^{60}Co, ^{56}Co, ^{109}Cd, ^{237}Np, and ^{238}Pu were performed. Radionuclide assays were also performed for ^{24}Na, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{76}As, ^{125}I, ^{131}I, ^{182}Ta, ^{183}Ta, ^{186}Re, and ^{198}Au. Over 7500 determinations were made on 1188 samples. (*J. F. Emery, K. J. Northcutt*)

14-MeV neutron-generator applications. The following samples were analyzed for oxygen by fast neutron activation analysis: Li metal (29), ^{58}Ni metal (1), Y metal (1), Ca metal (1), Li_3N (2), Li_2Se (4), WS_2 (3), and Li-Al alloy (5). In addition, oxygen was determined in 35 samples of lithium metal in a cooperative program with Argonne National Laboratory to determine the solubility of Li_2O in lithium metal as a function of temperature.

The neutron generator was converted to produce 2.5-MeV neutrons via the $D(d,n)^3He$ reaction to evaluate the performance of a neutron spectrometer developed by Kopp, McKay, and Borkowski of the Instrumentation and Controls Division. These tests were successful, and the detector has been set up in the Thermonuclear Division to determine the energy

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24 C. F. Bamberger, D. M. Richardson, and M. A. Bredig, "Thermochemical Decomposition of Water Based on Reactions of Chromium and Barium Compounds," *Science* 189, 725 (1975).

and origin of fast neutrons created in thermonuclear reactions. (*J. E. Strain*)

Decay heat project. This project aims at improving the accuracy and precision of the measurement of decay heat from radioactive fission products after reactor shutdown. Decay times of 0 to 10,000 sec are being studied. The heat produced during these periods is a primary determinant of reactor core shutdown cooling requirements. Several methods are being used: (1) a thermal calorimeter at LASL; (2) a nuclear calorimeter or total-absorption scintillation detector at IRT Corp.; (3) a scintillation spectrometer to measure the beta and gamma spectra at ORNL. With this variety of experimental approaches, it is hoped that a decay heat curve with an overall error of ±3 to 5% may be obtained.

The program at ORNL is to study ^{235}U, ^{239}Pu, and possibly ^{233}U. The experimental work on ^{235}U is complete and is summarized in a quarterly NUREG report;[25] the final report will be issued in the near future. Measurements on ^{239}Pu will be started by the end of 1976. Completion of the ^{239}Pu experimental work will depend on the continued operation of the Oak Ridge Research Reactor throughout calendar year 1977. The Neutron Physics Division has primary responsibility for the project. (*J. E. Emery, K. J. Northcutt*)

Trace alpha emitters in the environment. We are continuing the program[26] on low-level alpha emitters in environmental materials that is concerned with radiochemical behavior and analytical methodology for the elements from polonium to curium (and beyond if necessary). The program is in collaboration with, or in support of, the Environmental Sciences, Health Physics, Chemistry, and Chemical Technology Divisions, and other members of our own Division, particularly the Environmental and Radiochemical Analyses Laboratory (ERAL).

Methodology. Emphasis has been on simple simultaneous or sequential analyses of two or more elements in a given test portion. It was demonstrated that neptunium and plutonium could be isolated together by TTA extraction following nitrite oxidation of plutonium to the tetravalent state. Plutonium and thorium have been determined by sequential extraction of plutonium from 1 *M* HNO_3 and then thorium from 0.04 *M* HNO_3. Suggestions were made about determinations of ^{222}Rn in general, and about "emanating power" of solids. A consensus was reached on methods for identification and measurement of essentially all alpha emitters in air filters. In determining ^{226}Ra by separation with a barium carrier and correcting for its recovery, ERAL personnel obtained high radium results; the problem was found to be due to losses that occurred in precipitation of $BaSO_4$ from EDTA solution. Application of the classical logarithmic-distribution calculation with $\lambda = 1.8$ fitted the experimental data with an average deviation of 3%.

We have also studied methods which provide oxidation-state information. TTA extraction from 1 *M* HNO_3 or HCl is very selective for Pu(IV), but the HNO_3-TTA system was found to oxidize Pu(III) during the 10-min extraction period. Oxidation by HCl-TTA was much slower, and reduction of Pu(VI) was also slow; hence this system is preferred for Pu(IV) analysis. Hexone extraction is useful for Pu(VI) and U(VI), but oxidation of Pu(V) appears to take place if a 1 *M* HNO_3 – 4 *M* $Ca(NO_3)_2$ mixture is used for salting. We continue to develop procedures that are selective for specific species.

The equipment for counting and spectrometry described last year[26] has functioned very well. Assistance was given to the Environmental Sciences Division and ERAL personnel on setting up spectrometers, and two alpha detectors were evaluated on our system. Calculations were made of growth and decay of peaks in the alpha spectrum of ^{232}Th and its daughters.

Special analyses. A number of investigations by various groups required special analytical techniques or interpretation; some examples follow: (1) In collaboration with Environmental Sciences Division personnel, determination was made of the identities of alpha emitters and the valence state of plutonium in White Oak Lake water. Thorium-230 and various isotopes of U, Pu, and Cm were determined at 0.1 to 8 dis min^{-1} $liter^{-1}$; plutonium was found to be tetravalent and anionic. Neptunium was sought but not detected; it appears to be insignificant in all local environmental samples inspected. Plutonium leached from PuO_2 microspheres was shown to be radiolytically oxidized. This research may make a major contribution toward understanding how plutonium escapes from the inert oxide. (2) The U.S. Geological Survey submitted two samples from the Maxey Flats,

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25. J. K. Dickens, J. V. Love, J. W. McConnell, R. M. Freestone, D. E. Emery, and K. W. Peele, *Fission Product Beta and Gamma Energy Release Q Prog. Rep. July–September 1976*, ORNL-NUREG-TM-65.

26. S. V. Reynolds and J. C. Scott, "Radioanalysis of Environmental Materials," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1975*, ORNL-5100, p. 19.

27. R. C. Dahlman et al., "Plutonium and Related Transuranics," *Environ. Sci. Div. Annu. Prog. Rep. Sept. 30, 1975*, ORNL-5191, p. 99.

Kentucky, disposal facility for actinide analysis. In one, uranium was the dominant activity, while ^{239}Pu was largest in the other. (3) Samples of aluminum, nickel, and steel from Paducah were analyzed for neptunium and plutonium. Coprecipitation of the actinides with Pr(OH)$_3$ or PrF$_3$ was followed by TTA extraction. Significant actinide contamination was found only in an aluminum sample (Pu 0.3 dis min g^{-1}) that also contained uranium. In many cases our alpha spectrometer has been used to identify and quantitate alpha activities on plates prepared by others.

Quality control. Assurance of the quality of analyses of alpha emitters is maintained by use of reference materials. Many analyses involve the addition of known quantities of isotopic tracers of the desired nuclides, with ultimate measurement of the known and unknown activities by alpha spectrometry. If the tracers are NBS standard reference materials (SRM's) such as ^{239}Pu and ^{241}Am, measurements are traceable to NBS. In other cases, beta- or gamma-emitting isotopes are used to determine recoveries of alpha emitters. Reference materials are used to calibrate instruments; environmental materials of known contents are used to evaluate procedures. Finally, we participate in "round robins," so that our measurements may be compared with those of other participants (and sometimes certifications by the originators). The following paragraph contains examples of each of these.

In addition to NBS SRM's, a ^{210}Po preparation was obtained and calibrated for use in ^{210}Po analyses in the programs on tobacco, airborne activities, uranium mill wastes, and others. Neptunium-239 was used for ^{237}Np analyses; its gamma activity was counted in the final TTA extract, which was then evaporated and alpha counted for ^{237}Np. A ^{210}Po source from NBS was used to determine or confirm alpha efficiencies of proportional and scintillation counters and spectrometers. The counter efficiences were 50 to 51%, as expected, and efficiencies of spectrometers varied from 25 to 40%, depending on detector size. Analyzed samples of uranium ore and tailings were obtained from ERDA-Idaho; our analyses for uranium and ^{226}Ra agreed with those of ERDA. Suggestions were made with regard to an intercomparison on several environmental materials set up by the ERDA Health and Safety Laboratory. Some of those samples have been received, as well as a set for plutonium in water, prepared by Mound Laboratory for EPA. (*S. A. Reynolds*)

Low-level gamma spectrometry. The low-level gamma-ray spectrometry facility[28] in Building 4500N has been converted from lunar-sample and other NASA-sponsored analyses programs to the determination of low-concentration radionuclides in a wide variety of environmental sample matrices. High-resolution spectroscopy utilizing a Ge(Li) detector and computer-coupled pulse-height analyzer has been the system of choice for most of the environmental samples, but the NaI(Tl) systems[29,30] will be used extensively in a planned biological monitoring program for the in vivo determination of radionuclides in small animals. (*J. S. Eldridge*)

Radioactivity in trench water and suspended solids from the waste disposal site at Maxey Flats, Kentucky. Samples of water from five trenches at the Maxey Flats, Kentucky, radioactive-waste burial site and three suspended-particulate samples from three of those trenches were analyzed by high-resolution gamma-ray spectroscopy as part of a comprehensive study for determining the fate of radionuclides disposed of by shallow burial. Gamma-ray-emitting radionuclides in the water samples were ^{22}Na, ^{57}Co, ^{60}Co, and ^{137}Cs, and the suspended solids contained ^{241}Am in addition to ^{60}Co and ^{137}Cs. Contamination levels as high as 30,000 pCi liter in water and 350,000 pCi g of suspended solids were measured in some of these samples. Such levels of radioactivity in the trench water lead to the conclusion that leaching by infiltrating groundwater is an important factor in the movement of radionuclides in this important waste disposal method. This was a cooperative program with H. H. Behner, U.S. Geological Survey. (*J. S. Eldridge*)

Uranium milling operation residues. Residues from previous and current uranium milling operations (tailings) are present in large quantities at 22 locations in the western United States. An extensive survey is being conducted to determine present and potential health hazards attributable to these tailings piles to assist in possible remedial actions. A small concurrent program is being conducted to study the possible economic removal of the hazard-limiting ^{226}Ra by a simple nitric acid leaching process.

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28. W. S. Lyon et al., "Low-Level Gamma-Ray Spectrometry," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 16.

29. J. S. Eldridge et al., "Low-Level Gamma-Ray Spectrometer for Environmental Radioactivity Surveys," personal communication, Aug. 3, 1970.

30. J. S. Eldridge et al., "Nondestructive Determination of Radionuclides in Lunar Samples Using a Large Low-Background Gamma-Ray Spectrometer and a Novel Application of Least-Squares Fitting," *Nucl. Instrum. Methods* 112, 319 (1973).

Both the survey and the leaching study required the development of a reliable method for the determination of ^{226}Ra at the 1-pCi g level. We found that pulverized and blended soils from the tailings surveys or the leaching studies could be accurately analyzed with a 70-g aliquot in a 7.6-cm-diam plastic petri dish placed directly on the end cap of our new 23% Ge(Li) detector housed in a 7.6-cm-thick lead shield. This detector has a sufficiently high efficiency and low background to permit the time of counting to be as low as 1000 sec at the 1-pCi g concentration. A sophisticated computer program[31] for Ge(Li) detector spectral data resolution (MONSTR) is used on the IBM 360 for off-line data processing. Efficiency calibration of the Ge(Li) system is performed on a regular basis, and the resulting data are used for quality assurance purposes. New Brunswick Laboratory standards containing 0.05 or 0.5% uranium in a matrix of dunite are used as primary standards for the ^{226}Ra determinations.

Results from these extensive measurements have shown ^{226}Ra values ranging from approximately one to several hundred pCi g. A large selection of western states background samples were collected and analyzed in this program. These "background" samples average 1 pCi g ^{226}Ra. Associated ^{137}Cs levels are determined in the surface background samples. Levels of ^{137}Cs from atmospheric fallout range from a few tenths to 2 pCi g in those surface samples. These studies are in cooperation with F. F. Haywood of the Health Physics Division and F. J. Hurst of the Chemisty Division. A more detailed account of the survey has been described elsewhere.[32] *(J. S. Eldridge)*

Decommissioned and excess ERDA property surveys. The Assessment and Technology Section of the Health Physics Division has undertaken an extensive survey and sampling program to provide a radiological assessment of several sites that were contaminated to some degree by previous Atomic Energy Commission operations; these sites were declared excess property when they were no longer useful to the AEC program.

We have applied the ^{226}Ra measurement technique to the supportive analysis of several hundred samples from the first of these radiological surveys at the U.S. Marine Corps training center in Middlesex, New Jersey. This site was formerly a storage depot and sampling plant for uranium ore from the Belgian Congo during the 1940s and early 1950s. The site was surveyed in 1967 prior to decontamination and release to the General Services Administration in 1968. The present survey was conducted to determine the magnitude of residual radiation levels on the property and the extent of any off-site contamination. A significant discovery was the spread of ^{226}Ra contamination to property surrounding the 7-acre site, particularly to a low-lying region to the south of the site. The extent of the contamination is being evaluated.

A second survey has involved two sites, including the city garbage disposal area in Tonawanda, New York; analysis of these survey samples is under way. Results obtained so far are similar to those from the Middlesex samples. An exception is the presence of the actinium-series radionuclides in most samples in addition to the uranium-series daughters. We are revising our data analysis scheme to provide a measure of the ^{231}Pa and ^{230}Th content of these samples.

This is a cooperative program with H. W. Dickson of the Health Physics Division; a more detailed account of the work has been reported.[33] *(J. S. Eldridge)*

POLLUTION ABATEMENT OF TOXIC MATERIALS

During this period we completed our NSF(RANN)-supported project on the removal and recovery of cyanide and zinc from electroplating wastes by amine solvent extraction. The feasibility of the solvent extraction process for treating real-world cyanide wastes from the electroplating industry was evaluated in our laboratory-scale miniplant. Free cyanide and zinc cyanide were successfully removed, concentrated, and recovered in a series of demonstration runs. In addition to its pollution abatement applications, the new process shows considerable promise for the metal-finishing industry because of the potential savings through the recovered water, metals, and cyanide. Details of this work were presented in a recent article.[34]

This new approach opens the door to a host of possibilities with great potential for the metal-

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31. W. S. Lyon et al., "Activation Analysis," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 20.

32. F. F. Haywood et al., "Radiation Measurements and Assessments," *Health Phys. Div. Annu. Prog. Rep. June 30, 1976*, ORNL-5171, pp. 262-67.

33. H. W. Dickson et al., ref. 32, p. 267.

34. F. L. Moore and W. S. Groenier, "Removal and Recovery of Cyanide and Zinc from Electroplating Wastes by Solvent Extraction," *Plat. Surf. Finish.* 63(8), 26 (1976).

finishing industry. To cite the industrial demand for such technology, the response to the new process has been tremendous. Over 600 companies have contacted us for details of the process, and a number of technical personnel have visited us. We participated in two workshops on the subject. In spite of the apparent inability of various federal agencies to continue support of the project, several private companies have indicated interest in commercialization of the process; at least one company has begun work to exploit the process.

In connection with the above work, we developed an improved ion exchange resin method for the removal and recovery of zinc cyanide and cyanide from electroplating wastes. A major disadvantage in previous attempts to use anion exchange resins for cyanide removal was the difficulty of regeneration; the recent introduction by the Rohm and Haas Company of a new series of anion resins promises to alleviate that problem. Particularly interesting is Amberlite XE-275, a macroreticular, weakly basic anion exchange resin possessing tertiary amine functionality in a cross-linked acrylic matrix. Attractive features of this resin are its utility over a relatively wide pH range, rapid adsorption kinetics, good physical strength, and resistance to fouling.

We demonstrated that Amberlite XE-275 is an efficient tool for the removal, concentration, and recovery of zinc cyanide and cyanide from actual metal-finishing waste effluents. Although the resin column and feed solution pH's must be maintained in the range 6 to 7.5 (unlike the solvent extraction process), the method has applications for the analytical chemist and probably for the pollution abatement needs of the small electroplater. Details of the method were described in a recent article.[35] (*F. L. Moore*)

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[35] F. L. Moore, "An Improved Ion Exchange Resin Method for Removal and Recovery of Zinc Cyanide and Cyanide from Electroplating Wastes," *J. Environ. Sci. Health* A11(7), 459 (1976).

2. Mass and Emission Spectrometry

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The present programs of the Mass and Emission Spectrometry Section are basic and responsive to the needs of ORNL and the Nuclear Division, and as a result, the section is involved in a great variety of developmental work. It has been most gratifying to see technology developed within the section transferred immediately into a support function at ORNL and elsewhere. To cite an example of methodology transfer, the single-resin-bead technique for simultaneous determinations of plutonium and uranium in safeguards work for the International Atomic Energy Agency (IAEA) was followed by the installation of the ORNL-type two-stage mass spectrometer in the IAEA Safeguards Laboratory at Seibersdorf, Austria. This spin-off of ORNL-developed mass spectrometry techniques and hardware designs brings IAEA a giant step closer in fulfilling its safeguards analytical requirements. The resin-bead technique has been extended to other elements and is finding use in evaluating ^{240}Pu levels below the conventional counting capabilities. Another important example of technology transfer is the application of low-level techniques developed for spark-source mass spectrometry (SSMS) to the analysis of submicrogram samples of highly irradiated reactor materials for the full complement of fission products. Full advantage is being taken of the elemental coverage offered by SSMS and the multielement isotope dilution approach.

Our increasing competence in surface analyses using the ion microprobe mass analyzer (IMMA) has been accompanied by a growing awareness among investigators of the importance of studies of surface contaminants. This has resulted in increased section involvement in significant Laboratory programs. Experiments with IMMA, for example, for the Controlled Thermonuclear Reactor Program, paved the way for the preparation of metal oxide films that reduced tritium permeation 1000-fold. The problem of failure in high-temperature thermocouples was likewise elucidated; the effects of low trace-metals additions to alloy types can now be studied, since IMMA possesses extreme sensitivity and can detect small precipitates along grain boundaries.

During the past year, several isotope dilution procedures were developed and refined for spark-source and thermal-emission mass spectrometers to provide more reliable and efficient operations. Developmental and analysis work continues and has been expanded to include an organic effort for EPA under the "work-for-others" program. A collaborative trace-metals effort with the Paducah Gaseous Diffusion Plant was initiated.

As in the past, organic mass spectrometry support was given to investigators in the Biology, Chemical Technology, and Metals and Ceramics Divisions. The study of the mass spectra of nitrosamines was concluded with 147 published spectra. Techniques for both qualitative and quantitative analysis of gaseous hydrocarbons were developed for the Chemical Technology Division. A time-of-flight mass spectrometer was used to furnish support to the Metals and Ceramics Division for the study of reactions

occurring during fuel-coating experiments. Assistance also continues to Industrial Hygiene personnel at all plant areas in their studies of possible air pollution and exposure of workers to hazardous chemicals. Inorganic mass spectrometry service analyses were performed for 18 ORNL divisions and projects; over 80,000 analytical results were reported during this period. Major users are the Chemical Technology and Metals and Ceramics Divisions.

MASS SPECTROMETRY RESEARCH AND DEVELOPMENT

Ion microprobe mass analyzer. The high sensitivity of the ion microprobe mass analyzer (IMMA) has generated interest in the quantification of IMMA data. We investigated 13 National Bureau of Standards (NBS) glass and 5 NBS iron standards by two techniques with a view to establishing IMMA's capabilities in quantification. The two different kinds of standards are, hopefully, representative of nonconducting and conducting samples. IMMA was operated at the "standard" conditions recommended at an NBS workshop in January 1976. Accelerating voltage was 15 kV, and data were taken in fast raster mode from a 50- by 50-μm area. Settings for the various slits also conformed to the workshop's recommendations.

The two approaches we tried were (1) theoretical, in which concentrations are calculated on the assumption of local thermal equilibrium; and (2) empirical, in which sensitivity factors are used to calculate concentrations. The theoretical calculations are effected through the use of a computer program, CARISMA, and are based on a model developed by Andersen.[1] The assumptions upon which his model is based are open to question; however, it is the only working model available for these calculations. Concentrations that fall within a factor of 2 of the theoretical values are considered to be "good" analyses by this technique. Results from CARISMA fell within this range 63% of the time in our work. Obviously, under these conditions, IMMA is a semiquantitative technique.

The application of sensitivity factors to IMMA data presupposes the availability of a standard whose composition is not too different from the unknown. The phrase "not too different" has not yet been quantitatively defined. Although it is well known that sensitivity factors vary radically from matrix to matrix, no one has yet defined just what constitutes a "different" matrix. It is clear that conductors and nonconductors form two distinct classes. In our studies, it appeared that all the iron standards could be considered to have the same matrix; one glass standard, which was predominantly germanium oxide, gave results that showed it needed to be considered a different matrix from the remainder of the glasses, which were predominantly silicon, boron, or phosphorous oxides. Sensitivity factor calculations gave results accurate to within a factor of 2, 87% of the time, and within 20%, 45% of the time. It is obvious from these results that it is desirable to use sensitivity factors rather than CARISMA, when possible. The results obtained will be published as an ORNL report. (*D. H. Smith, W. H. Christie*)

The Controlled Thermonuclear Reactor (CTR) Program is concerned with how tritium diffuses in reactor construction materials. In a typical CTR concept, a heat exchange medium, possibly helium, will extract heat from the reactor and deliver it to a steam turbine to generate electrical power. The heat exchange medium will be contaminated with tritium. If this tritium becomes involved in the turbine steam cycle, it is considered lost to the environment, which is an unacceptable situation.

We have used the ion microprobe to investigate samples of as-received Incoloy tubing which show high tritium diffusion rates, and samples of the same material after oxidation in hot steam (similar to actual exposure in heat exchanger operation), where the tritium permeation rate is significantly reduced.

The ion microprobe revealed that both samples contained a region about 30 to 50 μm deep (measured perpendicular to the oxidized surface), where considerable perturbation of the aluminum and titanium distribution was noted. Furthermore, this region showed an approximately linear chromium depletion from the bulk material toward the surface. The second significant feature of the probe analysis was the surface segregation noted for chromium and manganese in both samples. Higher levels of these

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1. C. A. Andersen and J. R. Hinthorne, "Thermodynamic Approach to the Quantitative Interpretation of Sputtered Ion Mass Spectra," *Anal. Chem.* 45, 1421 (1973).

two elements, as well as a strong oxygen signal, were observed at the surface of the steam-oxidized sample.

The conclusions drawn from these data were as follows: During the manufacturing process the tubing undergoes oxidation damage, as evidenced by the aluminum and titanium subsurface segregation, chromium depletion, and the spotty noncontinuous oxide film on the surface. After undergoing steam oxidation, a more continuous, thicker oxide film is observed on the surface. That this film is thicker and more continuous accounts for the reduced tritium permeability.

This work suggested that removal of the 30- to 50-μm region damaged in the manufacturing process might be beneficial. Finally, the microprobe was used to show that electropolished surfaces grow thicker and the more continuous oxide films grow faster than those of the as-received Incoloy. This difference is probably due to the fact that the polished material has more chromium and manganese available at the surface with which to form the oxide film. These improved oxide films have shown a 1000-fold reduction in tritium permeation rates. In a continuing study, we plan to use the probe to establish the composition of the oxide film as a function of depth. This work will be the subject of a forthcoming publication.

As part of the Multiple Radiation Burst Test Program being carried out in the Engineering Technology Division, it is important to know the temperature of a reactor fuel cladding to within 2% during a temperature excursion. It has been observed during simulated testing that thermocouples used in the measurements decalibrate as much as 160° at 1300°C in 2 hr or less. We have used the ion microprobe to determine the cause of decalibration. The thermocouples are sealed in tantalum sheaths, and Al_2O_3 insulation permits service at elevated temperatures. Sections of the thermocouple wires at 3, 7, and 20 in. from the region of maximum temperature were removed and examined. The 20-in.-distant pair was used as a standard, because at this distance from the hot zone it was assumed that little or no alteration of the original wire composition had taken place. Mass spectra were taken in raster mode to determine what trace-level elements were present in the wires. Only aluminum was consistently observed to be present at levels ranging from trace to relatively high abundance. Based on this finding, the probe was used to determine transverse aluminum concentration profiles across a series of platinum and Pt 10% Rh wires. Semilog plots of the aluminum count rate vs transverse distance strongly suggested that the observed aluminum entered the wires via a diffusion mechanism. The 20-in.-distant standard showed very little aluminum diffusion. The 7-in.-distant wires showed considerable penetration, and the 3-in.-distant platinum wire appeared to be saturated. Independent optical-emission and spark-source analyses indicated that this wire had approximately 27 at.% Al present. In all cases the Pt 10% Rh wire exhibited significantly lower aluminum concentrations, suggesting much lower diffusion rates for aluminum in this material.

This work was repeated for another series of Pt 30% Rh Pt 6% Rh thermocouple pairs that were off calibration. The earlier findings were confirmed. It appears that, at elevated temperature, reducing conditions are set up that allow aluminum from the Al_2O_3 insulation to react with the thermocouple wires. The results of this study are being prepared for publication.

In collaboration with the Metals and Ceramics Division's High-Temperature Alloys for Space Isotopic Heat Sources Program, we have looked at a series of doped Ir 0.3% W alloys. Significant improvement in the high-temperature performance of these alloys has been obtained by doping with DOP-4 elements (Al, Fe, Ni, Rh, and Th). Auger analysis has indicated that of these dopants, only thorium segregates to grain boundaries at detectable levels. This work suggested that the solubility of thorium in this alloy was less than 1000 ppm, and alloy microstructure comparison studies suggest that it may be less than 30 ppm. We have used the ion probe to confirm that, of the DOP-4 elements, only thorium can be detected at grain boundaries: Ir 0.3% W alloy standards containing 25, 10, and 5 ppm, respectively, of thorium were studied. The extreme sensitivity of the ion microprobe clearly shows thorium segregated to grain boundaries and present as thorium-rich inclusions randomly distributed throughout the alloy. These features were clearly seen in the 5-ppm standard. It is of interest in this program to determine the solubility of thorium in this alloy. If the 5-ppm standard is correct, then we would estimate that the ion microprobe could be used down to about 0.5 ppm in this study. We plan to use isotope-dilution thermal mass spectrometry to assess the accuracy of the nominal thorium levels in the standards. In the alloys studied, the ion probe is considerably more sensitive for aluminum and iron than for thorium, so there is no question that these elements do not segregate at the levels involved. Sensitivity for nickel and rhodium are at least as good as for thorium. Further studies along this line should

establish the solubility of thorium in the Ir 0.3% W alloy. (*W. H. Christie, D. H. Smith*)

Actinides in environmental samples. Mass spectrometric procedures employing isotope dilution are being developed and applied to the determination of low levels of alpha emitters in environmental samples. The determinations of thorium, uranium, and plutonium in soil and plant uptake experiments have been done in cooperation with investigators in the Environmental Sciences Division. In such experiments, isotopic and quantitative information can be obtained using the resin-bead method. Spikes of ^{230}Th, ^{233}U, and ^{244}Pu are used for quantitative measurements.

In another effort a sample of "purified" plutonium from a waste trench was investigated for elemental content by spark-source mass spectrometry (SSMS) and for thorium and plutonium by isotope-dilution thermal-emission mass spectrometry (IDTEMS), using ^{230}Th and ^{244}Pu as isotope spikes. The main problem was to confirm or determine the alpha emitter or emitters giving rise to a large 5.50-MeV alpha pulse peak. Plutonium-238 was expected to be low in this sample; therefore, mass analysis was necessary for confirmation. A portion of the unspiked sample was analyzed by direct filament loading to see what, if any, other possible nuclides might be observed by thermal-emission mass spectrometry (TEMS). From this loading we confirmed the presence of ^{232}Th, ^{234}U, ^{235}U, ^{237}Np, and $^{239-241}$Pu. No unusual peaks were observed below $m/e = 232$, and no peak was seen at $m/e = 243$, thus suggesting the absence of thorium daughters and americium. It is usual to observe ^{243}Am in conjunction with ^{241}Am, if americium is present. A peak was observed at $m/e = 244$ and was confirmed as the ThC^+ ion.

A second aliquot was used for determining plutonium and thorium content. Spikes of ^{230}Th and ^{244}Pu were equilibrated with the sample, and then the elements were adsorbed on resin beads. The plutonium isotopic results from a single resin bead confirmed the observed alpha spectrometry peak at 5.50 MeV as ^{238}Pu. Thorium results by SSMS and TEMS checked within the expected analytical error. (*R. L. Walker, E. G. Miller, H. C. Smith*)

Americium decontamination in isotopic plutonium analysis using the resin-bead method. Experimental evidence based on the ion signals obtained from plutonium-loaded anion resin beads indicates satisfactory decontamination of americium from plutonium. This has been accomplished by scanning the ^{243}Am during plutonium analysis from direct filament loadings of dissolver solutions containing U, Pu, Np, and Am from irradiated fuels. These ^{243}Am data are compared with ^{243}Am ion signals obtained from plutonium analysis of the same solutions after anion resin-bead adsorption. The 241 mass position contains both americium and plutonium. Since americium emission occurs at lower temperatures than that for plutonium, a change in the 241/239 and 243/239 ratios is observed during the analysis. The estimated ratio of ^{241}Am/^{243}Am can be calculated from the high and low ratios. The results presented in Table 2.1 were obtained from direct filament loadings of dissolver solutions. As can be readily observed from the ^{241}Am/^{243}Am ratios in Table 2.1, this method is not very accurate. For the purpose of determining the decontamination of americium by the anion resin adsorption method, however, this approach toward estimating the amount of ^{241}Am observed in the unseparated solution seems adequate.

Ion signals of ^{243}Am (Table 2.2) were obtained when we analyzed for plutonium from anion resin beads loaded from the same 8 *M* HNO_3 dissolver solution used for straight-solution loading in Table 2.1.

Since the ^{243}Am noise-corrected counts are <0 and the ^{241}Am/^{243}Am ratio in the samples (determined from direct filament loading) is approximately 9 (Table 2.1), the decontamination of ^{241}Am in the

Table 2.1. Americium and plutonium in unseparated dissolver solutions

Loading	Sum of counts of			^{241}Am/^{243}Am
	^{239}Pu	^{241}Pu	^{243}Am	
1	3.3×10^6	1.7×10^5	2.75×10^3	7.3
2	4.4×10^6	4.9×10^5	5.78×10^3	9.4
3	8.7×10^5	9.6×10^4	1.98×10^3	10.8
4	6.4×10^5	7.1×10^4	1.41×10^3	8.0
5	4.3×10^5	4.8×10^4	3.7×10^2	9.9

Table 2.2. Test of americium decontamination in plutonium-loaded resin beads

Loading	Sum of counts of			Noise counts at mass 236.5	Net counts of ^{243}Am
	^{239}Pu	^{241}Pu	^{243}Am		
1	7.4×10^6	8.5×10^5	10	10	0
2	5.2×10^6	6.0×10^5	10	29	<0
3	8.7×10^6	1.0×10^6	12	20	<0
4	5.8×10^6	6.7×10^5	21	34	<0

^{241}Pu mass position is $>10^5$. These results (Table 2.2) indicate that americium would not contribute any significant interference in the ^{241}Pu isotopic analysis. Occasionally, very small signals at mass 243 are initially observed when analyzing for plutonium from anion resin beads. It is not known whether these counts in mass 243 are from hydrocarbons or americium; nevertheless, when this occurs, the plutonium analysis is delayed until the interference "burns off," as evidenced by a clean 243 mass position. Small quantities of ^{241}Am, whether from the lack of chemical purity or from the decay of ^{241}Pu, can be tolerated in the analysis, since, in the thermal-emission process, americium ionizes before plutonium, thereby affording some separation on the filament. (*R. L. Walker, E. G. Miller, H. C. Smith*)

Fission zirconium analysis—resin-bead method. A sensitive isotope dilution technique has been developed for the analysis of submicrogram amounts of zirconium. The analysis is based on the increased thermal ion emission for zirconium adsorbed on a single anion resin bead. Zirconium is isolated from a solution containing the sample and a highly enriched isotope spike. The detection limit depends upon the amount of the isotope spike added and the expected precision. Fifty nanograms of zirconium (sample and spike) produce sufficient ion signals for reliable isotopic analysis so that fission zirconium can be measured with blank correction to a precision of 3%. In the analysis for fission zirconium in single spent-reactor-fuel particles, contamination from normal zirconium and molybdenum can be corrected out by making isotopic measurements before and after spiking and by scanning masses 90 and 95 during the analysis. The intensities of these isotopes are used for correction based on the normal isotopic distribution. Zone-refined tantalum ribbon, essentially free of normal zirconium and molybdenum, was used as the ionizing filaments. This method could be adapted to a wide variety of samples. (*R. L. Walker, E. G. Miller, H. C. Smith*)

Isotope dilution method for gallium. A sensitive method for determining gallium water samples has been developed. Using 100 ml of solution, the method can measure as little as 2×10^{-10} g/ml of gallium. The isotope spike is ^{71}Ga, 99.7% enriched. The emission of the element loaded onto rhenium filaments is very efficient when loaded as the nitrate form. As little as 10^{-10} g of the element on a filament gives satisfactory emission for precise measurements. This method has been used to establish gallium toxicological concentration in environmental experiments being conducted by the Environmental Sciences Division. (*R. L. Walker, E. G. Miller, H. C. Smith*)

Uranium water solutions for the National Uranium Resources Evaluation (NURE) multilaboratory control program. Uranium solutions from natural lake water have been prepared, and the uranium concentration has been certified by careful isotope dilution analysis. The evaluation of these solutions for homogeneity and stability is continuing by monthly analyses. This work is in support of the multilaboratory control program conducted by the Y-12 Statistics Section. To meet the analytical requirements of the four participating laboratories and to simulate real-world samples, lake water was used as the starting material for making uranium solutions in concentration ranges fitting the real sample situation at the four NURE laboratory sites. Previous to this exercise, only synthetic solutions stabilized with 1% HNO_3 had been used in the internal UCC-ND control program.

Two 210-liter drums of Norris Lake water were analyzed by thermal-emission isotope-dilution mass spectrometry. Each drum was analyzed in duplicate, with each having a concentration of 0.22 ppb U. A uranyl nitrate spike solution was prepared from normal U_3O_8 and converted to the carbonate complex to more approximate the natural water system. By appropriate addition of uranium spike, three concentrations of uranium solutions were prepared to contain 0.82, 7.72, and 100.2 ppb

respectively. Four analyses by IDTEMS of each prepared batch were used as the certified value; the analyzed values for the three concentrations were 0.82, 7.79, and 99.7 ppb respectively.

These solutions are being mailed out to the four participating laboratories, where they are being analyzed along with NURE field samples by each laboratory's selected uranium method. The results are then submitted to the Y-12 Statistics Section for quality control assessment.

As a further check on stability and homogeneity, ORNL is making monthly checks of each control by taking aliquots from the bottom and top of the containers. Isotope-dilution results thus far (three months) do not indicate any significant change in concentration. The uranium contents of the three controls, based on eight measurements, are: 0.81 ± 0.03, 7.80 ± 0.05, and 100.0 ± 0.55 ppb respectively. These measurements compare favorably with the original certified values. In addition, this section continues to supply and certify uranium synthetic solutions for quality assurance for the UCC-ND NURE program. (*R. L. Walker, H. C. Smith, E. G. Miller*)

Age measurement studies on waste isolation site samples. Sandia Laboratories, Albuquerque, New Mexico, which is managing the search for an underground waste repository in southeastern New Mexico, has asked us to assist them by performing chemical characterization and age-dating experiments. This need arose when a brine pocket was discovered some 2710 ft below the surface in one of the test drill holes. At this depth, the brine pocket is reported[2] to be 200 ft below the proposed disposal facility. Our experiments involve the use of our two-stage thermionic mass spectrometers equipped with pulse counting for uranium and plutonium ion detection. The age-dating scheme being tested is the uranium disequilibrium approach commonly expressed by the relationship

$$[\alpha_m - 1] = (\alpha_0 - 1)e^{kt},$$

where α_m and α_0 are ^{234}U to ^{238}U alpha ratio at the present time and at intrusion time or time zero respectively, k is a decay constant, and t is the number of half-lives of ^{234}U. A number of brine samples have been measured isotopically, and the uranium and plutonium concentrations have been established. Alpha ratios were measured to be 1.35, which projects to an age of up to 10^6 years, depending on the α_0 value selected as reference. Mineral near the brine pocket where the uranium concentration was 10^3 times higher than the uranium in brines showed alpha ratios near unity, which signifies that the ^{234}U and ^{238}U are essentially in equilibrium.

The uncertainty of the α_0 is of great concern in determining age by the uranium disequilibrium technique. Values for deep-well waters in the literature vary from 1 up to 16. A feasible explanation for such a large variation has been given by Kronfeld.[3] This explanation involves the surface alpha recoil of ^{234}Th, a precursor of ^{234}U, as being a significant factor in the fractionation of uranium isotopes. Experiments on minerals and on controlled UO_2 microspheres are under way in an attempt to understand the mechanism. Additionally, some samples from deep wells, in which the uranium isotopic content was established by counting techniques, are being sought for verification by our mass spectrometry technique. (*J. A. Carter, R. L. Walker, E. G. Miller, H. C. Smith*)

ORGANIC MASS SPECTROMETRY

High-resolution organic mass spectrometer and data system (MS-50/DS-50). The DS-50 data system and associated peripheral input-output (I/O) devices for the organic mass spectrometers (MS-50 and the ORNL 12-in. single-focusing instrument) have been installed and have met initial specifications. The DS-50 system is not a time-shared system and is dedicated to one mass spectrometer at any one time for data acquisition and/or data processing.

The DS-50 system includes a 24K (16-bit word) Nova 2/10 computer. Input-output peripherals include a 4047/4049 Data General single cartridge-disk system (1.2-megaword capacity) for the storage of data and for processing software. Other I/O peripherals include a DEC DecWriter II, a Versatec 200-A printer/plotter, and an ASR-33 Teletype and Tektronix 4010 visual display unit (VDU). The 4010 VDU is the only I/O peripheral physically located with the ORNL instrument. An AEI (Kratos) analog data acquisition interface has been installed with eight additional multiplexed inputs for optional data capabilities (i.e., temperature and pressure measurements). A recent addition to I/O hardware is a four-track (1.4-megaword capacity) Tennecomp

2. "Radioactive Waste Site Search Gets into Deep Water," *Science*, p. 361, October 1975.

3. J. Kronfeld, "Uranium Deposition and Th-234 Alpha-Recoil: An Explanation for Extreme U-234/U-238 Fractionation Within the Trinity Aquifer," *Earth Planet. Sci. Lett.* 21, 327 (1974).

Data Pacer magnetic tape system that will be used for data storage as well as for disk backup.

The DS-50 software package is very comprehensive in that it can handle both low- and high-resolution data. Typically, data can be collected at high resolution (~10,000) on the MS-50 in a repetitive scan mode at a scan rate of 10 sec per decade. This capability has given us the opportunity to do high-resolution packed-column gas chromatographic mass spectrometric (GCMS) analyses. "Real-time" (post-scan) processing is another salient feature of the software, in that one may examine empirical formula, mass chromatograms, or total ion current in graphical or numeric formats during the course of a repetitively scanned gas chromatogram. Of course, post-run processing is also available in similar formats, in addition to user-selected mass spectral plots and background subtraction capabilities. Other software programs available on the system include text and data editors, interface diagnostics, data directory I/O, off-line time-to-mass conversion, and disk and central processing unit diagnostics. System capabilities can further be enhanced by user-generated FORTRAN software. An optional BASIC compiler is also available for user-generated software.

The MS-50/DS-50 combination system has been used for analysis at high resolution (~10,000) with the gas chromatograph (GC) inlet, the direct-probe inlet, and the gas-probe inlet. This type of data yields empirical formulas (within user-selected error limits) of every ion present in each mass spectrum. The metastable scanning circuitry of the double-focusing MS-50 has proved useful in identifying fragmentation pathways of selected ions. This technique allows one to examine only parent ions or daughter ions of selected ions in a mass spectrum. The technique improves "visualization" of the metastables seen in single-focusing magnetic instrument mass spectra because background peaks are virtually eliminated. Future organic applications of the MS-50/DS-50 system will involve low-ionizing-voltage high-resolution analyses of mixtures, high-resolution GCMS analyses, and metastable analyses of mixtures and individual compounds.

In addition to previously mentioned inlet systems, a quantitative gas inlet system has been designed, fabricated, and installed on the MS-50. The inlet system can be operated at temperatures up to 200° C. The pressure in the gas reservoir is measured by a capacitance manometer at pressures up to 1 torr. The 2-liter reservoir is equipped with a variable leak for variable flow rates into the mass spectrometer. The system is being evaluated for sensitivity and precision of operation. When used in conjunction with the DS-50, the system will provide accurate high-resolution mass data over the range 12 to 600. Present data indicate that accurate mass measurement at $m/e = 1$ to 12 will require development time and possibly hardware or software scan-rate modifications. The reproducibility of raw ion intensities from the system is about 3% at the 95% confidence level. (*W. T. Rainey, D. C. Canada, J. C. Franklin, J. R. Walton, L. K. Bertram*)

Du Pont 490B GCMS and data systems. A GCMS and data system was acquired this year and has been installed in Building 4500S as part of the organic structural identification facility. All standard specifications have been met or exceeded with the 490B mass spectrometer. These specifications include: a nominal resolution ($m/\Delta m$) of 600, xylene sensitivity of 7.1 C μg, maximum electron multiplier gain of 1×10^6, and a batch-inlet xylene mass flow rate of 1.5×10^{-3} μg/sec.

The 490B computer system includes a 16K, 16-bit word, 21 MX/H P computer. Software for data acquisition, storage, and processing is maintained on an H P 7900A dual-disk system (2.4-megaword fixed-cartridge disk). Peripheral I/O devices include a Tektronix 4012 CRT unit and a Tektronix 4631 hard-copy unit. A small mass-spectral library (Wiley) with software capabilities of spectral additions; a n identification aid has been supplied with the instrument.

Available 490B mass spectrometer sample inlet systems include a packed-column GCMS inlet, a heated batch inlet, and a direct-probe inlet. The heated batch-inlet system has been particularly useful for rapid m/e calibration of the instrument with perfluorokerosene. The batch inlet has also been used for qualitative analyses of gaseous samples (i.e., perfluorocyclobutane and nitrous oxide). A Perkin-Elmer (PE) 3920 gas chromatograph has been interfaced to the 490B mass spectrometer via an all-glass inlet system. The interface consists of a splitter followed by a Ryhage jet separator. At a helium carrier flow rate of about 30 cc/min, approximately 10 cc/min is split to the flame ionization detector and 20 cc/min to the spectrometer. The system, in general, has performed in a satisfactory manner for a wide variety of sample types.

Packed-column 490B GCMS work is being carried out. Initial GCMS analyses have included: Green River paraffin polynuclear aromatic hydrocarbon fractions, char-oil-energy development (COED) Syncrude fractions, trimethylsilyl (TMS) derivatives

of H-O scrubber solutions obtained from hydrocarbonization coal conversion processes, TMS derivatives of DNA hydrolysates, and fuel-particle coating scrubber solutions. (*D. C. Canada, E. H. McBay, W. T. Rainey, B. R. Clark*)

Organic mass spectrometry support activities. As in the past, the Organic Mass Spectrometry Group has given support effort to personnel requiring assistance in qualitative and quantitative organic analyses. The major support has been given to investigators in the Biology, Chemical Technology, and Metals and Ceramics Divisions. The study of the mass spectra of nitrosamines in cooperation with W. Lijinsky of the Biology Division has been completed. The spectra of 147 nitrosamines have been published,[4] and the thorough study of general fragmentation schemes of nitrosamines is being prepared for publication in the open literature. Assistance to the Chemical Technology Division has continued in the field of coal utilization, with analysis of a large number of gas samples from hydrocarbonization and other gasification studies and chromatographic fractions from various liquid fuels and effluent waters. We have also furnished support to the Metals and Ceramics Division in the use of the time-of-flight mass spectrometer to study reactions taking place in the Particle Coating Facility. This work is discussed in detail in Chap. 3.

In addition, we are assisting M. S. Judd of the Metals and Ceramics Division in evaluating possible personnel hazards in the recovery operation for perclene used in the effluent gas scrubber of the Particle Coating Facility. The use of the single-stage mass spectrometer coupled to a GCMS has enabled us to give probable identification to at least 53 chromatographic peaks present in the perclene removed from the scrubber after a variety of coating operations were carried out. These compounds are predominantly alkylated aromatic hydrocarbons varying in complexity from benzene to benzperylene derivatives. Our GCMS data have also been used to show that the recovery process removes many of the harmful polynuclear hydrocarbons. However, since this process involves distillation, it does not completely remove the low-molecular-weight hydrocarbons, even some of the methylated naphthalenes. Therefore, personnel protection will be required for those persons handling this product. We have also analyzed extracts of soot deposited in these processes. As expected, similar products were obtained, but in much lower concentrations. Only the lower volatility products were present, since the soot was collected from hot regions of the furnace facility.

We are improving our techniques for the collection and the GCMS analysis of volatile organic materials present in air. We have studied samples collected on activated charcoal granules from stack gases and in work areas and have identified large numbers of diverse compound types in these samples. These samples have been analyzed by extraction of the carbon with organic solvents, concentration of the solution, and subsequent injection into the GCMS. We have modified the inlet of the PE 3920 gas chromatograph to allow introduction of a sample collection tube containing adsorbent and sample directly into the injection port of the instrument. The glass liners used with the PE 3920 injector assembly are packed with adsorbent materials and used to collect volatiles from air. The tube is then inserted into a push-rod assembly replacing the septum and, after instrument stabilization, is inserted into the heated port for analysis. This system is being evaluated using Tenax GC as the adsorbent material, and we hope it will give us increased capability for studying environmental pollution problems.

We have also given support to F. F. Knapp of the Operations Division, who is involved in a developmental program leading to the preparation of organotellurium compounds of biological interest, specifically aimed at incorporating radioactive tellurium into compounds useful in nuclear medicine. Mass spectrometry has been very useful in proving the identity and purity of a series of dialkyl tellurides and ditellurides that will be used for synthesizing alkyltelluro steroids. Two of these products have been prepared and proved by mass spectrometry, nuclear magnetic resonance, and infrared to be 2,3-bisnor-A-telluro-5α-androstan-17β-ol and 24-nor-23-telluro-5β-cholan-3α-ol.

Continued work with Snyder and Rock of the Comparative Animal Research Laboratory has led to the identification of a major lipid component of the white portion of the rabbit harderian gland. This component has been shown to be a mixture of 2-(*O*-acyl)hydroxy fatty-acid esters in which the fatty-acid moieties are saturated and vary from C_{14} to C_{22} in

4. W. T. Rainey et al., *Mass Spectra of N-Nitroso Compounds*, ORNL TM-5500 (1976).

chain length. The *O*-acyl moieties are saturated and are predominantly C_{14} to C_{16} in chain length.[5]

Intradivisional developmental activities have also included assistance to the Bio-Organic Analysis Section. The PE 3920 gas chromatograph has been interfaced to the single-stage mass spectrometer, using a glass-jet separator with packed columns. The inlet jet has been adjusted to permit flow of 18 ml/min of helium carrier at 200°C, with the remainder of the carrier being split to the flame detector. All connecting lines are glass-lined stainless steel (except for that portion in the spectrometer source can) and are heated to prevent sample condensation. The yield of sample to the mass spectrometer appears to be about the same as that with the porous stainless steel separator used with the Varian 1200 chromatograph. However, the enrichment seems to be about 30 times greater in the jet system, resulting in source-can pressures in the 10^{-5}-torr range (as contrasted to 10^{-6} torr with the porous-tube separator). This increased enrichment is especially important in prolonging filament and heater life, in reducing background, and in maintaining lower pressure in the magnetic analyzer section during prolonged GCMS operation.

This system has been of value in analyses for our Tobacco Smoke Chemistry Program and in analyses for coal- and shale-oil-related problems. The GCMS has been of assistance in corroborating identifications proposed from chromatographic retention data and cochromatographic data in many samples. The proof of identity of the limonene, damascanone, and neophytadiene peaks in the terpene fraction of tobacco smoke condensate was accomplished with the GCMS. Another interesting problem resulted from discrepancies between the total alkaloid colorimetric and the gas-liquid chromatographic nicotine methods for analysis of certain tobacco variants. Mass spectrometric analysis showed the presence of triethylene glycol, which was not properly resolved from the nicotine peak when using aged Castorwax columns. We have also assisted in the identification of the components in the acid fraction from shale oil (a series of long-chain aliphatic acids) and in the polynuclear aromatic hydrocarbon (PAH) fraction from shale oil and shale oil process water. As expected, the latter samples were composed of aromatic hydrocarbons and their alkyl derivatives. As many as 40 components were given probable identities with complexities up to substituted pyrenes.

The increased interest in possible hazardous exposure of personnel led to the analysis of various process products such as fly ash, furnace residues, and pitch fractions. PAH fractions of these materials were generated within the Bio-Organic Analysis Section and analyzed by GCMS. The data generally confirmed the tentative identifications made from retention data, but often furnished identifications not possible otherwise. For instance, pitch and furnace residue fractions were shown to contain heterocyclic sulfur compounds (various thiophene, benzothiophene, and naphthothiophene derivatives) that undoubtedly originated from the pitch (1 to 2% sulfur content).

We have continued our contract with the Cyphernetics Corporation for use of the mass spectral search system resident in their computer system. Their search system has been of value in some cases of questionable identification made from interpretation of data for which we had no comparison with known spectra in our laboratory.

The organic mass spectrometry laboratory has analyzed approximately 400 samples during this year, many of them being very complex, multicomponent GCMS analyses. The single-stage instrument has been used with most of the samples, but increased use of the MS-50 system is expected with the more difficult analyses. (*W. T. Rainey, C. A. Pritchard, D. C. Canada*)

ISOTOPIC AND ELEMENTAL SPECTROMETRY

Evaluation of evaporated silver halide photoplates. The photographic detector in spark-source mass spectrometry is responsible for the high sensitivity of the method and also allows simultaneous detection of all isotopes from $m/e = 7$ to 245. The photoplate is also the source of analytical variations (plate sensitivity may vary by a factor of 10 within a batch of plates). The plates are easily damaged by temperature and pressure extremes, so that procurement and storage are continuous problems.

We are evaluating gelatin-free, evaporated silver halide plates[6] as ion detectors for spark-source mass spectrometry. Gelatin-free plates are commercially

5. C. O. Rock, V. Fitzgerald, W. T. Rainey, and F. Snyder, "Mass Spectral Identification of 2-(*O*-acyl) Hydroxy Fatty Acid Esters in the White Portion of the Rabbit Harderian Gland," *Chemistry and Physics of Lipids*, in press.

6. J. Masters, "Evaporated Silver Bromide as an Ion and Particle Selector," *Nature* 233, 611 (1969).

available and have been used primarily (in mass spectrometry) as detectors for high-resolution double-focusing organic mass spectrometry work at high mass. We purchased a group of these plates for evaluation after the vendor agreed to meet our mass resolution and sensitivity requirements. The grain sizes are small so that line images are very sharp and the plate background level is extremely low.

Preliminary studies have produced encouraging data. If clear glass is defined as 100% transmittance, a developed gelatin-free plate has an average transmission of 97%. Conventional gelatin plates are acceptable if the background is ≥85%. The gelatin-free emulsion has been calibrated using our standard Churchill two-line emulsion calibration program.[7] The emulsion characteristics are similar to gelatin plates; therefore, existing computer programs do not require significant modification. However, the slope of the curve in the gelatin-free plate is greater, and the linear portion of the curve does not cover as great a dynamic range as the gelatin plates. The response to ions is sufficiently high to warrant evaluation of these plates as alternate detectors for applications where low background and high-resolution mass spectral data are required. The low background makes the plate desirable as a detector for isotope-dilution spark-source mass spectrometry, especially where a very long exposure is necessary. Other possible applications in which the gelatin-free plates would be an advantage are in the search for super-heavy elements, and where spectral interferences can be eliminated by high resolution. (*J. C. Franklin, D. L. Donohue, L. Landau*)

Second computerized microdensitometer photoplate reader. We have designed and placed in operation a second, semiautomatic, microdensitometer system to read and analyze the photographic glass plates generated by spark-source mass spectrometers. The new system uses an 8K PDP-11/10 computer (16-bit), an LPS-11 laboratory peripheral system (contains a real-time clock, an analog-to-digital converter, and interfacing amplifiers), a Tennecomp Data Pacer (dual, magnetic-tape unit for bulk storage of programs and data), and an ASR-33 teletypewriter (for input/output).

The PDP-11 system makes use of a dual-beam principle to cancel the effects of any variation in light intensity. Measurements are made on sample and reference beams, with correction accomplished in software. Our first photoplate reader system used an 8K PDP-8/E (12-bit) computer and single-beam measurement.

Executive computer programs used by the PDP-11 system are KUS (keyboard utility system) and TIL (Tennecomp interpretive language), both furnished by Tennecomp Systems, Inc., for operation with the Data Pacer. TIL is very similar to FOCAL interpretive computer language. TIL software has been modified to incorporate overlay functions to operate with the Jarrell-Ash model 21-300 microdensitometer.

Computer programs written in FOCAL for the PDP-8/E must be translated to operate in TIL on the PDP-11 because of differences in computer design and machine instruction sets. Essentially, the same computer ideas and concepts are employed in the PDP-11 and PDP-8/E systems. Two basic types of progams are used: (1) isotope-dilution analysis and (2) internal standard addition.

Spark-source mass spectrometers are used to certify production quantities of nuclear reactor fuels, to assay transuranic materials, to characterize alloys, and to determine metallic elements in fuels and effluents from conventional power plants. (*R. W. Stelzner, M. T. Kelley, J. C. Franklin*)

Inductively coupled plasma system. Earlier this year we acquired a Plasma-Therm model HFS 3000-D inductively coupled plasma (ICP) source. This type of source has been used in optical-emission spectrometry for a number of years, but until recently, there have been no commercial units on the market. The technique and its capabilities have been adequately reviewed by Fassel and Knisely[8,9] at Ames Laboratory. Our interest in the technique involves the determination of parts-per-billion trace elements in aqueous and organic matrices.

To date, we have interfaced the source with our Paschen-mount direct reader and a 3.5-m Ebert photographic spectrograph. Both of these showed less than adequate sensitivity due to the long path lengths involved. The ICP is approximately 100 times less intense as an emission source than our conventional arc and spark sources. For this reason, short-path-length spectrometers are used exclusively by those workers reporting sub-parts-per-billion detection limits. We plan to acquire a 0.5-m Ebert

7. J. R. Churchill, "Techniques of Quantitative Spectrographic Analysis," *Ind. Eng. Chem. Anal. Ed.* 16, 653 (1944).

8. V. A. Fassel and R. N. Knisely, "Inductively Coupled Plasma Optical Emission Spectroscopy," *Anal. Chem.* 46, 1110A (1974).

9. V. A. Fassel and R. N. Knisely, "Inductively Coupled Plasmas," *Anal. Chem.* 46, 1155A (1974).

spectrometer to be used with the ICP for determining selected elements.

Our work with the ICP has included basic sensitivity studies for a number of elements in aqueous solutions. There has also been work on trace-element analysis of oils and other organic materials. Finally, modifications and redesign of Plasma-Therm's apparatus have been carried out to improve sensitivity and ease of operation. Work will continue in the areas of sensitivity and spectral interference (matrix) effects. (*D. L. Donohue, J. A. Carter*)

Analysis of fission product samples. We are attempting to determine, by further developing spark-source mass spectrometry capabilities, the concentrations of fission product isotopes in samples of reactor fuels that have undergone various separation procedures. We dilute samples until the radiation level is less than 200 mR per sample so that they can be handled in our spark-source mass spectrometer fitted with an alpha-containment glove box. The dilution sometimes leaves as little as 0.5 μg of sample for analysis and introduces large amounts of normal contaminants from the diluents. To aid in the analysis, we are adding a mixed ^{135}Ba, ^{125}Te, and ^{86}Sr spike to the undiluted samples and a normal erbium spike to the diluted samples. These isotope spikes are used to determine relative sensitivity factors for representative elements in the samples.

A synthetic waste sample was prepared containing 25 normal elements in the mass range of 75 to 160, with a concentration range from 0.03 μg ml to 1000 μg ml. This sample was diluted by a factor of 50 and analyzed using the same procedures as with the radioactive samples. For the exposures used, seven elements with concentrations less than 10 μg ml in the original solution gave lines too weak to be measured. The lines for the other 18 elements were used to determine relative sensitivity factors varying from 0.3 for easily ionized elements such as strontium and cesium to 1.5 for tellurium. These sensitivity factors and a computer-generated table of isotopic abundances for fuel irradiated two years and cooled two years provide analytical data with an estimated precision and accuracy of about 30% of the value. When fission product nuclei concentrations are <10 μg ml, the reliability of the data declines.

Some fission product elements can be determined from the characteristic decay of one of their isotopes, but most elements cannot; spark-source mass spectrometry is a good way to determine the concentrations of these elements in the various fractions from irradiated fuels. In the Laboratory's fuel reprocessing programs, tracing even the minor constituents through each separation is a necessity. (*J. C. Franklin, J. Landon, J. A. Carter, G. J. Gault*)

Elemental analysis. Emission spectrochemical and spark-source mass spectrographic analyses were provided to 16 ORNL divisions and related programs. A total of 61,836 analyses (2529 samples) were reported during the past year. Metals and Ceramics and Chemical Technology Divisions were the largest users of the elemental spectrometry services. In addition, we have provided analytical services to the Y-12 Plant, K-25, and the Environmental Protection Agency.

The spark-source mass spectrographic analyses of radioactive samples (^{237}Np, ^{129}I, ^{127}I, ^{239}Pu, ^{240}Pu, ^{244}Cm, ^{243}Am, ^{37}Cl, ^{119}Sn, and ^{254}Es) have continued this year. The section is heavily involved in the development of an analytical system for the analysis of dissolver solutions and residue leach solutions from cooled LWR fuel rods. The radiation associated with these samples has required analysis where major elemental concentrations are at submicrogram levels.

The Paschen emission spectrometer has provided certification analyses for aluminum, nickel alloys, and stainless steels. The method has been used to determine additives in LS-1 and related low-swelling alloys. We have ensured a precision of about 5% relative standard deviation by continuing analysis of NBS standard reference materials. Photoelectric measurements are being used as supplementary data in the determination of nickel in animal tissues.

The photographic emission spectrometers have contributed to the analysis of platinum metals and radioactive materials. We have extended our emission spectrographic procedures to support and confirm the spark-source mass spectrographic impurity analysis of platinum group metals (Ir 0.3%, W, Ir, Pt, Rh, W). Sensitivity of the ac method was not sufficient for the impurity analyses required; therefore, several dc excitation methods and buffer systems were investigated. From these studies, a modified LiF buffer dc arc method was developed with analytical capability for 18 elements at concentrations of 20 to 100 ppm.

The hot-cell-emission spectrograph has been used for support analyses for the Transuranium Research Facility laboratory, especially curium isotope product samples. The system has also been used to confirm aluminum determinations in ^{233}U solutions and solids. Additionally, qualitative spectrographic analysis on irradiated residues that remain after fuel-rod dissolutions is being done. Quantitative data are provided on a number of dissolved fission products;

the activity of certain samples exceeds 1000 R. To improve the operating conditions for the hot-cell emission spectrograph, we have installed a new grating and arc stand. The hot-cell interior has been cleaned, taped, and repainted.

This past year, two samples of an international nature were submitted for spark-source analysis. The first was a zirconium metal sample from the Bhabha Atomic Energy Center, Bombay, India. This sample is apparently going to be used as a standard reference material in India and was sent to ORNL for referee analysis. The elements Fe, Cr, Ni, Mo, Mn, and B were requested by isotope-dilution spark-source mass spectrometry at concentrations ranging from about 2 ppm for boron to about 200 ppm for iron. The results showed a higher amount of iron (1700 ppm) than was expected, and this value was verified by other techniques.

Food samples were submitted by the Canadian Agriculture Department in a round-robin study of arsenic and selenium. One problem encountered in the SSMS analysis of these samples was the necessity of ashing them to remove organic matter. This was done by wet-chemical oxidation, high-temperature, and low-temperature (rf) ashing techniques, with the latter providing the most reliable results. Another problem resulted from the high calcium and potassium levels present, which caused mass spectral interferences on the major selenium isotopes. We therefore only reported arsenic values, using an enriched minor selenium isotope as an internal standard. Again, one sample showed a high arsenic concentration (20 ppm) compared with the expected (1.2 ppm), and again other techniques provided substantial agreement. (*W. R. Musick, S. A. Macintyre, J. C. Franklin, L. Landau, R. C. Brown, E. H. Waters, G. I. Gault, L. K. Bertram*)

Mass spectrometry analysis. This laboratory performs mass spectrometric measurements on a wide variety of solids and gases. During the past year, over 19,900 results were reported, an increase of about 17% over the previous year and 50% over two years ago. About two-thirds of the analyses performed this year were for the Chemical Technology Division. The other third was split between 7 other ORNL divisions and five "work-for-others" programs. J. H. Shaffer of the Chemical Technology Division requested that we make uranium and thorium analyses for the HTGR Thorium Utilization Program. Because of the wide spread in uranium-thorium concentrations, we make two separate spikes and separate the thorium from the uranium by ion exchange before isotopic analysis. For the uranium analyses, a dilution is made and spiked with enriched ^{233}U (99.92% ^{233}U) before measuring the 238/235 ratio. The thorium analysis is made by spiking the original solution with enriched ^{229}Th (99.8% ^{229}Th). About 50 samples have been analyzed, and the uranium concentration has ranged from about 30 to over 200 mg/ml; the thorium concentrations have varied from 0.06 to 3000 μg/ml. The results on duplicate mixes indicate a precision of 1 to 2% when the thorium level is above 10 μg/ml.

E. E. McCoumbs of the Chemical Technology Division requested silver analysis for silver volatility studies. Normal silver is heated in a furnace, where the volatilized silver is removed by argon or other sweep gas. The product is spiked with ^{107}Ag and the isotopic ratio is used to calculate the amount of silver volatilized. Initial analyses indicated that about 250 μg of sample was required for a reliable analysis. However, loading the sample on silica gel, similar to the technique used for lead samples,[10] and closing the slits to give resolution from contaminating hydrocarbon peaks, enabled analyses to be made with less than 1 μg of sample.

Although the program is now complete, a large number of isotopic analyses were run this year on the ^{233}U for the LWFBR program. We have continued to make isotopic analyses on all actinides from thorium through californium. Additionally, this capability has been used to support research in other laboratories such as LASL, Ames, and the IAEA.

In the past year the analysis of gas samples has increased, primarily from expanded research activity in the Coal Technology Program. We have obtained standard saturated and unsaturated straight-chain compounds through C_6 and have obtained sensitivity factors and spectra for these compounds. These spectra and factors are used in a computer program (RESID) to calculate concentrations of 19 different components in the coal gas samples (H_2, CH_4, H_2O, N_2 + CO, O_2, H_2S, Ar, CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_4H_{10}, C_5H_{12}, C_5H_{12}, C_6H_{14}, benzene, and toluene).

We have received samples from J. F. Land of the Chemistry Division for solubility studies of mixed hydrogen isotopes in lithium for the Fusion Energy Division. We report the percentage of H_2, HD, and D_2 in these samples.

We have continued to supply the Y-12 Plant with specification analyses for argon and helium cylinders.

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[10] A. E. Cameron, D. H. Smith, and R. L. Walker, "Mass Spectrometry of Nanogram-Size Samples of Lead," *Anal. Chem.* 41, 525 (1969).

We also make analyses for tritium, krypton, and xenon from various Laboratory programs.

The number of analyses of stable isotopes for the Chemical Technology Division's Calutron Separations Program has decreased during the past year. Isotopic analyses were made on 28 different elements. Most of the samples analyzed were one of the following elements: Cl, Ge, Hg, Ni, Se, Sn, Te, Tl, and Yb. (*R. E. Ebv, L. Gunn, D. L. Whaley, W. W. Hemaker, R. L. Sherman, L. A. Bertram, J. R. Sites*)

WORK FOR OTHERS

Joint project with PGDP. We are engaged in a collaborative effort with the Paducah Gaseous Diffusion Plant (PGDP) Laboratory Division, the purpose of which is to improve the analytical techniques for determining trace impurities in both gaseous and hydrolyzed UF_6.

The initial objectives are (a) to evaluate the inductively coupled plasma (ICP) source for sensitivity vis-a-vis the methodology in use at PGDP, and (b) to study concurrently the application of gas-chromatographic techniques utilizing the arc emission detector (AED) reported in Sect. I. The AED has very high sensitivity for several elements and may offer the possibility of sequential or even simultaneous detection of certain trace metals in UF_6. Our responsibilities in this joint venture are the initial evaluation of the ICP for elements in samples furnished by PGDP and the assembly of a fluoride-resistant GC-AED system, plus assistance to PGDP personnel in optimizing spectral and chromatographic conditions.

In the Paducah Plant samples, five elements are of particular interest: Ta, Ti, Nb, Ru, and Sb. If possible, these elements must be measured at 100 ppb or lower in the presence of higher concentrations of uranium. Detection limits for these elements published by Fassel and others[1] indicate that the ICP optical-emission source should be capable of performing this task for Ta, Ti, and Nb. Little work has been published for ruthenium. Our scheme for evaluating this technique has been to interface the source with various spectrometers in our laboratory. Sensitivity studies for the five elements are run using standard solutions at concentrations ranging from 100 down to 0.1 ppm. The lowest concentration that produces a significant signal over background is taken as the detection limit. In addition, mixtures of these elements with higher amounts of uranium have also been studied. The conclusions reached thus far are that long-path-length spectrometers involve unacceptable light losses and degradation of sensitivity. With the shortest-path-length spectrometer (0.5-m Ebert), detection limits of 100 ppb have been achieved for titanium and niobium. Antimony, ruthenium, and tantalum are detectable at 0.5 to 1 ppm, but no lower with the present system. Computerized data collection involving signal integration techniques would decrease detection limits by a factor of 2 to 5, thus coming into agreement with published results. Finally, the presence of up to 10 ppm of uranium does not significantly change the response for the five elements of interest.

The GC-AED system utilizes a Micro-Tek MT-2000 GC, whose inlet and detector systems have been replaced by a sample loop of nickel tubing with Monel valves and the AED. The arc chamber is quartz and the electrodes are nickel. The chromatographic column is 2-m Teflon tubing packed with Krytox-143 AD-coated Chromosorb T. High-voltage power supplies for the arc and photomultiplier tube were built into the GC cabinet; a GCA McPherson instrument monochromator is mounted on a shelf attached at the top of the cabinet. A multiple-range, current-to-voltage transducer provides readout via a Honeywell 1-mV, 1-sec recorder. Separate ovens are provided for the sample loop and manifold. At present, only one sample container may be attached to the manifold; more may be added after the initial tests are completed. This system was constructed and tested at ORNL and then moved to Paducah in November 1976 for utilization and study by Paducah personnel. (*W. L. Maddox, D. L. Donohue, J. A. Carter*)

Platinum metals in air particulates by isotope-dilution SSMS. We analyzed for EPA composite dust samples for Pt, Pd, and Ru. The origin of the material was airborne dust particulates collected by filter banks that were located about 1.4 km from a busy eight-lane freeway interchange in Los Angeles. The major constituents of the ashed composite (50% wt loss) were Si, Al, Pb, Ca, Fe, Na, Zn, K, Mg, and Ti. Minor constituents (ppb range) including Pt, Pd, and Ru were not detectable by conventional excitation with radiofrequency spark followed by spectrometric measurement of the mass-resolved ion beams; gold was detected at the 1-ppm level. Therefore, to obtain adequate sensitive and quantitative Pt, Pd, and Ru results, we dissolved a large sample to equilibrate enriched stable isotopes of ^{196}Pt, ^{102}Pd, and ^{99}Ru, with each of these isotopically unaltered elements present in the samples prior to

platinum metal enrichment as a metal precipitate. Gold was added as a carrier. The gold and platinum-group elements were concentrated into a crude gold precipitate subsequently used in the isotope-dilution spark-source mass spectrometry (IDSSMS) measurements. The recovery of the gold by weight was near theoretical for blank acid samples, but was always less than 50% for the sample solutions. This fact did not alter the validity of the results, however, since equilibrium was established prior to the precipitation process. The range of results by isotope-dilution SSMS in micrograms per cubic meter of air are as follows: Pt, 1.5 to 3; Pd, <0.3 to 1; and Ru not detected, but <0.1. (*J. A. Carter, W. R. Musick, J. C. Franklin, G. L. Gaudet*)

Spectroscopic examination of slightly used catalytic converter beads. Under an EPA-ERDA Interagency Agreement, platinum-coated alumina catalytic converter beads have been examined by three techniques: IMMA, photoelectron spectroscopy, and SSMS. These techniques were used in the characterization of catalytic converter beads that had been exposed for about 1000 miles.

We used the ion microprobe to investigate platinum-coated alumina catalytic converter beads that appeared to have undergone different surface reactions. Many of the beads from the converter had turned partially or completely black, and the cause of this phenomenon was of interest. Sufficient ion emission could not be obtained from unmodified spherical beads. It was necessary to encapsulate them in epoxy and then grind and polish them to obtain flat cross sections suitable for analyses. Beads representing the two extremes, black and white, and several with black regions extending approximately halfway through were examined.

In all beads the black region was found to be heavily loaded with iron. Chromium and nickel were conspicuous by their absence. Aluminum was observed in both black and white regions. Based on our work with the NBS glass standards that are highly oxidized insulator materials and in a sense similar to the bead matrix, we used an aluminum-iron sensitivity ratio of 2.5. For the black region in the bead, this ratio would indicate iron concentrations up into the 20 at. % region. This high concentration would suggest that, under operational conditions in the catalyst bead, Al_2O_3 is being replaced by Fe_2O_3. The white regions of the bead exhibited iron levels several thousand times lower. The iron transverse concentration profile exhibited a very sharp gradient at the black-white interface, followed by an increasing iron concentration as one proceeds out toward the surface of the bead in the black region. This is suggestive of a diffusion process to account for iron penetration into the bead interior. Negative-ion spectra present an additional feature. Carbon peaks through C_4^- were observed, thereby indicating the presence of carbonaceous material in both the black and white portions of the bead. Independent analyses of the white beads (Al_2O_3) and black Fe_2O_3-rich beads gave 0.154 and 0.075 wt. % carbon respectively.

A separate black bead was allowed to stand two days in hot concentrated HCl. This resulted in essentially complete dissolution of the bead. Microscopic examination of a small amount of residue showed the bead to be possibly carbon and a very small amount of undissolved Al_2O_3. Chemical analysis of the solution gave an aluminum-iron ratio of 1.4, which verified the ion probe values for the iron-rich sphere. We were unable to detect platinum or palladium using an O_2^+ primary beam, and therefore, we are unable to make any statement concerning platinum or palladium distribution of the bead.

H. L. Richards of the Y-12 Laboratory Development Division analyzed several catalytic converter beads by the electron spectroscopy for chemical analysis (ESCA) technique to determine species present on the surface of the bead, and in particular, the oxidation state of platinum and palladium. The converter sample contained a heterogeneous mixture of light- and dark-colored beads. Low-resolution spectra were obtained from individual beads with both aluminum $K\alpha$ and magnesium $K\alpha$ excitation at 250 W (12.5 kV, 20 mA). Scans were made in three segments: 1200- to 1000-eV, 1000- to 500-eV, and 500- to 0-eV binding energy. The only peaks of any significance that were observed were Al, O, C, Fe, Na, and small amounts of S. However, two additional peaks, which appear to be the palladium $3d_{5/2,3/2}$ doublet, were observed on one bead. The presence of palladium was confirmed by SSMS. Efforts to observe platinum were unsuccessful. The strongest platinum photoelectron peaks, the $4f$ doublet, are superimposed on the aluminum $2p$ peak and would hinder the observation of platinum. The second strongest platinum peak at 314 eV, likewise, could not be observed.

High-resolution scans were made of the most intense photoelectron peaks so that precise binding energies could be determined. Iron was present in the beads as Fe_2O_3.

The platinum and palladium concentrations were measured by IDSSMS employing enriched ^{194}Pt and

^{194}Pd isotopes. The platinum-group elements were removed from the Al$_2$O$_3$ beads by aqua regia, and the platinum and palladium concentrations were measured after equilibrating the normal platinum and palladium removal from the bead with the known ^{196}Pt and ^{105}Pd spikes. The average platinum and palladium values for the beads were 510 and 150 ppm respectively. The average quantity of platinum per bead for the white and black specimens was found to be 13.0 and 18.5 μg respectively. Ruthenium was not observed by SSMS.

The combined studies employing the techniques of IMMA, ESCA, and SSMS showed that the catalytic converter beads have a platinum concentration of 510 ppm and that some of the Al$_2$O$_3$ beads may have reacted with the iron from the converter. The high concentration of iron in some beads suggests that the Al$_2$O$_3$ is being replaced by FeO. The FeO species was identified by the ESCA technique. Under the limited number of experiments conducted, the platinum concentration in the iron-containing beads has not decreased. Atom ratios of aluminum to iron are as high as 1.4, which probably indicates a severe corrosion condition within the catalytic converter.

With the existing state of the art, ESCA and IMMA techniques are not sufficiently sensitive to detect the level of platinum (510 ppm) on the coated Al$_2$O$_3$ catalytic beads. By the ESCA technique, the strongest platinum photoelectron peaks (4*f* doublet) are directly interfered with by the aluminum 2*p* peak; palladium peaks were observed. Platinum speciation by the IMMA technique at low concentration levels is impossible since, in the best cases, the speciation is established by a deduction and association process. Therefore, it would seem that future attempts to measure platinum oxidation states in automobile exhaust and ambient air need to await newer instrumental breakthroughs. (*W. H. Christie, J. A. Carter, J. C. Franklin, E. H. Waters*)

Gasoline and coals analysis—dry spike method. Work is continuing in the analysis of gasoline for the Environmental Protection Agency. The general technique was described in last year's annual report[11] and involves refluxing the gasoline with an aliquot of HCl containing 13 separated isotopes and normal erbium as an internal standard. Spark-source analysis is carried out by separating and drying the HCl onto graphite electrodes. The job of sample workup and spark-source analysis is being carried out in the Y-12 Plant's analytical laboratory. They provide us with the exposed photoplates from which we reduce and report the data. This arrangement is most advantageous in that it frees our personnel and equipment to perform other analytical duties while keeping close control over the data handling and interpretation.

Our joint ORNL-TVA study of coals from area steam plants has continued. We are currently reporting 12 trace elements by the use of a novel "dry-spike" isotope-dilution technique. Enriched isotopes of the various elements are dried from solution onto a high-purity silver powder. This silver is then intimately mixed with the coal ash or fly ash and formed into electrodes. In spark-source analyses, each element is measured against its enriched isotope "spike," as in normal isotope dilution. This method involves a minimum of sample preparation and reduces contamination effects. NBS standards are used as quality assurance monitors, and the results are usually within 10% of the NBS values. (*D. F. Bowman, J. C. Franklin, R. C. Brown*)

IAEA mass spectrometer installation. The mass spectrometer constructed for the International Atomic Energy Agency (IAEA) by the ORNL Mass and Emission Spectrometry Section has been installed in the IAEA's laboratory near Vienna. Three members of our group spent a month in Vienna during the installation and testing. The work went quite smoothly, largely due to rigorous quality control before the instrument left Oak Ridge.

The instrument has two magnetic deflection stages and is equipped with a pulse-counting detection system. The resulting combination of high abundance sensitivity and high sample sensitivity, coupled with good sample throughput capability, was required by the IAEA for their international safeguards program. Such an instrument was not available from a commercial vendor, and therefore IAEA negotiated a contract with Union Carbide Corporation, Nuclear Division, whereby we would build and install an instrument similar to the ones ORNL has had in operation for some years. The installation and meeting of performance specifications completes our responsibilities under this agreement.

Because the safeguards program requires the analysis (both isotopic and total) of several thousand uranium and plutonium samples each year, the

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11. D. F. Bowman et al., "Fuel Analysis by HDSSMS for EPA," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 53.

12. H. S. McKown et al., "Construction of a Two-Stage Mass Spectrometer for IAEA," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 50.

ability of the new instrument to analyze nanogram amounts of sample should significantly reduce the health hazard involved in handling fissionable materials. In conjunction with the resin-bead-sample loading technique recently developed at ORNL,[13] there is a good possibility of enormously reducing the quantity of fissionable material that needs to be shipped, thus saving the IAEA a substantial amount of money each year. Details of onsite sampling remain to be worked out.

The high abundance sensitivity of this spectrometer together with the programmable sweep of the mass spectrum allows high-precision measurements (better than 3%) of minor isotopes (< 100 ppm) to be made on small samples. Such measurements are of great importance in isotope calculation.

The following operational tests were met by the instrument:

1. Vacuum below 10^{-7} torr.
2. Two samples of NBS 010 uranium standard (≤10 ng each) were analyzed: internal precision was ~0.3%, for the 235:238 ratio and <2% for 234:235 and 236:235 ratios. Accepted values are 0.01014, 0.00538, and 0.00677, respectively.
3. Abundance sensitivity was measured to be $>10^{6}$.
4. < 0.5 ppm of ^{231}Pa was found in natural uranium.
5. Six samples were run on each of several days to demonstrate sample throughput capability.
6. Cross contamination (or lack thereof) was checked by analyzing ≤10 ng of NBS 010 (~1% 235) immediately after analyzing ≥100 ng of NBS 930 (~93% 235). The NBS 010 showed no contamination, giving a 235:238 ratio within 0.5% of theoretical.

The principal improvements in the instrument in comparison with those in use at ORNL are an updated ion source chamber pumping system and the inclusion of an on-line PDP-11 computer to accumulate and process the data. All computer programs were written within this section and were thoroughly tested before leaving Oak Ridge.

A documentation package consisting of program lists, electronic and mechanical component drawings, and an instruction manual[14] accompanied the instrument. (*H. S. McKown, W. H. Christie, D. H. Smith, L. K. Bertram, J. A. Carter, R. L. Walker*)

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13. 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 Analyzing Spent Reactor Fuels," *Anal. Lett.* 7, 563 (1974).
14. R. L. Walker, C. A. Pritchard, J. A. Carter, and D. H. Smith, *Practical Aspects of the Resin Bead Technique for Mass Spectrometric Sample Loading*, ORNL TM-4504, July 1974.
15. D. H. Smith, H. S. McKown, W. H. Christie, R. L. Walker, and J. A. Carter, *Instruction Manual for ORNL Tandem High Resolution, Symmetric Mass Spectrometer*, ORNL TM-4505, June 1974.

3. Analytical Services

L. T. Corbin, Head

During the past year, activities of the service laboratories included in-line monitoring of gaseous effluents from HTGR fuel preparation reactions, in-line monitoring of tritium in the Gas-Cooled Fast Reactor GB-10 capsule irradiation experiment, and surveillance of fission products in the Peach Bottom HTGR. In addition, we have continued our development program for the complete chemical characterization of HTGR fuel and have reestablished capabilities for the characterization of advanced LMFBR nitride fuels.

In February the Molten-Salt Reactor Program was terminated for budgetary reasons. Work during the remainder of fiscal year 1976 was directed toward an orderly conclusion of the in-line uranium monitoring program and research activities already in progress, which included electrochemical studies of tellurium and oxygenated species in molten fluorides, and transport and distribution measurements of tritium in the Coolant-Salt Technology Facility.

Concern about low-level radionuclide contamination from such diverse sources as stored waste, uranium ore tailings, and fuel reprocessing prompted us to expand and relocate a low-level alpha laboratory into the EGCR Building. Low-level radiochemical work often requires tedious chemical separations and/or long counting times; we have ordered an ND-6600 gamma-ray spectrometer system and a 19% relative-efficiency Ge(Li) detector to expedite this work. Other new equipment includes a Perkin-Elmer model 240 elemental analyzer, a model 3920B gas chromatograph, and a model 460 atomic absorption spectrometry system—all for the General Analyses Laboratory. We have also added an automatic sample changer to the graphite furnace AutoAnalyzer system in the Environmental Analysis Laboratory.

A major achievement this year was the development of a computerized data management system for records keeping and for computing and reporting results. Two terminals to the ORNL DEC system 10 have been acquired and are in use in two Analytical Services Section laboratories.

REACTOR PROJECTS

D. A. Costanzo, Group Leader

HTGR Monitoring Studies

Monitoring gaseous effluents from HTGR fuel preparation reactions, using a time-of-flight mass spectrometer. A time-of-flight mass spectrometer (TOFMS) has been used for the in-line monitoring of the gaseous effluents from the Fuel Particle Coating Facility in the preparation of HTGR fuel particles.[1] The purpose of these studies has been to optimize conditions for the production of sound fuel particles and assure occupational and environmental safety from possibly hazardous pollutants which may be produced. The identification and quantification of the reaction products have aided in the elucidation of

1. D. A. Lee, "In-Line Monitoring of the HTGR Fuel Particle Process Effluent Streams Using a Time-of-Flight Mass Spectrometer," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 36.

the chemical reaction mechanisms and kinetics relative to the physical properties of the finished particles.

During this period we prepared a paper, "In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer," which was published as an ORNL topical report and was submitted to *Nuclear Technology* for publication.[1]

Recently, we added to the TOFMS an all-metal carburization facility with a 4-in.-diam (10-cm) Inconel reaction chamber within its furnace. Samples from the effluent streams are diverted to the TOFMS through two lines, one directly at the exit of the furnace section and one after a trap that condenses liquids and tars at 0°C. This metal facility does not adsorb components of the effluent stream (e.g., H_2O) as readily as do the surfaces of the graphite-lined facility. Therefore, the mass spectra are more representative of the actual effluents, and there is less "memory" in successive samples.

There has been a continuing effort to quantify better the TOFMS data. To do this, we have made more detailed studies of sensitivity factors and fragmentation patterns of components known to exist in the effluent streams. A variety of standard gas mixtures has been used to help unravel the complex spectra in these systems. (*D. A. Lee*)

Tritium monitoring for capsule GB-10. The tritium monitoring program[2] to determine tritium production, molecular species (HT or HTO), cladding permeation, and release was terminated after capsule GB-10 attained the revised burnup goal of 100 MWd/kg of heavy metal. Fifteen tritium monitoring experiments were completed prior to postirradiation examination. Design, installation, and evaluation of the tritium monitoring system were reported.[3-5] In October 1975, tritium monitoring was terminated because of insufficient funding; development work on H_2 and H_2O monitoring and injection was also terminated. This development effort was directed toward evaluating Thermox and Meeco units for determining the H_2 and H_2O concentrations upstream and downstream of the irradiation capsule. A refrigerated moisture generator was being evaluated for controlled H_2O injection. With this equipment on line, the H_2-H_2O ratio and concentration could have been determined upstream and downstream. Thus, controlled levels of H_2 and H_2O could have been injected into the capsule sweep gas such that the oxygen potential of the capsule would not have been altered.

In July 1976, funds for the tritium program were again made available, but time did not permit installation of the H_2 and H_2O measurement and injection equipment. However, two series of experiments were conducted with the tritium monitoring system. The first series measured tritium release and transmission, using high-purity helium as sweep gas, and demonstrated that tritium is retained in areas exposed to fission product deposition. Relative release rates through the various capsule flow modes provided significant information on fission product behavior within the capsule. As expected, the highest tritium release was observed flowing through the fuel. Approximately 10% of the calculated production rate was observed in this flow mode, which suggests that high release rates can be expected during early stages of irradiation. An experiment using tritium in high-purity helium as sweep gas gave low transmission rates and confirmed the previous data.

The second series of experiments used sweep and calibration gas containing 10,000 ppm hydrogen. Tritium retained from high-purity helium was released when the sweep gas contained a hydrogen carrier. Complete transmission was observed when calibration gas containing a hydrogen carrier was passed through the capsule. Steady-state release was being approached after several hours when sweep gas containing hydrogen carrier was passed through the charcoal trap. However, this steady-state response was temperature dependent; therefore, the direct birth rate was not determined. Monitored tritium appeared to be predominately HT; however, data suggest that equilibrium and or interchange in the H_2, HT, HTO, and H_2O system may be occurring. Information on tritium production and cladding permeation could have been obtained by flowing a hydrogen carrier through the fuel region, but this was not possible because of a serious flow restriction in the fuel.[6]

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1. D. A. Lee, D. A. Costanzo, D. P. Stinton, J. A. Carpenter, Jr., W. T. Rainey, Jr., D. C. Cannada, and J. A. Carter, *In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer*, ORNL TM-5579 (August 1976).

2. J. A. Conlin and A. W. Longest, "GCFR Irradiation Experiments," *GCFR Program Prog. Rep. June 30, 1975*, ORNL-5119, pp. 51-76.

3. M. P. Pruett et al., "Tritium Monitoring System for a Reactor Experiment," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5000, pp. 98-99.

4. M. P. Pruett et al., "Tritium Monitoring System for the GB-10 GCFR Fuel Irradiation Experiment," *Trans. Am. Nucl. Soc.* 23, 116 (1976).

A complete description of the tritium monitoring program and experiments is being prepared for publication as an ORNL report. Since this program began, interest and concern about tritium production and behavior in fast breeder reactors have increased. Therefore, the real worth of the program is probably the background information required for evaluating the limitations and practicability of in-line tritium monitoring. Sufficient information is available for comprehensive tritium monitoring for the proposed capsule GB-11. (*M. E. Pruitt*)

Peach Bottom Reactor Studies

Surveillance of fission products in the Peach Bottom Reactor. We have continued to participate with the Chemical Technology Division in the HTGR fission product surveillance program. In this program the behavior of fission products in the primary circuit and fuel elements of the Peach Bottom HTGR (a 115-MW reactor owned and operated until October 31, 1974, by the Philadelphia Electric Company) is being studied. The purpose of this work is to compare measured and predicted behavior of fission products in an HTGR.

During this reporting period we completed studies of the primary circuit and finished a report describing all the results and the measurement methods for this phase of the surveillance program.[6] In work dealing with fuel-element examinations, we published a report describing results for an element irradiated to 384 equivalent full power days (EFPD),[7] prepared a report presenting findings for fuel element Eli-07[8] irradiated to 701 EFPD, continued examinations of two elements, E14-01 and F03-01, irradiated to reactor end-of-life (EOL), and began examination of two additional EOL elements, EOI-01 and FO5-05. (*F. F. Dyer, L. C. Bate*)

Examination of Peach Bottom primary circuit. This activity, pursued since 1970 and concluded this year with the above-mentioned reports,[6,7] consisted of four types of observations:

1. Measurements on four occasions of the axial distribution of radionuclide plateout on the primary-circuit cold duct.
2. Determination on three occasions of the concentrations of condensible radionuclides, for example, ^{131}I and ^{137}Cs, in the coolant. These measurements, carried out with samplers that withdrew coolant upstream and or downstream of the loop steam generator, were designed to determine both gas- and particulate-borne radionuclides. Separations of radioactive species according to their physical and chemical nature were effected by combinations of gaseous diffusion tubes, cascade impactors, and particle filters.
3. Measurement on three occasions of the krypton and xenon isotopes in the primary coolant and purge-gas helium.
4. Characterization—physical, chemical, and radiochemical—of dust specimens obtained on three occasions during core 2 operation from the reactor's cyclone dust separators.

References 6 and 7 contain details of the methods used and results found in this study. (*F. F. Dyer*)

Examination of Peach Bottom fuel elements. The procedures used in the examination of fuel element Ell-07 (701 EFPD) are generally those being used for all EOL elements. Details of the experimental methods have been published.[8]

Examination procedures focused on the determination of the total amounts and distributions of radionuclides in the graphite portions of the elements. The gamma emitters ^{60}Co, ^{110m}Ag, ^{134}Cs, ^{137}Cs, and ^{154}Eu were found in significant amounts in the graphite components of Ell-07. Gamma spectra acquired at 0.62-cm intervals along the sleeve and spine of Ell-07 permitted highly detailed distributions of these radionuclides to be derived. From these data it was found, for example, that the sleeve contained 17 Ci and the spine 8.3 Ci of ^{137}Cs. Radial distributions of these gamma emitters plus the beta emitters ^{3}H, ^{14}C, and ^{90}Sr were obtained at six axial locations, four within the fueled region and one each above and below the fueled region. Radial dissection was accomplished by the use of a lathe in a hot cell operated remotely by manipulators. Radial profiles reveal that ^{134}Cs penetrated the graphite sleeve and spine to a larger extent than did ^{137}Cs, due, evidently, to a longer time spent as a xenon precusor of ^{134}Cs.

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6. F. F. Dyer, R. P. Wichner, W. J. Martin, and H. J. deNordwall, *Distribution of Radionuclides in the Peach Bottom HTGR Primary Circuit During Core 2 Operation*, ORNL-5188, in review for publication.

7. F. F. Dyer, R. P. Wichner, W. J. Martin, L. L. Fairchild, R. J. Kedl, and H. J. deNordwall, *Post-Irradiation Examination of Peach Bottom HTGR Driver Fuel Elements E06-01*, ORNL-5126 (April 1976).

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, in review for publication.

Examinations of EOL fuel elements E14-01, F03-01, E01-01, and F05-05 are at various stages of completeness. Visual, photographic, and metrology phases of the examinations on all components of each element are complete. Also complete are measurements of the gamma-emitter inventory in the fuel of each element as well as axial gamma scanning of the graphite components of E14-01 and F03-01. Currently in progress is the measurement of radial distribution of beta emitters in the graphite components of E14-01. Preparation of a report presenting the results found for E14-01 is in progress, and reports for the additional EOL elements will be started soon. (*F. F. Dyer*)

Lathe modifications for hot-cell machining. To measure the radial fission product distribution in highly radioactive sleeves and spines from the Peach Bottom fuel elements, a lathe was modified for hot-cell operation to machine and contain samples. Modifications consisted of the following:

The motor was replaced with a variable-speed motor with external speed control mounted behind the lathe. Collets were machined to the proper diameter for holding either the sleeves or spines in the lathe.

The control knobs for power feed, cross-feed carriage, and the tail stock were changed to square blocks that the fingers of the manipulators can grip and turn. A tool block to hold the cutting tool was mounted on the cross feed with a micrometer dial attached to measure depth of cut. The normal cutting tool was used for sleeves, and the extended cutting tool was used for the spines.

An arm with a centering dial was attached to the frame and was movable, permitting it to be turned to position over either the sleeve or the spine so as to center the piece prior to machining. The sleeve or spine was adjusted to the center by using the centering dial. After use, the centering dial was moved to a rest position out of the way.

The sleeve specimens were filled with epoxy, and a metal rod was centered in the epoxy and used to manipulate the specimen. The epoxy gave the sleeve enough strength so that it would not crumble when the interior wall of the sleeve was machined. Since the sleeves are not perfectly round, some epoxy was machined on the last cuts and was removed from the sample.

A basket was designed to attach to the lathe frame and enclose the collet and sleeve or spine specimen and contain the machined sample. The basket was made of two sections, with the top hinged for opening to retrieve the sample. A scoop was made to fit the bottom of the basket to collect samples and transfer them to the tared bottles with a funnel. A screen was sealed in the funnel to facilitate the separation of the graphite and epoxy during the final cuts of a sleeve. (*L. C. Bate*)

Defective particle fraction of Peach Bottom fuel. A method was developed to determine directly the failed fuel-particle fraction of irradiated driver-element fuel from the Peach Bottom Reactor. The method consists of the following steps:

1. Cut surfaces of a core sample taken from a fuel-element compact are electrolytically cleaned to remove damaged particles.[9]
2. The sample is weighed and hot-chlorine leached at 1000°C to remove the thorium and uranium exposed in the failed particles.[10]
3. The sample is electrolytically deconsolidated after leaching, the particles separated from the matrix graphite, and the total number of particles determined from the total particle weight.

Four Peach Bottom archive compact samples, weighing approximately 9 g each and containing about 15,000 particles, gave a mean failed-particle fraction of 0.28% with excellent agreement between the determination by thorium and uranium mass from each sample. The number of failed particles is determined from the weight of the leached thorium or uranium and the average amount of heavy metal per particle. (*J. L. Botts*)

Methods Evaluation and Development

Determination of the defective-particle fraction in HTGR fuels. The high-temperature (1500°C) chlorine leach method for the determination of the defective-particle fraction in HTGR fuels[11] has continued to be applied successfully throughout the year to a large number and variety of samples. The installation of a new and more powerful (10-kW) induction heating unit has not only added to sample

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9. D. A. Costanzo et al., "Gas-Cooled Reactor Programs," *Anal. Chem. Div. Annu. Prog. Rep. Sept. 30, 1974*, ORNL-5006, p. 35.

10. D. E. LaValle, D. A. Costanzo, W. J. Lackey, and A. J. Caputo, *The Determination of Defective Particle Fraction in HTGR Fuels*, ORNL TM-5483 (September 1976).

11. D. E. LaValle, "Determination of Particle Failure Fraction," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 33.

analyses capacity but has also made possible the chlorination of larger specimens such as the ½-in. commercial HTGR fuel rod design and large segments of 3-in.-diam Peach Bottom fuel compacts. The question of whether the SiC layer in Triso-coated fuel particles may prevent the detection of defects in the inner low-temperature isotropic (LTI) pyrocarbon coating was resolved. Particles with a permeable inner LTI coating enclosed by only an outer SiC coating were subjected to the chlorine leach. In 1 hr the silicon was removed as $SiCl_4$; the residual carbon[12] presented no barrier to the removal of uranium through the permeable inner LTI coating.

We prepared a paper entitled "The Determination of Defective Particle Fraction in HTGR Fuel" which was published as an ORNL topical report and has been submitted to *Nuclear Technology* for publication.[13] (*D. E. LaValle*)

Heavy-metal assay for HTGR fuel particles. We also investigated the possibility of adapting the chlorine leach to the total assay of thorium and uranium in coated fuel particles. In this determination the two chief problems are the removal of the coating layers and the dissolution of the refractory ThO_2 kernels. In the past, coatings have been removed by crushing and burning, followed by dissolution of the ThO_2 in alkali or borate fusion or by an acid leach. More recently a method[14] has been developed using oxygen and chlorine to remove the pyrocarbon and SiC layers of the coating, but still dissolving the fuel kernel by fusion or acid leaches. These procedures have been lengthy and cumbersome; more desirable would be an extension of the chlorine leach to convert the ThO_2 to easily soluble $ThCl_4$.

We carried out a preliminary study using the existing horizontal system[12] as designed for the hot cell at 1000°C. The conditions for removal of the coatings were quickly established: 1 hr in a 1:1 mixture of O_2 and CO_2 at 800°C for each pyrocarbon coating and 1.5 hr in Cl_2 at 1000°C for the SiC for 5-g samples of fuel particles. The attempted conversion of the bare kernels was unsuccessful, however. Using a gas mixture of CO and Cl_2 in a ratio of 2:1 at 1000°C, conversions ranged from 20% in 4 hr to 75% in 12 hr.

We turned to the more favorable design of a vertical system in which the sample, resting on a sealed-in frit in the quartz tube, allowed an upward flow of gas to create a fluidized bed. The chlorinating agent was phosgene ($COCl_2$) used alone, or with added carbon (soot) on the sample, or in combination with CO. The high-fired ThO_2 kernels used, in 1-g samples, were virgin material and had never been incorporated in fuel particles; the samples assayed 99.6% ThO_2. Runs were made of 7 hr duration with fairly uniform results of ~95% conversion. Another apparatus of vertical design incorporated a loop of 8-mm-OD tubing to hold the sample and keep it concentrated in one spot exposed to maximum heat. Results were the same, and an examination of the residual kernels under the microscope showed the majority to be practically undiminished in size. The reason for this resistant fraction is unknown.

Resistance furnaces may be obtained (Kanthal-wound) that operate as high as 1300°C in air. However, we investigated conversions at this temperature, using induction heating and adapting the particle failure fraction apparatus to a downward flow of gas into a collector flask below for the $ThCl_4$. In these runs, 5-g samples of coated fuel particles were treated in the horizontal 1000°C apparatus to remove the coatings, the bare kernels then being weighed before transfer to the induction heating apparatus. The conversion was accomplished at 1300°C in a gas mixture of CO and Cl_2 in the optimum ratio of 3:1. In a series of nine runs, conversions of 98.0 to 98.5% were obtained on the assumption that the kernels were 100% ThO_2. However, in each sample, approximately 100 kernels were black and were found to contain quantities of uranium and minor impurities. The time for conversion of approximately 2.7 g of ThO_2 kernels from 5 g of fuel particles was 3.5 hr. Total time, therefore, including coating removal, is ~7 hr, in contrast to the crush-burn-leach method, which requires up to 44 hr. (*D. E. LaValle*)

Determination of defective SiC coating fraction. Because the ignition-acid leach procedure for determining the defective SiC coating fraction of HTGR fuel particles has proved unsatisfactory, a technique[15] which employs mercury penetration and radiography to detect defective SiC coatings was

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12. J. Nickl and C. Braunmühl, "Chlorierung und Analyse hochschmelzender Carbide," *Z. Anal. Chem.* 221, 223 (1966).
13. D. E. LaValle, D. A. Costanzo, W. J. Lackey, and A. J. Caputo, *The Determination of Defective Particle Fraction in HTGR Fuels*, ORNL-TM-5483 (September 1976).
14. S. R. Reeder et al., "Analysis of HTGR Coated Fuel Particles for Uranium and Thorium," *Anal. Chem. Branch Annu. Rep. October 1974*, ICP-1056.
15. D. M. Hewette and W. R. Laing, "Detection of Defective SiC Layers in Coated Nuclear Fuel Particles," *Nucl. Technol.* 21, 149 (1974).

evaluated as a possible method for routinely determining the defective SiC coating fraction of Triso fuel particles. Particles from which the outer LTI pyrocarbon coating has been removed by ignition are pressurized at 1.034×10^8 Pa (15,000 psi) in an Aminco porosimeter. Mercury forced through any defects in the SiC layer is detected by radiography. Five-gram samples containing approximately 30,000 particles were employed in order to statistically improve the value obtained for the defective fraction. This technique is being routinely used to study the effect of various coating-process parameters on the defective-particle fraction. (*F. L. Layton*)

Silicon carbide removal by chlorination. In the determination of defective-particle fraction and in the procedure for converting Triso-coated fuel particles to a solution form amenable to the measurement of heavy-metal content, chlorine gas at 1000°C is used to leach the heavy metals from the fuel particles. Questions have been raised as to whether hot chlorine gas will react with and destroy SiC, and about the conditions necessary for quantitative removal of the SiC.

Test portions of a Triso-coated HTGR fuel sample [uranium-loaded weak-acid resin (WAR) kernels, no outer LTI] were chlorinated at 900, 1000, and 1500°C for 1 to 3 hr. After chlorination, the test portions were radiographed. Microscopic examination of the radiographs revealed that chlorination at temperatures of 1000°C or greater is required to completely remove the SiC coating in 1 hr or less. At 900°C for 2 hr, the SiC coating was completely removed in only 10% of the particles; however, at 900°C and 3 hr the SiC coating was completely removed from 90% of the particles; the SiC coatings which remained were extremely thin. Those particles that were chlorinated at 1000 and 1500°C had the SiC coating completely removed in 1 hr. Examination of the radiographs of these particles revealed a layer of carbon resulting from the removal of the SiC coating. This carbon layer was readily distinguishable from the inner LTI coating. No attack of the kernels was observed, indicating that the inner LTI coating was intact.

A number of the particles that were chlorinated at 1000 and 1500°C were ignited in air at 900°C for 4 hr. Microscopic examination of these ignited particles revealed only uranium oxide (U_3O_8) kernels, a further indication that all SiC had been removed. (*F. L. Layton, D. E. LaValle*)

Coating densities determination. Density measurements of Triso-coated HTGR fuel particles are required to qualify the particle at each coating stage and to ensure the acceptability of the final Triso particles; it is necessary to interrupt the coating process at each stage to determine this density. It would be advantageous if the coating process could proceed without interruption and the densities at the various stages could be determined by using the final Triso particles.

By means of mercury porosimetry, the densities of Triso fuel particles were determined at the outer LTI pyrocarbon coating, again at the SiC coating after removal of the outer LTI by ignition in CO_2 atmosphere at 900°C, and finally at the inner LTI pyrocarbon coating after removal of the SiC by chlorination at 1000°C. Density values obtained at the outer LTI and SiC stages compared favorably with values previously obtained during the coating process. The values at the inner LTI stage differed by approximately 11% from the value obtained after the inner LTI coating had been applied. This was found to be due to carbon that remained even after chlorination of the particles.

Published reports have indicated that when SiC is chlorinated below 900°C, $SiCl_4$ and carbon are produced, but chlorination at 1000 to 1100°C produces $SiCl_4$ and CCl_4.[16] Several samples were chlorinated at 1050°C to see whether the SiC would be quantitatively removed at this temperature. Microscopic examination of radiographs of these samples revealed that carbon did remain. In order to accurately determine the density of fuel particles at the inner LTI stage, this carbon must be removed.

Removal of the carbon by selective oxidation was investigated. Previous studies indicated that the inner LTI is not oxidized by ignition in air at 400°C. Weighed samples of HTGR fuel particles which had been chlorinated at 1050°C were therefore ignited at 400°C for 20 hr and then reweighed. The weight losses indicate that only about 50% of the theoretical amount of carbon present due to the SiC is removed by this procedure. In addition, an excessively large number of fuel particles are cracked during ignition at 400°C. This is probably due to permeation of the inner LTI and oxidation of the UC_2 kernel. These two facts make the accurate determination of the density at the inner LTI an impossibility. Other means of removing the carbon without disturbing the inner LTI must be found. (*F. L. Layton*)

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16. A. C. Lea, "III. The Oxidation of Silicon-Carbide Refractory Materials," *Trans. Br. Ceram. Soc.* 40, 198 (1940).

HTGR procedures manual. A manual entitled "Laboratory Procedures for the Analysis of HTGR Fuels and Materials" was compiled and is being prepared as a GCR report. This manual provides information concerning some analytical methods used by the Division in the chemical characterization of various HTGR fuel materials. As new methods pertaining to HTGR-type samples are developed and demonstrated to be reliable, they will be included in this manual. (*F. L. Layton*)

Advanced reactor fuel development: Characterization of nitride fuels. The compounds of UN, PuN, and solid solutions of these compounds are of interest for application in LMFBR advanced fuel systems. As a part of the advanced reactor fuel development program in the Metals and Ceramics Division, suitable analytical methods and techniques for characterization of these fuels were reestablished. The feasibility of an accurate chemical analysis of the major elements and contaminations in these compounds has been demonstrated in the past.[17]

Using a well-characterized uranium mononitride material, the following methods were evaluated: uranium by a sequential oxidation-reduction-oxidation method, nitrogen by a modified Dumas technique, oxygen by the Leco inert-gas fusion method, and carbon by the Leco oxygen combustion method. The precision for these methods was found to be as follows: uranium, 94.46 ± 0.02 wt %; nitrogen, 5.46 ± 0.02 wt %; oxygen, 526 ± 29 ppm, and carbon, 350 ± 22 ppm.

Using the same material referred to above, methods have also been evaluated for characterizing mixed plutonium and uranium nitride materials. These methods and their precisions are as follows: uranium by coulometric titration, 94.59 ± 0.02 wt %; nitrogen by Kjeldahl-acid titration, 5.48 ± 0.04 wt %; carbon by Leco combustion, 419 ± 17 ppm; and oxygen by Leco inert-gas fusion, 593 ± 76 ppm. Plutonium by coulometric titration is still under evaluation.

The UN material used in these evaluations was characterized in an extensive round-robin program to contain these elements: uranium, 94.46 ± 0.02 wt %; nitrogen, 5.46 ± 0.02 wt %; oxygen, 335 ± 21 ppm; and carbon, 389 ± 29 ppm. (*J. L. Botts*)

HTGR Process Development Studies

Solvent extraction studies. In support of the HTGR Fuel Reprocessing Development Program, laboratory studies have been initiated to determine the effect of temperature on the extraction of thorium and nitric acid in the system $Th(NO_3)_4$–HNO_3–30% TBP–NDD and to determine extraction conditions for third-phase formation. These studies will provide data to develop a mathematical model for use with the SEPHIS-Thorex computer program.[18] will be used to simulate the Acid Thorex flowsheet.[19] will correct for the effect of temperature on the contactor system, and will provide a signal to indicate when a third phase will form. The experimental conditions to be studied and which are required to bracket the flowsheet condition are these: 20 to 60°C, 0.05 to 1.5 *M* $Th(NO_3)_4$, and 0.0 to 3.0 *M* HNO_3. Extractions at 30°C have been completed, and the densities, free acid, and thorium content of the aqueous and organic phases have been determined. The conditions under which a second organic phase appears were also determined. Studies will be conducted at 10°C intervals from 20 to 60°C. (*A. J. Weinberger*)

Uranium recovery. For the preparation of HTGR fuel, WAR is loaded with uranium from acid-deficient uranyl nitrate.[20] The acid-deficient solution is prepared by extracting the nitric acid with an organic amine that is regenerated. The process produces wastes, the uranium content of which should be low because ^{233}U will be loaded. It also introduces carbonaceous and nitrogenous organics into the aqueous resin-loading streams that could be detrimental. The reduction of the amount of uranium sent to waste and the determination of the amount of organic carbon in the aqueous process streams were investigated in the laboratory.

It was found that the introduction of a second water-scrub step in the amine regeneration system to reclaim uranium for recycle was beneficial. Use of 0.01 *M* nitric acid or carbon dioxide–saturated water did not significantly improve the extraction. A second water-scrub step was introduced into the engineering-scale equipment. It performed approximately in agreement with the laboratory results.

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17. V. J. Tennery and J. L. Botts, "The Chemical Characterization of Uranium Nitrides," *Nucl. Technol.* 13, 264 (1972).

18. J. H. Rainey and S. B. Watson, "Modifications of the SEPHIS Computer Program for Calculations of the Acid Thorex Solvent Extraction System," *Trans. Am. Nucl. Soc.* 22, 315 (1975).

19. R. H. Rainey and J. G. Moore, "Laboratory Development of the Acid Thorex Process for Recovery of Thorium Reactor Fuel," *Nucl. Sci. Eng.* 10 (1961).

20. P. A. Haas, *HTGR Fuel Development: Loading of Uranium on Carboxylic Acid Anion Exchange Resin Using Solvent Extraction of Nitride*, ORNL TM-4955 (September 1975).

The organic content of the aqueous process stream was determined with an Oceanography International model 0524 carbon analyzer. The total organic carbon, which could be due to the resin, organic amine, or organic solvent, ranged from 22 to 100 ppm. The insoluble or suspended carbon varied from 4 to 13% of the total. Data indicated that the resin absorbed some of the organic material in the early stages of the process. (*A. J. Weinberger*)

Materials Preparation

Preparation of inorganic materials for Solid State Division research continued at about the same level as last year. For the Neutron Diffraction Group, 300 g of the ferrite $(Sr_{0.5}Ba_{0.5})_2Zn_2Fe_{28}O_{46}$ was prepared by thorough mixing of the oxides or carbonates of the elements and firing at 1300°C in air for 8 hr. Also for this group, 20 g of the isotopic compound Li^7H was made by combination of the elements at 700°C over a period of 7 hr. The alloy $LaNi_5$ was prepared in a 50-g quantity for studies in hydrogen storage. This compound is able to take up a quantity of H_2 equivalent to its own volume of the liquid gas. For the Neutron Spectrometry Group, a 200-g quantity of palladium was purified by ion exchange methods. The purified palladium was used to make four alloys containing manganese in amounts of 0.25, 0.50, 1.00, and 2.00 at. %. For the same group, approximate 1-g quantities of the valuable isotopes ^{160}Gd, ^{164}Dy, and ^{170}Er were recovered, and approximately 20 g of ^{62}Ni. For the Pure-Materials Group, 20-g quantities of the following compounds were prepared by well-known methods: BaO_2, VO_2, NbO_2, RuO_2, and ReO_2.

The group in the Chemical Technology Division concerned with LWR reprocessing required a nitrocompound of ruthenium with <10 ppm of Cl^-. A satisfactory compound selected was $Na_2[RuNO(NO_2)_4OH]$. We prepared it according to the method of Fletcher *et al.*[21] Soluble $RuCl_3$ is dissolved in a restricted amount of 1 *N* HCl and treated gradually over a period of time with $NaNO_2$ at elevated temperatures until the orange-red solution of the compound is obtained. The solution is carefully evaporated to dryness, and the compound is extracted with acetone to remove it from the by-product NaCl. A second extraction reduces the chloride concentration to the desired level. (*D. E. LaValle*)

Molten-Salt Reactor Program Studies

Electrochemical studies of tellurium in molten $LiF-BeF_2-ThF_4$ (72-16-12 mole %). Tellurium occurs in nuclear reactors as a fission product and causes shallow intergranular cracking in structural metals and alloys.[22] Efforts were continued to characterize this substance electrochemically and to ascertain the feasibility of in situ monitoring by electroanalytical means.

As previously reported,[23] lithium telluride, Li_2Te, was added to molten $LiF-BeF_2-ThF_4$ that was contained in a cell equipped with viewing ports in addition to the electrode ports. Subsequent voltammograms did not reveal waves that could be attributed to soluble electroactive tellurium species. Chemical analysis indicated <5 ppm Te in the melt. Following cleanup of the cell and recharging with $LiF-BeF_2-ThF_4$, standard additions of $LiTe_3$ were made in the form of pressed pellets. The pellets disappeared more rapidly from the melt surface than did the Li_2Te pellets. A grayish metallic-looking film formed on the surface. Subsequent voltammograms did not show significant changes over background scans. The equilibrium potential remained the same, which was different from that for the Li_2Te additions where the melt became more reducing. This is indicative that $LiTe_3$ is not stable under our operating conditions. Bamberger et al.[24] revealed, in their experiments on spectral measurements of what was reported to be $LiTe_3$ in $LiF-BeF_2$, that isothermal conditions were necessary to hold the characteristic color for any length of time. Under nonisothermal conditions the color quickly disappeared, with evidence of tellurium metal formation. Since our conditions are nonisothermal, the $LiTe_3$ probably decomposed immediately after contacting the melt. The grayish metallic-looking crust on the melt surface apparently tended to short out the electrodes after a few hours, because the voltammograms became extremely noisy and nonreproducible. However, there was no change in the equilibrium potential.

Thus we have been unable to detect stable electroactive telluride species in molten $LiF-BeF_2-$

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21. J. M. Fletcher, I. L. Jenkins, F. M. Lever, F. S. Martin, A. R. Powell, and R. Todd, "Nitrato and Nitro Complexes of Nitrosylruthenium," *J. Inorg. Nucl. Chem.* 1, 385 (1955).

22. H. E. McCoy, "Materials for Salt Containing Vessels and Piping," *The Development and Status of Molten-Salt Reactors*, ORNL-4812 (February 1975), p. 207.

23. A. S. Meyer et al., "Electroanalytical Studies of Tellurium," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 29.

24. C. F. Bamberger, J. P. Young, and R. G. Ross, "The Chemistry of Tellurium in Molten Li_2BeF_4," *J. Inorg. Nucl. Chem.* 36, 1158 (1974).

ThF_4 following standard additions of Li_2Te and $LiTe_3$ compounds under these conditions. It appears that these tellurides are, for the most part, relatively insoluble and or thermally unstable under these experimental nonisothermal conditions.

In the absence of meaningful voltammograms, experiments were initiated to determine the decomposition potential of elemental tellurium ($mTe + ne^- \rightarrow Te_m^{n-}$) relative to the half-wave potential of the U(IV) $\rightarrow$ U(III) electrode reaction. This should provide some insight on the reducing power [U(IV) U(III) ratio] required to favor the existence of tellurides (if stable) over elemental tellurium in MSBR fuel salt. For these experiments, the molten LiF-BeF_2-ThF_4 was contained in a pyrolytic boron nitride cup. The holder for the small tellurium-pool electrode ($\frac{1}{16}$ in. diameter) was fabricated from spectrographic-grade graphite. Cathodic polarization curves (recorded on the tellurium-pool electrode right after it was dipped into the melt at ~650°C, and for the next hour or so) revealed a decomposition potential of about +1.15 V vs the melt limit. It was observed that ~100 mg of tellurium volatilized from the graphite holder in approximately 1 hr. The half-wave potential for the U(IV) $\rightarrow$ U(III) reduction is about +0.40 V, which corresponds to a U(IV) U(III) ratio of ~150 at 650°C. From these measurements it appears that a relatively reducing melt is required to favor the existence of stable telluride species over elemental tellurium in molten LiF-BeF_2-ThF_4-U(IV) at 650°C.

In order to obtain additional information on the formation and stability of tellurides under nonisothermal conditions, studies were conducted on the telluride species produced in situ from cathodizing elemental tellurium ($mTe + ne^- \rightarrow Te_m^{n-}$). Chronopotentiometric and double-potential-step[24] voltammetric experiments conducted at a tellurium-pool electrode contained in a graphite cup revealed that the telluride species generated does not appear to be stable at ~650°C. Instability was indicated from the chronopotentiometric experiments by comparing the ratio of the forward and reverse transition times.[25] According to theory, generation of a stable but insoluble substance yields $\tau_f/\tau_r = 1$; for a soluble and stable species, $\tau_f/\tau_r = 3$. For an unstable species, on the other hand, τ_f/τ_r should be greater than 3. For these experiments the current was reversed at a time $t < \tau_f$; however, the above conclusions remain valid as long as $t \leq \tau_f$. Potential-time curves recorded at the tellurium-pool electrode produced a $\tau_f/\tau_r \gg 3$ in all the runs, indicating that the telluride species generated is not stable, at least within the time frame of the experiment (seconds).

In the double-potential-step[26] experiments, the anodic-cathodic current ratio (i_a/i_c) is plotted vs a function of time [$F(t)$] that the potential step is applied and removed. For a stable system the ratio i_a/i_c is unity when $F(t)$ is extrapolated to zero. For the generation of an unstable species, the ratio i_a/i_c is less than unity. This was observed for the tellurium experiments.

Plots of log i vs E from potential-step experiments revealed an n value close to unity. The validity of n-value determinations by this method is discussed by Armstrong et al.[27] and by Bacarella and Griess.[28] Thus if $n = 1$, the telluride generated can be represented as $mTe + e^- \rightarrow Te_m^-$ ($m \geq 1$). Bronstein and Posey[29] also obtained an n value of unity from polarization studies of tellurium in molten chlorides, using a different method.

A stable telluride of the type Te_m^- should exhibit a color when dissolved in the melt.[24] In an effort to observe this effect, we cathodized elemental tellurium in molten LiF-BeF_2 at ~480°C. The melt was held in a quartz tube to permit visual observations. Upon applying a current of 150 to 300 mA for several seconds or longer, a dark brownish-looking substance was observed streaming from the tellurium electrode; however, the material appeared to be insoluble, and a colored melt was not produced. After the material diffused away from the electrode a short distance (~1 cm), the color could no longer be detected. These results also indicate that we generated an unstable species that under nonisothermal conditions will undergo a decomposition reaction. Reasonable reactions are as follows:

$$2Te^- \rightarrow Te_2^{2-} \quad ,$$

$$Te_2^{2-} \rightarrow Te^- + Te^0 \ (m = 1) \quad ,$$

$$2Te_m^- \rightarrow Te^- + (2m - 1)Te^0 \ (m > 1) \quad .$$

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25. Arnold Weissberger, Ed., *Physical Methods of Chemistry, Part IIA, Electrochemical Methods*, Wiley-Interscience, New York, 1971, p. 502.
26. Ref. 25, p. 620.
27. R. D. Armstrong, T. Dickinson, and K. Taylor, "The Anodic Decomposition of Copper(I) N-Methylhexamethylenetetramine Bromide," *J. Electroanal. Chem.* 66, 155 (1975).
28. A. L. Bacarella and J. C. Griess, Jr., "The Anodic Dissolution of Copper in Flowing Sodium Chloride Solutions Between 25° and 175°C," *J. Electrochem. Soc.* 12, 459 (1973).
29. H. R. Bronstein and F. A. Posey, "Porous Electrode Studies in Molten Salts: Electrochemical Studies of Tellurium in the LiCl-KCl Eutectic System," *MSR Program Semiannu. Prog. Rep. Feb. 29, 1976*, ORNL-5132, p. 29.

The Te^{-} species does not appear to be soluble in fluoride, at least to the extent that voltammetric detection is feasible. (*D. L. Manning*)

Electrochemical studies of oxide ions and related species in molten fluorides. The electrochemistry of oxide ions (free or complexed) was studied in molten LiF-BeF_2-ZrF_4 (65.6-29.4-5.0 mole %) and LiF-BeF_2-ThF_4 (72-16-12 mole %) at gold, iridium, and glassy carbon electrodes in the temperature interval 500 to 710°C. Well defined and reproducible voltammograms and chronopotentiograms could be obtained only at gold electrodes. Cyclic voltammetric and chronopotentiometric results indicate the following electrochemical reaction pathway:

$$O^{-} = O + 2e \quad ,$$

$$O + O = O_2 \quad ,$$

$$O + O^{-} \rightarrow O_2^{-} \quad .$$

Peroxide species were oxidized further, producing a voltammetric postwave which increased with Na_2O_2 additions. Peroxide ions also gradually decomposed in these media; the decomposition was more rapid in the Zr(IV)-containing melts as compared with the Th(IV)-containing melts. The results provide the basis for an in situ electrochemical determination of small amounts of dissolved oxide.

A more detailed report of this work has been submitted for publication in the *Journal of the Electrochemical Society*. (*D. L. Manning, G. Mamantov*)

In-line analysis of molten fluoride salts. Corrosion test loops and creep test machines, described previously,[30] were operated with reference fuel salt LiF-BeF_2-ThF_4-UF_4 (71.7-16-12-0.3 mole %) until the shutdown of the program in June 1976. These experiments were under the general supervision of H. E. McCoy of the Metals and Ceramics Division and were designed to test the compatibility of Hastelloy N and other container materials with fuel salt under various conditions. Correlations were made with respect to U(IV)/U(III) ratios, fuel composition, and temperature.

Ratios of U(IV)/U(III) in thermal convection loops NCL-21A and 23 showed no unusual trend in the redox behavior of the melt with time. A temporary rise in the ratio was observed in response to the addition of new corrosion test specimens, but within a short time the ratio returned to the initial value. The U(IV)/U(III) ratios were about 5.4×10^{1} and 4 for loops 21A and 23, respectively, at shutdown.

The U(IV)/U(III) ratios in loops 18C and 24, which were operated with Hastelloy N corrosion specimens, showed a gradual decline to final values of about 1.7×10^{2} and 80 respectively.

Forced convection loop FCL-2B was charged with new salt and was placed back in operation after a shutdown period. The U(IV)/U(III) ratio at startup was about 5.3×10^{1}, which indicated that the melt was oxidizing. The ratio decreased to about 90 at shutdown, as the melt came in contact with new metal surfaces installed in the loop.

The measurement of U(IV)/U(III) ratios was initiated in November 1975 on eight creep test machines located in Building 2011. Since the initial measurements, the melts have tended to become more reducing. For comparison, first measurements and final U(IV)/U(III) ratios are shown in Table 3.1.

Table 3.1. Ratios of U(IV)/U(III) in creep test machines

Machine identity	U(IV)/U(III) ratio	
	Initial	Final
15	4.6×10^{1}	1.4×10^{2}
16	3.9×10^{1}	450
17	2.3×10^{1}	38
18	3.5×10^{1}	46
19	3.5×10^{1}	25
20	5.3×10^{1}	30
21	65	26
22	3.1×10^{1}	64

Tellurium as Cr_2Te_3 (~50 mg) was added to machines 19 to 22, and no detectable change in the redox behavior was observed.

TeGen experiments, a series of ORR poolside experiments set up to irradiate prospective MSBR container materials, were designed to produce a fission product inventory similar to that produced in the MSRE when intergranular cracking was observed. Our role was to determine the U(IV)/U(III) ratio in situ in the salt charge prior to irradiation. Voltammetric measurements were made on the fill salt used for TeGen 4 after a 4-hr period of hydrogen treatment. It was not possible to record voltammograms on the melt contained in the treatment vessel because potential control could not be maintained. It is believed that this difficulty was caused in part by

30. H. E. McCoy, "Materials for Salt-Containing Vessels and Piping," *The Development and Status of Molten-Salt Reactors*, ORNL-4812 (February 1975), p. 207.

film on the surface of the melt that was conducting and shorted the electrodes. After transferring the melt into the fill vessel, reasonably well-defined voltammograms were obtained from which a U(IV) U(III) ratio of 100 was calculated. Following pin filling and blow-back into the fill vessel of a portion of the melt for recheck, the U(IV) U(III) ratio was within the range 100 to 130. The voltammograms recorded on the blowback material were poorly defined; thus U(IV) U(III) values could not be calculated as precisely as for the original fill solution. However, the U(IV) U(III) ratios were well within the desired limits set for this experiment. (*D. L. Manning, R. F. Apple*)

Tritium transport experiments at the Coolant-Salt Technology Facility. The Coolant-Salt Technology Facility (CSTF) was operated for testing $NaBF_4$-NaF (92-8 mole %) for its suitability as a possible secondary coolant for the molten-salt reactor. In cooperation with the Engineering Technology Division, we participated in experiments to determine the fate and distribution of elemental tritium when it is added directly to the salt to simulate, at least in part, the predicted transport of tritium in the coolant system via diffusion through the primary heat exchanger. The methodology and the results from the first two tritium injection experiments were described previously.[31] This section presents the results of the third tritium injection experiment.

About 80 mC. of tritium (diluted about 1:1000 with protium) was introduced into the salt over a period of about 11 hr. Tritium concentrations were measured in the cover gas and salt from the beginning and for several days thereafter.

Preliminary evaluation of the data indicates that about half of the injected tritium experienced significant holdup in the salt but was eventually removed in the off-gas stream. Very little tritium in the off-gas was in the elemental form; the majority was in a water-soluble or combined form, which is advantageous from the standpoint of tritium trapping by the salt. Also, there appears to be evidence at low concentrations that some tritium is captured by the salt and has a tendency to escape on standing. A general discussion of the behavior of tritium in the CSTF and more complete analysis of the injection experiments are given elsewhere.

A fourth tritium injection experiment was started in February 1976, using more sophisticated gas addition and sampling techniques. Tritium was added in this experiment until a steady state was reached. The experiment was conducted for a period of several months, ending in July. The results are being evaluated by Engineering Technology Division personnel. Some preliminary results, however, have been presented elsewhere.[32] (*R. F. Apple*)

GENERAL ANALYTICAL LABORATORIES

W. R. Laing, Group Leader

Chemical Technology Division personnel began several programs in support of the reprocessing of spent reactor fuels.

In the head-end treatment for light-water reactor (LWR) reprocessing, the fuel bundles were sheared into 1-in. sections for acid dissolution of the UO_2. The designers of the shear equipment would like to know the amount of stainless steel cladding in each size fraction of the chopped fuel. This measurement was usually made by dissolution in HNO_3-HCl and determination of the iron content. A need arose to test for iron in 50 samples/day, but the leach-analysis method was too slow. H. H. Ross and L. N. Klatt developed a monitor based on the change in frequency of an oscillator when a sample containing stainless steel is inserted into the center of the coil. Details are given in Chap. 1. Over 500 samples have been analyzed with this instrument.

Equipment was assembled to prepare a manifold for the Arsenazo III spectrophotometric thorium method for the Technicon AutoAnalyzer. The calibration range was 1 to 10 μg of thorium per milliliter. Four hundred samples were analyzed over a period of four weeks. Half of the solutions contained tributyl phosphate, and the thorium was stripped with 0.01 *M* HCl before analysis.

A gas-sampling system was constructed for use with the Microtek 222 gas chromatograph for sampling glass or metal gas containers. The apparatus consisted of a vacuum pump, low-volume manifold, mercury manometer, Hastings gage, sample valve, and manifold-to-sample fittings. This system allowed gas samples to be taken with little waste because of the large manifold volumes. Gases have been analyzed for CO_2, N_2, CO, and CH_4.

The Waste Management Program included formulation of special cements for borehole plugging. Standard ASTM procedures were used to determine 12 components of these mixtures. Fly-ash composition was also measured.

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31. A. S. Meyer et al., "Tritium Transport Experiments at the Coolant-Salt Technology Facility," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 24.

32. J. R. Engel et al., "Tritium Behavior in the Coolant-Salt Technology Facility," *MSR Semiannu. Prog. Rep. Feb. 29, 1976*, ORNL-5132, p. 2.

Uranium mine tailings were analyzed for U, V, and Ra. Ores which had been treated with H_2SO_4 were especially difficult to prepare for radium determination; several percent SO_4 remained and formed insoluble $RaSO_4$. A suitable procedure involved grinding the tailings to 100 mesh, followed by treatment of a 1-g aliquot with HNO_3 and HF. The solution was diluted to a volume of 200 ml with 2 *M* HNO_3; $RaSO_4$ was more soluble in a higher concentration of HNO_3. The radiochemical analyses were done by the Environmental and Radiochemical Analyses Laboratories.

Bacteriological decomposition of acetates to H_2O and CO_2 was tried by Chemical Technology Division engineers as a solution to a waste-effluent problem. These wastes contained mg ml amounts of $Ca(NO_3)_2$, $CaCO_3$, and HNO_3, and 50 to 500 ppm of acetate. In this method the aliquot was passed through H^+-form Dowex 50 resin, which eluted the HNO_3 and HAc. After neutralizing the bulk of the HNO_3, the acids were titrated in 90% acetone, using a recording titrator. The second break in the curve corresponds to the titration of the HAc.

Work for the Environmental Sciences Division included the analysis of 75 samples of wood from individual tree rings for C, H, and N determination. The Perkin-Elmer model 240 elemental analyzer was used for this measurement. Samples of 0.5 to 2 mg were taken, and based on duplicates, relative standard deviations of 0.6% for C, 1.8% for H, and 10% for N were obtained. Nitrogen levels were generally <0.5%, which accounted for the higher relative standard deviations.

Environmental Sciences Division personnel indicated a need to measure the reducing sugar content of tulip poplar bark and wood. This value was thought to be associated with the production of CO_2 by the tree. The wood was ground thoroughly with ethyl alcohol in a Waring blender, and the reducing sugars were extracted into the alcohol. Next, cupric ion was added which was reduced to cuprous ion by the sugars. The cuprous ion, in turn, reduced an arsenatomolybdate complex to molybdenum blue for a spectrophotometric measurement. A calibration curve was prepared using glucose, and the sample results were reported as ppm glucose. Thirty-six samples have been analyzed with a range of 800 to 9000 ppm. Two sample extracts have been separated into individual components by high-pressure liquid chromatography. The total amount of reducing sugars found was approximately the same as with the spectrophotometric procedure. Half of the sugar was glucose, with the remainder split into fructose, xylose, and galactose.

In another Environmental Sciences Division program, we have measured the organic carbon content of snails and snail eggs. In the procedure used, similar to a chemical oxygen-demand test, the snails were digested in an H_2SO_4-$K_2Cr_2O_7$ solution, and the remaining Cr(VI) was measured spectrophotometrically. The "as-received" snails, preserved in formalin, were carefully washed with water before the analysis. The shells were crushed between glass plates and dropped into the oxidizing mixture.

The Coal Technology Program included stability studies for coal-derived liquids. Four containers, to be stored under different conditions, were analyzed for C, H, N, S, BTU, forms of S, ash, density, solids, cresol insolubles, viscosity, and gel chromatography. Additional samples were analyzed every two months during the year.

ASTM method D2887, Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, has been set up on the Microtel 222 gas chromatograph, using a 6-ft by $\frac{1}{4}$-in. Dexsil 300 column. A calibration curve was prepared using compounds with boiling-point ranges from 60 to 327°C. Column bleed was negligible over this temperature range. Samples of solvent-refined coal (SRC) liquid product have been analyzed. The boiling-point curves were similar in shape and showed a distillation of 150 to 375°C.

Fractionation of coal-derived liquids by solvent separation was used for SRC product. Benzene, cyclohexane, and nitromethane were used to separate asphaltenes, heavy oil, and aromatic and nonaromatic fractions. Methylene chloride was used to extract water-soluble organic compounds from aqueous condensate. Acetone and *m*-cresol were used as solvents for coal-derived liquids.

Encouraging results in the solids separations from coal-derived liquids caused a large increase in the number of samples for ash determination. As many as 500 samples month have been received. Several modifications have been made in the procedure to increase the efficiency. Samples are handled in groups of 12, evaporated under a battery of heat lamps, flamed as a group in a stainless steel tray, and ignited in a muffle furnace. Ash contents range from 0.05 to 10%.

Several samples of monazite sand were analyzed for uranium by the dibenzoylmethane spectrophotometric and fluorometric procedures. The key to a successful analysis was in the sample preparation. Some monazites contain materials of varying densities, and it was necessary to quarter these samples to size and grind them to −100 mesh, using the shatterbox grinder. The uranium was dissolved

with H_2SO_4, using a sealed tube. Some residue, about 10%, remained and was fused with pyrosulfate. Negligible amounts of uranium were found in the fused portion. Results on a very inhomogeneous Georgia monazite were as follows:

Sample	Percentage of uranium		
	Spectrophotometry	Fluorimetry	Mass spectrometry
A	0.41	0.43	0.431
B	0.41	0.43	0.435
C	0.39	0.42	0.417

Mass spectrometry was used to check the chemical results.

The Civil Defense Group worked on methods of iodine removal from water that might be used in case of a nuclear emergency. Complexing the I_2 with flour and filtering the water through 6 to 8 in. of soil was very effective in removal of I_2, but removed only 50% of the iodide. Further tests showed that household bleach could be used to oxidize the iodide to iodine for more complete removal.

The Nuclear Safety Pilot Plant has been reactivated. The first tests were to determine sodium transport, and samples were analyzed on the Perkin-Elmer 460 instrument. Either atomic absorption or flame emission modes could be used, plus a built-in microprocessor to linearize the calibration curve. In the flame emission mode, a calibration curve from 1 to 25 μg of sodium per milliliter was set up, and most samples were read without further dilution. With 40 to 60 samples per set, this resulted in a saving of 2 hr over the use of atomic absorption.

A chemist worked with Chemistry Division personnel to establish the operating and sampling conditions for a geothermal test loop. The effects of acidity, salt content, and waiting time on the polymerization of SiO_2 were studied. A procedure for routine operation was written, and a Technicon AutoAnalyzer was set up for the on-line determination of silica.

Water samples from tanks in the Annual Cycle Energy System experimental house, designed to use solar energy, were submitted on a regular basis. Tests for total hardness, total alkalinity, pH, conductivity, Mg, Ca, and Al were done.

New instruments obtained during the year were a Perkin-Elmer model 240 elemental analyzer, a model 3920-B gas chromatograph, and a model 460 atomic absorption instrument.

ENVIRONMENTAL AND RADIOCHEMICAL ANALYSES LABORATORIES

R. R. Rickard, Group Leader

Environmental Analyses Laboratory

A microcosm study undertaken by the Environmental Sciences Division for the Environmental Protection Agency (EPA) was the largest program in which the Environmental Analyses Laboratory was involved during the past year. Another sizable analytical effort was made toward providing analyses for six to eight trace elements in support of the Environmental Fate of Emissions from Coal-Combustion Plants Project. The measurement of mercury in a variety of environmental samples continued at about the same level as that last year.

The microcosm project required analyses for Ca, Mg, K, NO_3, NH_3, PO_4, and dissolved organic carbon (DOC). Arsenic was found to interfere in the PO_4 analyses unless the sample was pretreated with HBr. The DOC analyses involved sealed-vial oxidation conditions employing elevated temperatures and pressures to convert carbonaceous materials to carbon dioxide. The failure of a pressure vessel led to a radical change in the sample treatment procedure relative to temperature and pressure control. Redundant temperature controls are now in use on the pressure vessel and the heating oven. A pressure relief valve is also a safety feature added to the pressure vessel. These changes were achieved at a high cost of man-hours and materials.

An automatic sampler for the graphite furnace was acquired and is being evaluated for its effectiveness. The graphite furnace is dedicated mostly to the analytical work supporting the Emissions from Coal-Combustion Plants Project. With an increase in the use of the furnace technique, this sampler unit should improve sample injection reproducibility of microliter aliquots. Results of trace-element measurements in both EPA water standards and "unknown" quality assurance standards have been gratifying.

The NSF-sponsored study of a mercury mine in Spain produced samples of vegetation, fish, birds, stream sediments, and mice for organic and inorganic mercury analyses. Local water, fish, and air provided the other samples analyzed for mercury this past year. Depending on sampling locale, the mercury levels varied from ng g to μg g.

Radiochemical Analyses Laboratory

Most of the low-level radiochemical work has been consolidated in one remotely located laboratory.

This action became necessary with an increased need for low-level actinide analyses, more definitive environmental monitoring analyses, and special radium and radium daughter analyses. New instrumentation has been acquired to improve our capabilities for low-level activity measurements. Strontium-90, gamma-emitting nuclides, and alpha-emitting actinides have been determined in soils and sediments, water, vegetation, and air filters.

Studies involving the behavior of ^{99}Tc (a pure beta emitter) required numerous radiochemical separations for ^{99}Tc throughout a small-scale treatment system.

LWR fuel reprocessing studies placed heavy emphasis on determining the fate of ^{3}H, ^{14}C, and ^{129}I during fuel dissolution. Procedures employed were either distillation, evolution, or solvent extraction coupled with neutron activation to isolate these nuclides of interest. The LWR work also required the assay for gamma-emitting nuclides in dissolver solutions and dissolver trap solutions. This was accomplished by gamma-ray spectrometry coupled with computer resolution of gamma-ray spectra.

The fission product surveillance study on components of the Peach Bottom Reactor involved analyses for ^{3}H, ^{14}C, and fission product ^{90}Sr. Special dissolution and combustion techniques were used to prepare samples for analyses of interest.

HTGR work necessitated the greatest number of difficult radiochemical separations; this work involved the isolation of ^{106}Ru, ^{110m}Ag, ^{125}Sb, and ^{154}Eu from other fission products many orders of magnitude higher in concentration. Numerous gamma-ray spectra were analyzed for the more predominant gamma-photon emitters by gamma-ray spectrometry, using J. F. Emery's MONSTR program.

A new liquid scintillation counter was acquired to increase our productivity in ^{14}C and ^{3}H analyses. A 19% relative efficiency Ge(Li) detector was obtained and placed in a lead-shielded facility to enable us to perform analyses of intermediate- to low-level gamma-emitting nuclides. Plans have been made to obtain a new gamma spectrometer that will not only replace the older unit but will also free the old system (ND 3300) for multiple-detector alpha spectrometry.

RADIOACTIVE MATERIALS ANALYTICAL LABORATORIES

J. H. Cooper, Group Leader

The LWBR Assistance Program of the Chemical Technology Division provided the major portion of our work during the past year. This program is drawing to a close and consists primarily of recovering scrap and waste from the production of fuel pellets. The production of transuranium elements has become fairly routine and consists of about two runs per year.

We have assisted the Chemical Technology Division in studying problems in the reprocessing of LWR fuels. Solids that arise from incomplete dissolution of the fuel, that precipitate upon storage of the fuel, or that appear at the interface during solvent extraction have been investigated. Portions of these solids were isolated for x-ray studies and possible identification; other portions were dissolved for radiochemical and spectrographic analyses.

Another important study in LWR fuel reprocessing is the behavior of plutonium. Exhaustive extraction of plutonium from the fuel solution is done, and all of the resulting organic and aqueous solutions are analyzed for plutonium. Radiometric methods of plutonium determination are used; often the levels of plutonium are very low (less than 10^{3} dis min^{-1} ml^{-1}), and the levels of fission products are high. Extraction of plutonium by thenoyl trifluoroacetone has been very successful under these conditions.

Measurement of the transuranium elements is usually done by counting the gross alpha activity and performing an alpha pulse-height analysis. In cases where the salt concentration is very high (samples that have been dissolved by carbonate fusion), gross alpha measurement by direct evaporation of aliquots is not satisfactory. Cleaner counting planchets were made by carrying the actinides down on ferric hydroxide and plating a portion of this mixture. This scavenging technique also helped to make better sources for alpha pulse-height analysis. Neptunium-237 was measured in the LWR fuel solutions by a combination of ion exchange and solvent extraction after spiking the sample with ^{239}Np for recovery calculations.

We participated in another study to analyze the depletion of acid in stored LWR waste solutions. These extremely radioactive solutions were titrated remotely with a standard base. Erratic results caused us to closely inspect our procedure for determining free acid; we discovered that restandardizing the pH meter after each titration greatly improved the precision. Evidently the high levels of radiation caused excessive drift of the electrodes. Future studies in LWR fuel reprocessing will be made on determining nitrogen, ^{14}C, and tritium in the spent fuel.

During the past year we experienced a large increase in demand for our nuclear-coatings testing

service, largely because we are the only independent testing laboratory capable of performing the recently updated specifications tests to meet rigid quality assurance standards. As a result, improvements have been made to our design basis accident test chambers. We have also added a second air irradiation facility at the HFIR spent-fuel storage area. We have maintained close liason with the Utilities Nuclear Coating Work Committee as an advisory board member and with the ASTM subcommittee on "Coatings for Power Generation Facilities." A continued increase in the work load is anticipated for the coming year.

DATA MANAGEMENT SYSTEM

R. W. Stelzner and J. S. Stanton

In cooperation with the Computer Sciences Division, we are designing a data management system to assist the Analytical Chemistry Division in creating and keeping records of the results of chemical-physical analyses. During the 12-month period ending September 30, 1974, the Division reported 178,411 results from its various service laboratories; by 1975, this number had increased to 223,751. A computerized data management system will reduce the large amount of manual data handling and increase both efficiency and effectiveness.

The Computer Sciences Division is designing the record-keeping facility, using the assembly and machine languages of the ORNL DEC system 10 time-sharing computer. Access to the computer is by means of "intelligent" remote terminals (Texas Instruments model 742) via telephone lines. One such terminal has been placed in operation in Building 2026; a second unit is used in Building 4500S.

We are designing programs using high-level languages (BASIC, FORTRAN IV) to perform some of the calculations that will be used on the remote terminals. One such program calculates the ppm of ^{235}U present in ^{238}U. Input information for the terminal consists of the alpha count for ^{238}U and the total alpha count for the sample; output from the remote terminal is the ppm amount of ^{235}U.

A FORTRAN IV computer program calculates gamma-ray detector efficiencies over a range of energies. Program execution on the DEC system 10 computer results in successive calculations of linear, quadratic, and cubic equations to fit the energy-efficiency data set. For each curve, a CHI-SQUARED value is calculated to test "goodness of fit." The best fit is computer selected for computation of the polynomial coefficients; the coefficients created have been used successfully in calibrating a new gamma-ray detector.

We have placed on the disk a general-purpose, least-squares curve-fitting program that will allow selection of the degree of the polynomial equation. This FORTRAN IV program is employed for particle density determination, using the gradient-density method. The original version of the program had no provision for incorrect keyboard entries, making it necessary to retype an entire input data set; we have introduced new coding to permit retyping of only the incorrect entries.

A BASIC language program to calibrate specific-ion electrodes for the determination of F^- and NO_3^- concentrations has been written and placed on the disk. The same program has been written in FOCAL for execution on a PDP-8 computer.

We are working at present on programs that will correct radioactivity measurements for decay, and on a program to simulate distillation curves for complex organic mixtures, using gas chromatographic data as input.

4. Bio-Organic Analysis

M. R. Guerin, Head
J. R. Stokely, Associate

We are experiencing a period of transition, both in organization and in areas of research. We continue to be involved almost solely in programmatic research and services, our funding base has broadened, however, and traditional objectives of tobacco-smoke-related projects are changing. The National Cancer Institute Smoking and Health Program has effectively abandoned smoke condensates and skin carcinogenicity bioassay models in favor of whole smokes and inhalation bioassays. Our objectives for the Council for Tobacco Research USA, Inc., are nearing completion, and reprogramming is being discussed. Methodologies and philosophies developed as a result of tobacco-related work have been effectively transferred to emerging ERDA concerns in the area of synfuels technologies. Methodologies and facilities derived from synfuels research promise to expedite progress in newly defined areas of research related to the biological effects of tobacco smokes for the traditional sources of support.

The Bio-Organic Analysis Section is divided into four groups: Quantitative Methods and Projects, Separations and Identifications, Bioanalytical Methods and Projects, and Inhalation Exposure Chemistry and Instrumentation. The Quantitative Methods group is primarily committed to the characterization of experimental cigarettes, but includes research and services in the area of occupational exposure to organic constituents of complex mixtures, in cooperation with the Laboratory Industrial Hygiene staff. A challenging expanded responsibility for the group accompanies an NCI decision that chemical characterization will constitute the primary parameter for prioritizing cigarette types for biological study. New approaches and methodologies are required to adequately meet this expectation. The Separations and Identifications group was formed to meet the need for carefully defined materials from synfuels processes for biological and environmental study. It has generated methodologies of general use to those interested in environmental toxicology, including that associated with cigarette smoking. The Bioanalytical Methods group continues to provide expertise in the areas of uptake and impact of smoke constituents, and approaches are readily transferred to other sources of environmental insult. The Inhalation Exposure group has provided the tools required to meaningfully dose animals with tobacco smoke and to chemically monitor the exposures. Attention is directed toward advanced exposure and monitoring methods and toward transferring these methodologies to studies of general environmental contamination.

This report period has included an increased interest by new sources of support in the unique analytical chemistry - life sciences viewpoint of the section. We are involved with the Masonite Corporation in a study of an agricultural feed supplement to isolate and identify beneficial ingredients. We have recently accepted responsibility for a branch of the Environmental Protection Agency to provide its contractors with materials related to alternate energy sources for biological and environmental study. In-house interactions with process developers on potential problems of occupational exposure to organic

chemicals are increasing. Methods developed in support of life-sciences problems appear to be readily transferable to interests of process developers, and we look forward to an increasing interaction with the engineering staff of this and other institutions.

Our efforts continue to be typified by closely collaborative interactions with other institutions and groups. We continue to interact closely with National Cancer Institute Smoking and Health Program contractors and anticipate an even broader interaction with other institutions sponsored by the Council for Tobacco Research. Collaborative studies with J. L. Epler of the Biology Division have been particularly productive and are leading to unique capabilities for ORNL. We have been particularly pleased with the cooperation of colleagues at the Pittsburgh and Laramie Energy Research Centers. We look forward to new interactions with university researchers on the problems of agricultural feed supplements.

The topics included in this report were chosen by the group leaders as being illustrative of ongoing activities and capabilities. We anticipate an increasing need for multicomponent organic analytical methods to provide a maximum chemical characterization and an increasing demand for unambiguous organic structural identification. Bioanalytical and separations methodologies require attention to meet these needs and extend section capabilities. The following reports illustrate our capabilities to address organic- and bioanalytical problems.

QUANTITATIVE METHODS AND PROJECTS

Advanced organic-analytical services. Quantitative analytical capabilities have evolved from the expertise developed in analyses of tobacco smokes. A number of compounds being routinely determined were listed last year.[1] New methods added this year include procedures for the analysis of paraffins and carboxylic acids. A procedure for the direct analysis of the latter in aqueous samples is described elsewhere in this report.[2] New gas-phase constituents that can be determined include methane and hydrogen; polynuclear aromatic hydrocarbons (PAH's) are being determined for the Industrial Hygiene Department, using methods developed in smoke-related work.

The largest user of these services has been the National Cancer Institute (NCI) Smoking and Health Program (SHP). A series of experimental cigarettes and their corresponding smoke condensates have again been submitted for extensive chemical characterization. Approximately 40 varieties of experimental cigarettes and condensates were examined for more than 30 routine protocol constituents or parameters in this report period. This characterization required approximately 4000 analyses.

An increasing part of our effort has involved responding to special requests from the NCI. Studies have included the measurement of tar, nicotine, water, carbon monoxide, and carbon dioxide deliveries of 11 varieties of commercial cigarettes purchased in Brazil and Hong Kong. A more detailed analysis of smoke constituents from 17 domestic commercial brands is in progress. The smokes are being analyzed for tar, nicotine, carbon monoxide, nitrogen oxides, hydrogen cyanide, and acrolein. The data are to be used by the NCI SHP management to postulate levels of smoking that produce an acceptably low health risk.

We have also completed examining smoke condensates generated, using 24 experimental cigarettes to compare a new bioassay, the sebaceous gland suppression test, with the mouse skin-painting bioassay. Our assignment was to determine if these condensates were chemically identical to those generated and used earlier for skin testing. Statistically significant compositional differences were found. Two causes of this difference are possible: (1) the smaller number of cigarettes available for use produced an insufficient amount of condensate to properly condition the cold-trap assembly for maximal collection efficiency, and (2) the cigarettes had aged up to three years and may have yielded a chemically different smoke in spite of freezer storage. These data indicate that a direct comparison of bioassays is not possible by use of this experimental design.

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1. W. H. Griest and H. Kubota, "Polynuclear Aromatic Hydrocarbons," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 57.

2. *C-h. Ho, B. R. Clark, and M. R. Guerin, "Direct Analysis of Organic Compounds in Aqueous By-Products from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification and COED Coal Liquefaction," J. Environ. Sci. Health* A11(7), 481 (1976).

As the priorities and requirements of the NCI SHP change, our services and capabilities also change. The future direction of this NCI program will include heavy reliance on multicomponent analytical procedures for an efficient, maximum characterization of a smaller number of experimental variants. Newly developed or improved methods to meet such requirements are described in the following sections. (*R. B. Quincy, H. Kubota*)

Characterization of occupational exposure to PAH-containing fugitive emissions. Operations involving the pyrolysis of petroleum pitch produce large amounts of hydrocarbons as by-products. The chemical composition of such by-products and their release as fugitive emissions into the workroom atmosphere have not been well characterized. We have been involved in a study of PAH-containing airborne fugitive emissions associated with an ORNL project involving pitch pyrolysis.

A cooperative effort was established with the operating division and the Industrial Hygiene Department of ORNL to collect air samples during normal operations. A standard air-filter cassette was employed with a backup dry-ice trap on a 20-liter/min sampler. Samples of workroom air were collected at suspected emission points for each operation. Personnel exposure was defined by a personal monitor carried by one worker.

The samples were ranked for analysis by examination of the fluorescence exhibited by the gross unpurified filter extracts at benzo[*a*]pyrene (BaP) emission wavelengths. Those samples whose fluorescence indicated more than 0.2 μg of BaP per m^3 of air (the proposed air concentration limit for BaP)[3] were selected for specific BaP determination. Selected samples will be subjected to a multi-PAH analytical procedure for a more complete assessment of airborne PAH content.

Results from the first set of samples allow several conclusions to be drawn. (1) The standard filter cassette employed for the collection of air samples appears to be at least 95% efficient for BaP-containing particulates in the range of particle sizes encountered in these operations. The cryothermal backup trap was therefore eliminated from subsequent sampling operations. (2) Comparison of the results for the final specific BaP analysis with the initial gross sample fluorescence measurement suggests that use of the latter may allow a rapid, rough estimate of the BaP content of a sample. However, more samples are required to quantify this relationship. (3) The manner in which a worker performs a given operation has a major effect on the emissions generated. This effect may seriously complicate efforts to predict exposures for the various work operations. (4) Most important, certain operations were found to produce BaP-containing emissions. Particle-size analysis of the emissions of one operation showed that approximately 70% by weight are ≤ 10 μm in diameter; hence a significant portion are in the respirable range.

The operation that appears to offer the greatest emission is being characterized in greater detail. Emissions have been sampled hourly during the course of a work shift at three workroom points. Hourly personnel exposure was defined by a separate personal monitor carried by a worker. The intent of this study is to develop methods for monitoring the release and spread of emissions and for defining some relation to worker exposure. (*W. H. Griest, H. Kubota, R. W. Holmberg, L. B. Yeatts, Jr.*)

PAH analysis methodology and correlation with biological activity. Interest in methods that allow the simultaneous determination of many PAH's continues as new information on the biological activity of various isomers indicates a synergistic carcinogenic effect.[4-6] Our multicomponent PAH method has undergone several improvements in this report period. The initial procedure [serial extractions with cyclohexane, dimethylsulfoxide (DMSO), and cyclohexane] has remained the same. However, a volume reduction step has been added prior to the DMSO extraction to improve the recovery of alkyl naphthalenes. Extraction of 80 ml of cyclohexane with 5 × 20 ml of DMSO allows only one-quarter of the alkyl naphthalenes to be transferred into DMSO. Reduction of the cyclohexane volume to about 5 ml by evaporation under nitrogen at reduced pressure prior to DMSO extraction improves recovery to at least 95%. The residue is subjected to Florisil column chromatography as before.

The major change in our method is that we now divide the subsequent alumina column effluents into two subfractions prior to analysis. This separation is accomplished by using a solvent program consisting of 100 ml of hexane/benzene (6/1) followed by 300 ml of hexane/benzene (2/1) on the alumina column. The

3. Standards Advisory Committee on Coke Oven Emissions, *Occup. Saf. Health Rep.* 4(50), 639 (1975).

4. R. Schoental, pp. 133–60 in *Polycyclic Hydrocarbons*, ed. E. Clar, Academic Press, New York, 1964.

5. *Particulate Polycyclic Organic Matter*, Committee on Biologic Effects of Atmospheric Pollutants, National Academy of Sciences, Washington, D.C., 1972, pp. 4–12.

6. E. L. Wynder and D. Hoffmann, *Tobacco and Tobacco Smoke*, Academic Press, New York, 1967, pp. 225–32, 330–51.

subfractions are defined by the elution of ^{14}C-labeled naphthalene and benz[*a*]anthracene (BaA) tracers, detected by liquid scintillation counting. The two subfractions are separately concentrated and analyzed by high-resolution gas-liquid chromatography (GLC). Recoveries are calculated from liquid scintillation measurements of the tracers. We have applied this method to the analysis of a variety of sample types. Samples analyzed include several coal-derived liquids, a natural crude oil, petroleum pitch, tobacco smokes, and air particulates.

Experiments comparing the PAH's collected in total particulate matter (TPM) (glass-fiber filter) and cold-trapped condensate showed widely varying collection efficiencies on the standard glass-fiber filter. Collection efficiency by the filter is a function of PAH volatility. Sixty-two percent of the naphthalene was lost from the TPM, while losses were lower for the less volatile PAH's such as anthracene (28%) or a methylpyrene (4%). TPM cannot, therefore, be used to reliably determine the smoke deliveries of PAH's less than four rings in size. The experiment suggests that analysis of industrial air-filter samples will produce unrealistically low results for smaller PAH's.

Smoke condensates from five experimental cigarettes were used in a direct correlation ("blind assay") of GLC profile-peak areas with biological activity of the whole condensate. The biological activity, as determined by skin painting elsewhere of these condensates, ranges from 0.19 to 0.52 P_f (probability of survival without tumor for 18 months at 25-mg dose level). PAH fractions were isolated from these condensates, and GLC profiles were generated. The PAH profiles for three of these condensates, ranging from the highest biological activity condensate (upper trace) to intermediate (center trace) and lowest biological activity condensate (bottom trace), are shown in Fig. 4.1. The general features of the profiles appear quite similar, but the intensities vary directly with the biological activity of the condensate, suggesting a group correlation. Thirty-one visually selected peaks were chosen for correlations of peak-area vs biological activity. Resulting simple correlation coefficients are presented in Table 4.1. The highest correlation with biological activity (+0.97) was found for an unidentified peak (3) which may be 2- or 3-methyl fluorene, judging by its retention time. Fluoranthene, 2,3-benzofluorene, and perylene (possibly with a coeluting species) also produce significant correlations, as did the total integrated 3- to 6-ring PAH-fraction peak area. The latter result is consistent with the long-known fact that the majority of the carcinogenic activity of tobacco smoke resides in its PAH-containing neutral fraction. Fluoranthene is cocarcinogenic with BaP; pyrene, which also is a cocarcinogen, did not correlate so well. Surprisingly, the 1,2-isomer of benzofluorene yielded the best correlation, +0.99, an excellent correlation *against* biological activity. This result is just opposite that of the 2,3-isomer.

A very low correlation was observed for BaP or BaA; however, this was not unexpected, since correlations of the routinely determined BaA/BaP data with bioassay

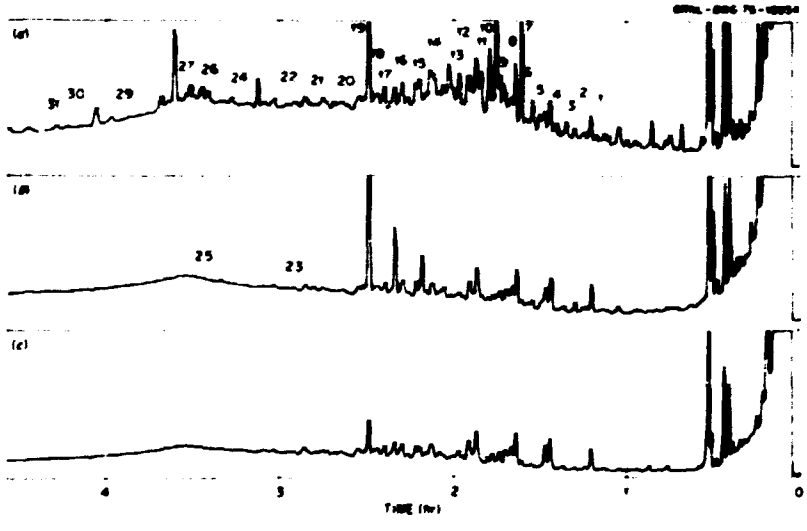

Fig. 4.1. Three- to seven-ring PAH profiles for three experimental cigarette smoke condensates of known biological activity. (*a*) high activity, (*b*) intermediate activity, and (*c*) low activity. Tentative peak identifications are listed in Table 4.1.

Table 4.1. Tentative peak identifications and correlations with skin-painting bioassay data

Peak No.	Tentative identification	Correlation[a] coefficient
1	Fluorene	-0.38
2	9,10-Dihydroanthracene	-0.23
3	Unknown-1	-0.97
4	9-Methyl fluorene	--
5	1-Methyl fluorene	-0.58
6	Unknown-2	-0.80
7	Unknown-3	-0.74
8	Phenanthrene	-0.77
9	Anthracene, impure	-0.60
10	Unknown-4	-0.70
11	Unknown-5	-0.75
12	2-Methyl anthracene	--
13	1-Methyl phenanthrene	--
14	Unknown-6	-0.77
15	Fluoranthene	-0.92
16	Pyrene	-0.80
17	1,2-Benzofluorene	0.99
18	2,3-Benzofluorene	0.91
19	Unknown-7	-0.65
20	1-Methyl pyrene	--
21	1,2-Benz[*a*]anthracene (BaA)	0.05
22	Chrysene	-0.10
23	2,3-Benz[*a*]anthracene	--
24	Unknown-8[b]	-0.65
25	1,3,4-Triphenylbenzene	-0.12
26	1,2-Benzo[*a*]pyrene (BaP)	0.62
27	Perylene	-0.95
28	Unknown-9[b]	--
29	*o*-Phenylene pyrene	--
30	1,12-Benzoperylene	--
31	Anthanthrene	--
Total	3- to 6-ring PAH fraction peak area	-0.94

[a] -- signifies that these PAH's were not found in a sufficient number of condensates to allow calculation of a confident correlation coefficient

[b] These unknowns are each isostructural with 7,12-dimethyl-1,2-benz[*a*]anthracene (24) and 3-methyl cholanthrene (26), neither of which have been identified in tobacco smoke

results for previous experimental cigarettes have never been good. The results of this study suggest that a better indicator of the PAH fraction and its relationship to biological activity would be the unidentified peak (3). The next step of this study is structural identification of the correlating constituents of the PAH fraction. Gas-liquid chromatographic mass spectrometric (GLC-MS) examination of the sample is planned in the near future. (*W. H. Griest, G. Olerich*)

Polyglycol multicomponent analytical method. Polyglycols such as glycerol are usually present in tobacco smoke at relatively high levels. They originate for the most part from polyglycol humectants added to the tobacco in the manufacture of cigarettes. Although polyglycols are not expected to be biologically active, it is possible that their presence in smoke at elevated concentrations could affect the absorption and uptake of carcinogenic constituents of smoke. Our recent observation of unexpectedly high levels of polyglycols in certain tobacco smoke condensates of the current NCI series suggested a need for an analytical method for identifying and quantitating polyglycols in smokes.

We have developed a rapid analytical technique capable of identifying and quantitating several polyglycols in tobacco smoke. The procedure is a slight modification of our standard multicomponent TPM or condensate profiling method similar to the humectant analysis developed by Carugno et al.[7] One milliliter of a 25 wt % solution of tobacco smoke condensate in

7. N. Carugno et al., "Gas Chromatographic Determination of the Trimethylsilyl Derivatives of Polyhydric Humectants in Tobacco and in Tobacco Smoke," *Beitr. zur Tabak.* 6, 79 (1971).

acetone water (95:5) and a known amount of undecane internal standard are pipetted into a 5-ml volumetric flask and then diluted to volume with redistilled pyridine. After mixing, a 400-μl aliquot is reacted with 200 μl of bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane for 30 min at 65°C. A 5-μl aliquot is injected into a 20-ft × ⅛-in.-OD glass GLC column packed with 4% OV-101 on 80/100-mesh high-performance Chromosorb G, temperature programmed from 100°C (8 min isothermal hold) to 280° at 2°/min. Appropriate attenuations are made to keep all polyglycol peaks on scale. Application of this method to certain smoke condensates of the current series confirmed our initial observation of elevated polyglycol concentrations. For example, in one condensate, three polyglycols – glycerol, 1,3-propylene glycol, and triethylene glycol – were present in even greater concentrations than that of nicotine (64.8 mg/g), and at least one other polyglycol was present at about one-third the nicotine concentration. The total weight of the identified polyglycols constituted almost 20% of the condensate.

The importance of such multicomponent screens is thus demonstrated. NCI is now supporting such methods to establish the integrity of experimental variants. *(W. H. Griest, G. Oberich)*

Phenol multicomponent analytical method. Methods have been devised for the multicomponent determination of phenols in tobacco smoke and other sample materials such as Masonex, a by-product of hardboard manufacturing. Interest in the phenols arises from the observation of significant tumor-promoting activity in the weak-acid fraction of tobacco smoke condensate.[8,9] The phenols may exhibit tumor-promoting activity. Certain phenols, such as catechol, are considered cocarcinogenic.

Our multicomponent phenol method involves both solvent extraction and column chromatography. The sample in ether is spiked with a ^{14}C-labeled phenol tracer and is extracted with 1 *N* NaOH. The aqueous layers are pooled, neutralized to pH 6.1, and back-extracted into ether to obtain a weak-acid fraction.[10] This fraction can be directly analyzed following trimethylsilyl (TMS) derivatization by GLC for a few phenolics and phenol. Many more phenols can be visualized and measured, apparently free of interferences if the weak-acid fraction is further subfractionated on a silica-gel column. At present, a solvent program consisting of benzene, various ratios of benzene and methylene chloride, ether, and, finally, methanol is employed.[9] The first subfraction, as defined by the ^{14}C phenol tracer, consists of simple phenols and their methyl derivatives; the second subfraction is defined as the material eluting up to the methanol solvent step; and the final subfraction consists of the material eluted with methanol. The second subfraction contains some carry-over of simple phenols such as hydroquinone from the first subfraction. The use of a ^{14}C-labeled hydroquinone tracer instead of the phenol is being considered for defining the simple phenolic subfraction. The identities of the remaining constituents of the second and third subfractions are not well known, but are thought to be carboxylic acids, cyclopentenoids, pyridinols, and other constituents. Each subfraction is examined by GLC after preparation of a TMS derivative by reaction with bis(trimethylsilyl)trifluoroacetamide.

Initial application of this procedure was to the same five tobacco smoke condensates as were used in the PAH blind assay study. GLC profiles were generated for each subfraction. The simple phenolic subfraction was found to contain at least 20 phenols, with phenol, the three cresol isomers, and certain ethyl- and methoxyphenols as the major constituents. Several dimethyl and higher alkyl phenols and catechol derivatives also were tentatively identified. The second and third subfractions were complex, but little identification was possible.

Blind assay correlations were applied to the profiles, but no readily apparent correlations were observed for any of the subfractions. Two explanations are possible. The constituents visualized in the profiles may not actually be contributory to smoke-biological activity, and further subfractionation may be necessary to visualize the active constituents. Alternatively, it is possible that the active constituents of this fraction are on a "saturating" plateau region of the dose-response curve, and, therefore, the concentrations of other constituents are controlling the differences in biological activity of these condensates. Considerable differences in the PAH contents of these condensates were observed, suggesting that the PAH's might be among the controlling factors. Further work will be necessary to confirm this explanation. *(W. H. Griest)*

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8. E. L. Wynder and D. Hoffmann, *Tobacco and Tobacco Smoke*, Academic Press, New York, 1967, pp. 626–27.

9. S. S. Hecht, R. L. Thorne, and D. Hoffmann, "A Study of Tobacco Carcinogenesis. XIII. Tumor Promoting Subfractions of the Weakly Acidic Fraction," *J. Nat. Cancer Inst.*, in press (1975).

10. A. P. Swain, J. F. Cooper, and R. L. Stedman, "Large Scale Fractionation of Cigarette Smoke Condensate for Chemical and Biologic Investigations," *Cancer Res.* 29, 579 (1969).

Arc-emission detector for gas chromatography. Gas chromatographers have long recognized the potential that a versatile, multielement detection system would hold. Several systems have been investigated with varying degrees of success.[11-15] With increasing interest in organohalides and organometallics, an element-specific detector should have broad application in areas such as tobacco-smoke chemistry and environmental studies related to synthetic fossil fuels production. We are studying a technique that we hope will lead to a true multielement detection capability. The project, involving both spectroscopic and chromatographic methodologies, has been one of close cooperation between the Bio-Organic Analysis Section and the Analytical Instrumentation Group.

The detector, based on a helium glow discharge, is a modification of a system described in last year's annual report[16] and in detail elsewhere in this report (Chap. 1). The arc has been interfaced to a high-resolution gas chromatograph to provide for a maximum separation capability. The chromatograph has been modified by a 50:50 split of the column effluent to the arc emission detector (AED) and a conventional flame ionization detector (FID). Thus the output of the system is a dual-trace chromatogram, with one trace responding to all hydrocarbon-containing components (FID) and the other (AED), ideally, responding only to components containing the element in question.

Most of the initial studies were conducted using the system as a silicon-specific detector, monitoring photometrically the 288.2-nm silicon emission line. Using mixtures of trimethylsilylated fatty acids and similar normal hydrocarbons, selectivity for silicon was determined to be ~37. (Selectivity refers to the AED's ability to discriminate between a compound containing the atom of interest and a compound of similar structure without the particular atom.) Silicon-specific detection was applied to samples of TMS-derivatized tobacco smoke condensate. Response comparisons of the conventional FID with the AED illustrated both the strengths and weaknesses of the "first-generation" AED system. Since most constituents in the smoke condensate possess active hydrogens and thus become TMS-derivatized, most compounds are visualized by the silicon-specific detector. Constituents which are at moderate concentration, contain no active hydrogens, and are not TMS-derivatized (e.g., neophytadiene) are readily identifiable, since they are visualized by the FID but not the AED. However, for nonactive hydrogen-containing constituents present at high concentrations, such as nicotine, there is still a small response by the AED. This is presumably due to an increase in overall spectral background radiation, since relatively large amounts of hydrocarbons pass through the discharge. In order to alleviate the problem of small, false, positive responses and to substantially boost the system's selectivity, spectral background corrector modifications have been made in a "second-generation" system. These modifications are described in Chap. 1 of this report.

The preliminary tests of this second-generation system have been completed. With the background corrector, it has been possible to completely suppress background radiation resulting from pure hydrocarbons that are at least one to two orders of magnitude more concentrated than the species containing the sought-for element. High element selectivity and good sensitivity have been verified for organic compounds containing Si, As, and I. Some preliminary studies with a nonbackground-corrected system indicate that moderately sensitive element-specific detection appears feasible for compounds containing Al, Cl, P, S, Cl, Br, and F.

We are using this detection system to investigate and quantify the possible existence of arsine in the vapor phase of tobacco smoke. Arsenic is present in cigarettes in microgram quantities and presumably could be converted to arsine in the highly reductive atmosphere of the burning cone of the cigarette. Some preliminary nonchromatographic experiments have indicated that about 35% of the arsenic in the cigarette transfers to the mainstream vapor phase and the sidestream smoke during normal smoking. About 30% remains with the unsmoked butt, 30% remains in the ashes, and about 5% transfers to the mainstream particulate matter. Given the inherent sensitivity of the helium-glow discharge method for arsine,[16] these arsenic levels should be within the detection capabilities of the

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11. A. J. McCormack, S. C. Tong, and W. D. Cooke, "Sensitive Selective Gas Chromatography Detector Based on Emission Spectrometry of Organic Compounds," *Anal. Chem.* 37, 1470 (1965).
12. R. S. Braman and A. Dynako, "Direct Current Discharge Spectral Emission-Type Detector," *Anal. Chem.* 40, 95 (1968).
13. R. W. Morrow, J. A. Dean, W. D. Shults, and M. R. Guerin, "A Silicon-Specific Detector Based on Interfacing a Gas Chromatograph and a Flame Emission or Atomic-Absorption Spectrometer," *J. Chromatog. Sci.* 7, 572 (1969).
14. W. B. McLean, D. L. Stanton, and G. F. Penketh, "A Quantitative Tunable Element-Selective Detector for Gas Chromatography," *Analyst* 98, 432 (1973).
15. Y. Talmi and A. W. Andren, "Determination of Selenium in Environmental Samples Using Gas Chromatography with a Microwave Emission Spectrometric Detection System," *Anal. Chem.* 46, 2122 (1974).
16. C. Feldman, "Determination of Arsenic," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, p. 6.

system, allowing a definitive answer to the question of arsine in tobacco smoke. We have already attempted some gas-chromatographic visualization of arsenic-containing compounds, and these preliminary experiments indicate that good selectivity (>55) is attainable using the arsenic-emission line at 228.8 nm, even without the "second-generation," background-corrected AED. We are involved with determination of GLC conditions and procedures necessary to separate arsine from other smoke-vapor-phase constituents. (*R. A. Jenkins, C. Feldmann*)

SEPARATIONS AND IDENTIFICATIONS

Large-scale chemical class fractionation of synthetic crude oils. Available separations methods for fossil-derived materials are predominantly of an analytical scale. There exists a substantial need for chemical class separations methods which are preparative in scale and broadly applicable. Our own concern in this regard arises from the need to produce samples large enough for extensive biological and chemical characterization of coal liquids, crude shale oils, natural petroleums, and various by-products. In addition to the problem of sample size, attention must be given to the preservation of the sample integrity; that is, the method should be gentle.

Encouraging progress has been made in the development of a separation scheme that appears to fulfill the criteria outlined. The heart of the scheme is a Dextran-derived gel: Sephadex LH-20 (Pharmacia Fine Chemicals, Sweden). This is a gel that was especially developed for low-molecular-weight gel filtration applications where it is desirable to use organic solvents.[17] Earlier publications[18,19] have suggested the possible utility of LH-20. Most useful among the properties of this gel are the behavior features observed when the gel is swollen and eluted with different solvents. By judicious choice of solvent systems, one can achieve lipophilic-hydrophilic, aliphatic-aromatic hydrocarbon, or molecular-size separations. Gentleness, with respect to chemical or physical stresses upon sample components, has always been a positive factor with polysaccharide gels; sample integrity should be maintained much better than in cases where heat, strong acids, strong bases, or ion exchange resins are used in separation steps.

Crude shale oil obtained from an above-ground retort of the Laramie Energy Research Center has been used as a model material to develop the methodology and is to be used here to illustrate the procedure. First, a sample of the oil is dried by azeotropic distillation with benzene at reduced pressure and low temperature (40°C). This step would, of course, tend to reduce the amounts of volatile constituents left in the sample, but in the case of shale oil, few constituents are lost by this dehydration step. The sample is placed on an LH-20 gel column (5 cm × 1 m) in which the gel has been swollen with an 85% methanol 15% water mixture. Up to several hundred grams have been placed on the column at one time with no apparent loss of separation or yield in this initial column separation. *n*-Hexane is used to elute the sample (500 ml/hr); in this process, the lipophilic components distribute more readily in the hexane phase than in the gel-supported, polar, methanol-water phase. Hydrophilic components are distributed more readily in the polar phase and cannot be eluted with hexane, even after extremely large elution volumes. Thus a very rapid, large-scale, high-yield (virtually 100%) separation is achieved into the broad classification of lipophilic and hydrophilic materials. The hydrophilic material left on the column is easily recovered by back-flushing with methanol or eluting with acetone or mixtures thereof. No further work has been done with the hydrophilic fraction.

The lipophilic material (~40% in shale oil) is next subjected to a separation procedure employing an LH-20 column in which the gel has been swollen with tetrahydrofuran (THF). THF is used to elute the sample (up to 4 g at one time); a refractive index detector reveals three distinct peaks which are highly reproducible when 4-g sample loads are placed successively on the column (a sample can be placed on the column before the previous one is eluted with no overlap). Examination of the materials corresponding to each of the peaks has indicated that the first material is polymeric with respect to the gel pore size (molecular weight: >5000) and is eluted with the void volume. The bulk of material is eluted next; this is the low-molecular-weight (>5000) lipophilic material. Elution occurs in approximate order of molecular size, since the gel behavior is that of a filtration gel or sieve when operated with THF. A small weight of material is found in the third fraction. This is a class of compounds which can hydrogen-bond to gel sites and is substantially retarded. Since this material did not distribute in the hydrophilic phase initially, it must have lipophilic

17. M. Joustra, B. Soderquist, and T. L. Fischer, "Gel Filtration in Organic Solvents," *J. Chromatog.* **28**, 21 (1967).

18. S. Marm-Mudrovcic, J. Mubl, and M. Sateva, *Nafta (Zagreb)* **23**, 593 (1972).

19. H. J. Klimisch and D. Ambrosius, "Gel Chromatography of Polycyclic Aromatic Hydrocarbons," *J. Chromatog.* **90**, 311 (1974).

character, for example, long alkyl chains with oxygen or nitrogen functional groups. Details of this step require further study.

Following treatment on the THF–LH-20 column, the lipophilic (sieved portion) fraction is eluted with isopropanol through an LH-20 column with the gel swollen by isopropanol. This system now separates, according to aromatic-aliphatic and molecular size, properties of the eluate components. The first portion eluted contains more polymeric material eluted because the gel pore size is somewhat smaller in isopropanol than in THF. Next come the aliphatics, in reverse order of molecular size, followed by aromatics in order of ring size (monoaromatics first). A remarkable separation is achieved between the aliphatic and aromatic components. This is true even when the aromatics are highly alkyl substituted, a factor which lowers the elution volume. Heteroatomic groups substituted on aliphatics or aromatics increase the elution volume, so overlap is expected if this fraction is not composed entirely of hydrocarbons. But most heteroatomic species should have been separated at this point by the lipophilic-hydrophilic initial separation step or by the THF step (hydrogen-bonded fraction).

Although this separation scheme appears highly promising, its general applicability to a wide range of fossil-derived material remains to be demonstrated. There is a likelihood that a method exists here for isolating PAH and heteroatomic aromatic compounds for biological studies and chemical characterization. (*A. R. Jones, B. R. Clark*)

Chemical-biological characterization of synthetic crude oils and aqueous by-products. This Division and the Biology Division have been working closely to develop an approach for screening a large variety of fossil-derived materials to determine their relative biological activities. Several biotesting methods are being explored to find an economical and rapid means for predicting, on a relative scale from bioactivity data, whether a potential health hazard exists. Fractionation of whole samples is an integral part of this approach, since repeated fractionation, biotesting, and chemical analysis function in a feedback loop, which allows us to converge on those specific components of a mixture that produce a high rate of biological activity. In this way, guidance is provided to direct further fractionation and identification effort toward the identification of "culprits" in a complex mixture without need to rely on previously established toxicity data.

One separation procedure[20] for the fractionation of coal-derived liquids into reproducible-class fractions has been improved and put into semiroutine use. The procedure has also been adapted to the fractionation of the organic matter in aqueous process streams from fossil-fuel conversion processes. Samples which have been thus treated include char-coal-energy development (COED) separator liquor from coal liquefaction, synthane condensate from coal gasification, and shale-oil product water from oil-shale retorting.

In conjunction with fractionation procedures, it is desirable to have available methodologies for specific class analyses. PAH's constitute one important class of compounds which can be isolated by the procedure used with tobacco-smoke condensates described earlier. This method was applied to the determination of PAH's in five liquid fuels (shale oil, Synthoil, COED Syncrude, Louisiana Mississippi Sweet-petroleum, and mixed petroleums) and three synthetic-fuel by-product waters (shale oil water, Synthane water, and COED Syncrude water). Five microliters of the PAH fraction were injected into a gas chromatograph equipped with a packed 3% Dexsil 400 column. The tentative identifications were made by cochromatography, and quantification was achieved by using standard solutions. Structural confirmations were made using GLC-MS. The concentrations of 30 PAH's in eight fossil-derived samples were calculated and compared. LMS-petroleum or mixed petroleums contain PAH's in the 2- to 3-ring range with alkyl-substituted naphthalenes predominating. Shale oil is similar in this range but has about a seven times higher distribution of PAH's in the 3- to 6-ring category, for example, 4300 ppm pyrene, 270 ppm benz[*a*]anthracene, 380 ppm picene, and 1500 ppm benzo[*g,h,i*]perylene. The overall PAH concentration in Synthoil is somewhat less than in shale oil (~⅔), but still about five times greater than in petroleum crudes. COED Syncrude shows relatively low concentrations of PAH's. Shale oil retort water shows a broad spectrum of PAH materials, but the larger proportion falls into the 2- to 4-ring category. Synthane by-product water contains principally 2-methylnaphthalene with no detectable PAH's of more than three rings. Only trace amounts of PAH's are found in COED-Syncrude by-product water.

Paraffins, a major compound class of liquid or synthetic fuels, can be isolated by the following conventional procedure: an oil sample (~1 g) is dissolved in benzene, or a synthetic-fuel by-product water (1 liter) is extracted with benzene. The benzene solution or combined benzene extracts are washed with

20. I. B. Rubin, "Fractionation of Synthetic Crude Oils from Coal for Biological Testing," *Anal. Chem. Div. Annu. Prog. Rep. Nov. 30, 1975*, ORNL-5100, pp. 61–62.

NaOH and HCl solutions. The paraffin fraction is isolated by alumina column chromatography (neutral activity I), using hexane as the eluting solvent. This method has been used to determine the concentrations of *n*-alkanes in the five oils discussed above and the three synthetic-fuel by-product waters. The most satisfactory separation of the paraffin fraction was obtained on a ½-in. by 10-ft glass column packed with 3% Dexsil 400. Tentative identifications were made by cochromatography, and quantification was achieved using standard solutions. Structural confirmations were obtained using GLC-MS. *n*-Alkanes detected ranged from $C_{11}H_{24}$ to $C_{36}H_{74}$.

The concentrations of *n*-alkanes in petroleum crudes are similar to those for shale oil. The overall *n*-alkane concentrations of COED Syncrude are somewhat less than in petroleum crude or shale oil (~⅓). Synthoil contains only one-tenth the total found in shale oil. The concentrations of *n*-alkanes in shale oil by-product water range from 2 to 106 ppb. Such concentrations are about 10 times greater than in COED-Syncrude or -Synthane by-product water.

Sufficient biological data have been gathered by J. L. Epler (Biology Division) to indicate the next direction in chemical characterization. Most of the data have been obtained on fractions generated by the acid-base-neutral fractionation scheme mentioned earlier.[20] The Ames test,[21] a microbiological mutagenesis test, appears to be the most useful. Mutagenic activity data are shown in Table 4.2. These values show the relative mutagenic activity of the various fractions in each sample. The numbers are calculated from the relative weights and the specific activities of each fraction. This factor is based on the number of colonies of bacteria growing on the nutrient medium per milligram of test substance. The fractions which have high relative activity vary from sample to sample. However, the ether-soluble base fraction (fraction 9) in all of the samples except one does contain significant activity, as does the neutral fraction of all of the oils. These would appear to be the most fruitful subjects for further investigation. As noted in a previous report,[20] the neutral fraction is divided into four portions by column chromatography, and each of these, in turn, is subdivided into three subfractions. Mutagenic activity was found in virtually all of these neutral subfractions in all four oils tested. Because many of the fractions are insignificant portions of the whole material by weight, the relative effect of those fractions is slight. The base fraction can be further subdivided by chromatography on alumina columns[22] and the resulting subfractions

21. B. N. Ames, "The Detection of Chemical Mutagens with Enteric Bacteria," p. 267 in *Chemical Mutagens: Principles and Methods for Their Detection*, vol. 1, ed. A. Hollaender, Plenum, New York, 1971.

22. J. F. McKay, J. H. Weber, and D. R. Latham, "Characterization of Nitrogen Bases in High-Boiling Petroleum Distillates," *Anal. Chem.* 48, 891–98 (1976).

Table 4.2. Distribution of relative Ames test activities of fractions of fossil-derived oils and aqueous samples

Fraction	Coal-derived oil A	Coal-derived oil B	Shale-derived oil	LMS crude	Scrubber water, coal process A	Coal gasification condensate, process B	Shale-derived product water
1. $NaOH_I$		6.6	1.7		NT	NT	NT
2. WA_I		0.2	0.2		NT	28.2	7.1
3. WA_E		0.4	0.3		76.4	3.9	9.7
4. SA_I					NT	31.8	
5. SA_E		0.2	0.3	0.8		27.0	
6. SA_W		0.2	0.6	0.3			
7. B_{Ia}	3.3	69.3	1.7		NT		0.1
8. B_{Ib}		0.2	1.1		NT	0.1	2.2
9. B_E	7.6	14.2	38.6	0.6	23.6	8.2	62.0
10. B_W		0.2	0.4		NT	NT	17.1
Neutral	88.9	9.5	55.1	101		0.9	1.8

Note: NT = not tested, I = insoluble, a, part a, b, part b, E = ether soluble, W = water soluble.

reexamined (C. A. Hill, I. B. Rubin, B. R. Clark, J. L. Epler)

Airborne exposure system for gaseous contaminants. The effects upon terrestrial plants of various gases, known or suspected to be effluents in coal conversion processes, are being studied by members of the Environmental Sciences Division. The Analytical Chemistry Division is providing the technical assistance necessary to develop the gas metering and monitoring systems for a plant exposure chamber (a controlled atmosphere containment facility) designed for these studies.

In order to accumulate interpretable environmental data, gas concentrations introduced into the chamber must be known with reasonable precision. Furthermore, any uptake or expulsion of gases from plants must be detected by periodic sampling of the atmosphere. Careful measurements can provide a mass balance that affords a means of determining the extent of plant exposure to, or uptake of, the gases metered into the system. The system has been designed so that a single gas or a mixture of up to nine gases may be introduced at steady-state delivery rates.

One serious handicap in designing plant exposure experiments is the lack of knowledge regarding both kinds and levels of gaseous effluents that will be produced by a coal conversion facility. Nevertheless, some indication of likely effluents can be inferred from past experience with research-scale conversion apparatuses. For present purposes a metering system has been developed that can supply the following gases: methane, ethylene, methylamine, benzene, xylene, phenol, and hydrogen sulfide.

Modes of delivery to the exposure chamber vary according to the properties of the materials. Benzene and xylene are held in gas-bubbler trains through which metered volumes of air are passed. Quite reproducible concentrations of these vapors are produced in this manner, although the available concentration ranges are small. Phenol, a solid at room temperature, is heated to a melt, and the headspace volume is swept into the manifold at a steady rate. It was necessary to heat this delivery line to prevent condensation of the phenol vapor prior to reaching the manifold, where dilution can sustain the vapor phase.

A series of tests has been completed to establish the delivery characteristics of the various gas metering devices. Likewise, many gas samples have been withdrawn from the chamber to test the reproducibility of sampling and to investigate the behavior of various gas mixtures in the empty chamber. The chamber has a 15-ft^3 volume and a set flow rate of air through the chamber of 37.5 ft^3 min (1062 liters, 2.5 changes per min). A synthetic stack gas, limited to 4.7 Vppm methane, 1.5 Vppm ethylene, 0.94 Vppm methylamine, 2 Vppm benzene, 1 Vppm xylene, 0.8 Vppm phenol, and 4.7 Vppm H_2S, can be introduced into the chamber.

Samples are withdrawn by vacuum pump through a 1-ml loop attached to a pneumatic gas-sampling valve and rapidly transferred to a 10% DC-200 column in a Perkin-Elmer 3920 gas chromatograph. The column is held at −60°C for 2 min, then heated at 32°/min to +180°C and held for 4 min. Methane and ethylene are eluted at −60°C as very sharp peaks, with a 5% valley at 1 min after injection. The retention time of benzene is 7 min, of xylene, 9 min, and of phenol, 9.75 min. Sulfur compounds are analyzed using a 15-ft × ⅛-in. column packed with 20% FFAP on 60–80 mesh Chromosorb W-AW-DMCS. A flame photometric detector is used to obtain maximum sensitivity for sulfur compounds.

Calibration curves for liquids were obtained gravimetrically by cold trapping the generator vapors and weighing. The curves for gases were obtained by use of standard gas mixtures. Data were compared with samples withdrawn from the chamber after introducing predetermined amounts of the individual components. The latter were in good agreement with the former except for methylamine, which did not appear in the chromatograms even at the 10-ppm level. Detector response vs concentration was linear for all components except H_2S. The calibration curve for H_2S shows a response approximately proportional to the square of the concentration. The detector response of each component in the mixture in the presence of, and in the absence of, H_2S was measured.

Several conclusions were drawn as a result of these studies:

1. In a mixture of all components (except H_2S), methane, ethylene, benzene, and xylene responses were constant 1 hr after introduction into the chamber.
2. Phenol did not give a measurable response before 2 hr. The response was erratic and gradually increased for about 6 hr until it became constant within ±15%. After the phenol bubbler was turned off, the decay of the phenol response was about twice the rate of the buildup, and it dropped by a factor of 2 in 1 hr.
3. There were no significant changes in the levels of the known organic components upon introduction of H_2S into the chamber. However, three unknown component peaks that were present in the high-boiling region of the chromatogram (max T = 180°C) increased in the presence of H_2S. The

fluctuation of these peaks was very large from run to run, and they varied in magnitude from <1 to ~9%, based on the peak height of benzene.

4. The response of H_2S only in the presence of each of the organic components individually and collectively was constant except in the presence of methylamine, where the magnitude of the H_2S response was reduced about 25%. No sulfur component peaks, except H_2S, were detected in the presence of the organic components either individually or collectively. The concentration of all components during these tests was intentionally at, or near, the minimum limit of detection. Therefore, if any sulfur components were formed by the reaction of H_2S with an organic component, they would be below the limit of detection. The tests must be repeated at higher concentrations of all components with an excess of H_2S to determine whether reaction products containing sulfur are present.

The next stages of development will include installation of a humidity control device and gas sampling under final operating conditions. Some varieties of legumes will be placed in the chamber for the first exposure tests. These will probably commence with only ambient air to determine background conditions, followed by introduction of one gas at a time. (*A. D. Horton*)

Analysis of organic compounds in fossil fuel by-product waters. An increasing concern with water quality and potentially hazardous contaminants has generated a serious need for analytical methods capable of determining organic compounds over wide ranges of concentration. Meeting this need becomes more urgent with the likelihood of widespread construction of fossil-fuel conversion facilities. Since all the existing conversion technologies plan to use water within the various processes, some additional contamination of present water resources will inevitably result. Protection of health and the environment will necessitate a strict, accurate, and rapid monitoring program to assure that unacceptable levels of contamination are avoided.

The identification and determination of organic pollutants in water have been approached in a variety of ways. The methods of choice are usually governed by the concentrations and properties of the compounds of interest. Since low concentrations pose the severest difficulties, a concentration step usually precedes the analysis. Frequently used concentration methods include solvent extraction, activated-carbon adsorption, headspace sampling, adsorption on macroreticular resin beads, and lyophilization. We have performed a series of studies to determine the utility of a variety of these methods when applied to real samples from oil-shale retorting and coal conversion processes.

Activated carbon adsorption was looked at as a possible removal method that could be applied to the broadest range of compounds. These studies were not encouraging, however, because low-molecular-weight polar compounds were poorly adsorbed, especially when the aqueous samples contained high concentrations of salts (up to 5% by weight in shale retort water). Also, activated carbon gives incomplete recoveries of many important compounds when back-extracted in a Soxhlet apparatus.

It appears that a method for removal of most compounds in a single step is not available. One must resort to applying a method which gives good removal of a particular class of compounds of interest. Relatively high concentrations of organic compounds (several ppm or more) are amenable to direct analysis with a packed Tenax-GC column. Since a preconcentration step is not required, samples can be analyzed rapidly and very reproducibly. This method would be well suited to any sort of monitoring program to provide rapid screening for major contaminants in effluent streams.

In this method of direct analysis, a Perkin-Elmer model 3920 gas chromatograph equipped with a flame ionization detector (FID) was used with a 15-ft × ⅛-in.-OD glass column fabricated and packed with 60/80 mesh Tenax-GC. Instrument parameters were set as follows: column temperature programmed from 100°C (3 min hold) to 320°C at a linear rate of increase of 2°/min, inlet temperature at 350°C, detector temperature at 350°C, helium carrier gas inlet pressure set at 60 psig. The column was baked out overnight at 320°C and gave a constant low-level baseline at the most sensitive settings. All sample volumes were 8 μl. Tentative identifications were made from retention time data and cochromatographic comparisons with reagent-grade compounds. Some chemical identifications were confirmed from gas chromatographic mass spectrometric (GC/MS) data. Quantitative measurements were made from the integration of peak areas; working curves were obtained from injections of standard solutions.

Chromatograms obtained from the direct injection of some aqueous samples onto Tenax-GC are shown in Fig. 4.2. The most prominent feature of these data is the similarity of the two coal liquid chromatograms and the difference between the shale and coal liquids. A homologous series of carboxylic acids constitutes the major organic compound class in the shale water (peaks 1, 2, 3, 4, 7, 10, 13, 19, 21), whereas phenol (9),

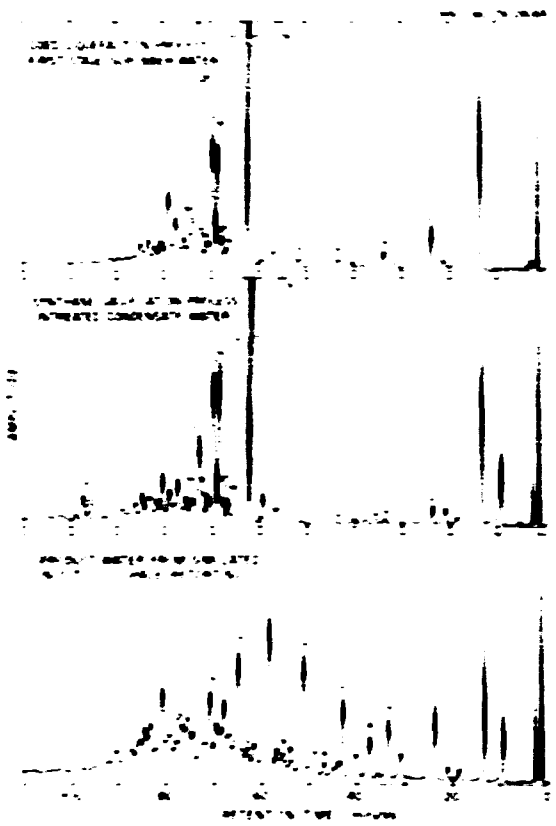

Fig. 4.2. Gas chromatograms of major organic components present in aqueous by-products from fossil-fuel conversion processes.

o-cresol (10), and *m*+*p*-cresols (12) are major components in the coal waters. Other significant compounds in the coal waters are dimethyl- and ethyl-substituted phenols. One coal water contains measurable amounts of α- and β-naphthols (22 and 23 respectively).

The remaining peaks in the chromatograms have not yet been identified. Since the major portion of dissolved organic material is polar, this technique using direct analysis is not expected to reveal the relatively small amounts of nonpolar components. Low-molecular-weight nonpolar compounds, for example, benzene, are obscured in the background; higher-molecular-weight compounds, for example, polycyclic hydrocarbons of three or more rings, are retained by the column and would be undetectable in any event at the low levels governed by their slight solubilities. Nonpolar compounds require some preconcentration before analyses.

Tenax-GC appears to be the most suitable column packing if aqueous samples are to be injected directly. Other packing materials retain water and give poor results. In addition to its low affinity for water, Tenax-GC has the advantage of a high operating temperature. The data reported here demonstrate the utility of Tenax-GC for the direct analysis of aqueous samples from fossil-fuel sources. (*P. R. Clark, C.-k. Ho*)

INHALATION EXPOSURE CHEMISTRY AND INSTRUMENTATION

Monitoring the NCI inhalation bioassay exposures. The Smoking and Health Program of the National Cancer Institute is developing and using inhalation bioassays to determine the relative biological effects of tobacco smoke from experimental cigarettes. The complexity and developmental nature of the tobacco smoke inhalation bioassay require sophisticated chemical and instrumental methods to adequately define exposures. It has been our responsibility to provide this support and to monitor the bioassay studies. NCI is sponsoring four inhalation bioassay studies: the rat inhalation model is being tested in studies at two laboratories, ORNL and Battelle Northwest Laboratory, Richland, Washington; beagle dogs are being exposed at two other laboratories, Hazleton Laboratories, Reston, Virginia, and the Veteran's Administration Hospital (VAH), East Orange, New Jersey. The three primary objectives of our work are:

1. to define and document exposure conditions to permit confident interlaboratory comparison of bioassay results,
2. to identify and/or resolve problems as they occur during the bioassay experiments, and
3. to develop methodologies required by the SHP to extend inhalation bioassay capabilities.

Each laboratory is visited periodically by at least two ORNL staff members. Hazleton Laboratories has been visited twice since March 1976; VAH has been visited four times since November 1975. One visit to discuss inhalation bioassay protocols was made to Battelle Northwest. During these visits, inhalation exposures are observed, measurements are made on the smoke generation devices, 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 later returned to ORNL for analysis. Results of the site visits are reported to both bioassay laboratory personnel and NCI management through informal topical reports. Routine monitoring is performed on a monthly basis for the ORNL exposure study.

One of our interests is to estimate the average dose of tobacco smoke offered to the experimental animal. 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 during each site visit to evaluate these factors. Measurements related to puffing characteristics (duration, frequency, and volume) are made on selected exposure devices to determine if the machines are performing according to specifications. Smokes generated by the exposure devices are collected on standard Cambridge filter pads, weighed to determine TPM, extracted with ethanol, and returned to ORNL for nicotine determinations and or multicomponent chromatographic profiling. Samples taken at the inlet of the machines permit comparison of the exposure devices on the basis of their ability to generate a consistent smoke aerosol. Samples taken at the point at which the smoke is delivered to the animal allow estimation of the quantity of smoke offered the animal and the efficiency of the machine to deliver the smoke which it generates. Measurements of temperature, relative humidity, and air flow in the exposure area aid in estimating the importance of environmental effects on variation of smoke dose.

Data gathered on the site visits serve not only to document tobacco-smoke dose levels but also to support on-site observations by staff members concerning potential problems in the exposure studies. For example:

1. Measurements of cigarette static burn rate verified that an excessive ventilation air flow rate in an exposure ward was responsible for reduced particulate deliveries of the cigarettes smoked.
2. An inadequate smoking machine air supply at one laboratory caused substantial variation in machine puffing characteristics and was corrected.
3. Large batch-to-batch variations in cigarettes used in one of the rat inhalation studies was discovered.
4. Enrichment of gas-phase smoke components occurred as a result of internal particulate deposition in one group of the exposure devices used.

Careful documentation of these kinds of difficulties permits more valid interlaboratory comparisons of inhalation bioassay results. It also demonstrates the need for monitoring on a more frequent basis, perhaps with the aid of continuous-monitoring instrumentation.

We are investigating the possibility of changes in the chemical composition of smokes produced by two exposure devices, since such changes could have a deleterious effect on the relevance of the bioassays. Studies are made on gas- and particulate-phase components, using both conventional and cryothermal gas chromatography. Preliminary findings suggest that there are no gross compositional differences between the smokes generated by the exposure devices and those generated under analytical conditions. However, the nicotine content of the smoke generated by one of the exposure devices is slightly higher (13%) than that of analytically generated smoke, which may be significant.

With current sampling methodologies, it is not possible to sample smoking-machine outputs while the animals are being exposed. It is necessary to substitute an artificial respirator for the animal in order to sample at the cannula exit of the machines. We are investigating the effects of simulated breathing patterns on the amount of smoke reaching the cannula exit. Again, the results are preliminary, but they seem to suggest that short, shallow breaths may not remove from the exposure system all of the smoke particulates available for inhalation.

Ideally, routine monitoring operations would be performed by the bioassay laboratory at a much greater frequency than is possible with periodic site visits. Because of the inefficiency and time requirements of the present sampling procedures, however, this is not practical. During the report period, we have had a modest effort under way to improve the routine monitoring operations of the dog-inhalation exposure machines. Our initial objective is to automate the procedure for measuring total smoke that the exposure device generates. A second, and more difficult, objective would be the automated determination of the amount of smoke that the animal inhales. Related studies in this group have shown that an optical light sensor can be used to detect and quantitate tobacco smoke in intermittent and continuous inhalation exposure devices. The sensor is described in detail later in this report; the device appears promising for routine dog-inhalation exposure systems. We are constructing a portable model, which we expect to field test on a site visit in the near future. (*R. A. Jenkins, R. B. Quincy, J. R. Stokely*)

Addition of microquantities of chemical carcinogens to cigarettes for inhalation cofactor studies. We have initiated a study to determine whether large quantities of chemical carcinogens can be added to cigarettes for transfer to the smoke without appreciable decomposition. Animals would be exposed to such cigarettes in an attempt to induce respiratory-

tract tumors in a short period of time (weeks). This would allow comparison of this dosing method with other supposedly less relevant techniques (intratracheal installation, pellet implantation).

Our initial work was concerned with loading BaP in Kentucky reference cigarettes. Previous biological studies indicate that intratracheal installation of approximately 10 mg of BaP administered over a 10-week period produced high percentages of tumors in mice at 30 to 40 weeks. With the Walton smoking machine we estimate that this same BaP dose can be attained by a 10-week exposure to 10 cigarettes day with 10 mg of BaP loaded in each cigarette. Attempts were made to load cigarettes with this level of BaP by injecting solutions of BaP along the tobacco rod with our tracer loading apparatus used previously for loading ^{14}C compounds in cigarettes for dosimetry studies. Some modifications were found necessary in the loading technique because larger volumes of solutions are required. It was necessary to use a lower injection rate and to blow air through the cigarette during the loading to rapidly evaporate the solvent. With these modifications, at least 10 mg of BaP could be added to cigarettes without difficulty. Cigarettes loaded in this manner were smoked to established the recovery of BaP in the smoke. The smoke particulates were collected, dissolved, and analyzed for BaP by both gas and liquid chromatography. Approximately 30% of the BaP loaded in the cigarettes was found in the particulate matter of the mainstream smoke. No other large peaks were found in the chromatograms, indicating that there is probably no major decomposition of the BaP during smoking and that the BaP is simply distilled out of the cigarette unchanged.

Similar studies with 3-methylcholanthrene (MCA), a potent tumor initiator, showed that MCA in milligram quantities is also effectively transferred from the tobacco rod to the mainstream smoke. Approximately 10% of the MCA added to the cigarette was transferred. With cigarettes loaded with 10 mg of MCA, it is estimated that tumors can be initiated in mice in approximately three to four weeks, using inhalation exposures to ten cigarettes per day on the Walton smoking machine.

Experiments have been started to determine whether 12-*O*-tetradecanoyl-phorbol-13-acetate (TPA), the most potent tumor promoter known, can be used in a manner similar to that used with BaP and MCA. Because of the high molecular weight and polar characteristics of TPA, there may be difficulty in transferring TPA from the cigarette to the smoke. Studies indicate there may be some transfer, but TPA is at least partially decomposed during the smoking process.

Results obtained have been sufficiently promising to encourage the funding agency to equip another laboratory for animal inhalation exposure experiments using modified cigarettes. If these inhalation experiments show that respiratory-tract tumors can be induced in a short time, this new technique could be used to study the effects of chemical cofactors on the biological effects of smoking. Detailed organic analytical studies would be required to unequivocally determine the fate of added constituents in both mainstream and sidestream smoke. This would constitute a new research effort for the section. (*J. H. Weisburger, J. R. Sanders*)

SEM II tobacco smoke inhalation system. The SEM II (smoke exposure machine, model II) is a new tobacco smoke inhalation exposure system designed by Process and Instruments Corporation for the Council for Tobacco Research USA, Inc. The machine is designed to produce a continuous stream of fresh tobacco smoke for large-scale inhalation exposure studies to be conducted at Microbiological Associates in Bethesda, Maryland. Many features of the SEM II resulted from our evaluation of the prototype, SEM I. We are engaged in an exhaustive evaluation of the system. Figure 4.3 illustrates the

Fig. 4.3. Photograph of the SEM II tobacco smoke inhalation system.

SEM II and a prototype monitoring unit (described elsewhere in this report) developed here to document smoke generation.

The SEM II is a positive-puff, constant-pressure smoking device. Thirty cigarettes are loaded automatically into a drum under a sealed dome. The drum rotates and positions the cigarettes consecutively at a slider block that opens to the smoke delivery tube. Positive pressure in the dome forces air through the cigarette, generating the puff; puff volumes are regulated by the dome pressure. Each puff is of 2 sec duration with a 1-min cycle for the drum. Smoke generated by the system may be diluted to the desired concentration and directed either continuously to one animal exposure unit or alternately to as many as four exposure units within a 1-min cycle.

Due to the constant-pressure puffing mode of the SEM II, it was found that puff volumes vary inversely with the resistance-to-draw of the individual cigarettes. Other smoking devices are essentially constant-volume puffing systems and do not have this limitation. A flow measuring device incorporating a sensitive pressure transducer was fabricated to define puff characteristics. The response of the measuring device is such that we were able to profile individual puffs and measure their volumes. It was shown that the cigarettes were not sealing in the diaphragm holders, which permitted air to leak around the cigarettes and generate low smoke concentration. Corrective measures were provided by the designer. Puff volume variations, caused by resistance to draw differences, were found to lie within ± 5 cc of the average puff in over 90% of the tested cigarettes.

Puff volumes are calibrated using a bellows system. The bellows is attached to the smoke delivery tube of the SEM II and draws air through the cigarettes at a nearly constant volume. The pressure differential across the cigarettes generated by the bellows is monitored, and an average differential is determined. The average produced by the bellows system is then established in the positive puffing mode of the SEM II. The previously mentioned flow measuring device was used to establish that the bellows system is acceptable for calibration.

Design of the animal restraint and exposure units for the SEM II is new. The animals are mounted in groups of five in holders with neck slots and spring neck restraints. Racks are positioned in the exposure system so that the nose of each mouse enters the smoke stream through a rubber diaphragm; several such racks are mounted linearly along a central smoke delivery tube. The design of the restraint system evolved from interaction of our personnel, the designer, and users of the system. A head-restraint spring was added to prevent loss of animals through improper positioning at the diaphragms. Leakage of smoke at the diaphragms has been lowered by providing tray adjustments to accommodate animals of varying sizes. Spread of animal wastes is controlled by using an open-lattice support tray; body wastes fall through the lattice and are caught in a support pan.

To ensure that all the mice receive unaltered smoke, a study was performed to determine the maximum number of animals that could be effectively exposed in one smoke stream of the containment system without affecting smoke composition. Using carbon monoxide as a smoke component indicator, we determined that if all the smoke from the SEM II is directed to one smoke outlet, up to 100 mice could be exposed simultaneously without significant animal effect on the carbon monoxide level; with this number of animals, smoke entering the exposure tube would be depleted by the mice by less than 10%. By alternately directing the smoke stream in 30-sec exposure periods to two confinement systems, 200 mice could be exposed during one exposure cycle of the SEM II.

To prevent dehydration of the animal's respiratory system during an exposure and to maintain constant relative humidity in the smoking chamber, all air supply to the SEM II passes through a humidification system. Temperature changes under the dome of the SEM II cause a sharp drop in absolute humidity in the dome; this change could affect the smoking characteristics of the cigarettes. A separate study has shown that the moisture content of cigarettes drops rapidly at elevated temperatures even though relative humidity is held constant. Cigarettes held in the loading hopper during continuous operation could lose 2 to 3% by weight due to loss of moisture in 1 hr. A more detailed study of the effect of humidity upon the delivery of smoke is being performed to be certain that chemical changes in the smoke do not result from moisture changes in the tobacco. (*J. H. Moneyhun, J. R. Stokely*)

Design and testing of smoke monitoring unit for the SEM II exposure system. A monitoring unit for use with the SEM II has been designed, built, and extensively tested. A second unit, specifically tailored to actual field testing and based on experience gained with the prototype unit, has been designed and is being fabricated for use in large-scale inhalation studies at Microbiological Associates, Bethesda, Maryland. A concern in the use of the SEM II for large-scale inhalation experiments is the possible

effect of either machine malfunction or operator error. It is likely that occasional malfunctions or errors will occur that may cause high levels of smoke to be presented to valuable test animals. In such cases, death of animals could result from nicotine and or carbon monoxide poisoning. The monitoring units for the SEM II incorporate alarms and automatically actuate safety systems to prevent accidental overexposure. The sensor instrumentation is interfaced with integrating and recording systems to provide data documenting exposure conditions.

The three detectors used in the monitor are: (1) a light-scattering device for particulates, (2) an infrared carbon monoxide analyzer, and (3) a thermal conductivity sensor for gas-phase hydrogen. The optical sensor, developed especially for tobacco-smoke particulate measurements, consists of a light-emitting diode and a high-gain phototransistor that measures backscatter from the smoke particulates. The sensor is housed in a short section of 12-mm-diam tubing, and the total smoke flow for one bank of animals passes through the unit. The sensor provides the basic rapid signal for animal safety, and its continuously recorded output gives the operator a measure of machine performance. Basic studies of the sensor showed that its response is directly proportional to the concentration of particulates in the immediate vicinity (within 1 cm) and that it is easily calibrated. While the unit is subject to minor drift with time as a result of the buildup of tar coatings on its sensitive optical surfaces, this has not been an impediment to its practical application.

Gas-phase measurements are made by drawing a sample from the smoke stream through a standard Cambridge filter and through a scrubber to remove carbon dioxide and water. The scrubber is necessary only for a valid hydrogen measurement; the carbon monoxide analyzer is immune to these components. The hydrogen measurements are made using a diffusion-type filament cell with tungsten-rhenium elements, while a nondispersive (4.7-μ) dual-beam infrared analyzer is used for carbon monoxide analysis. A small vacuum pump with an external flow-control system is used to pull the sample through the filter, scrubber, and detectors.

For purposes of recording and display, each of the three detector outputs is electronically amplified to a signal level of 0 to 100 mV. In addition, each channel is provided with continuous signal integration; panel meters continuously indicate each signal level as well as the integrated totals. A patch-panel network allows any signal or integrated total to be displayed digitally and or recorded on a two-pen strip-chart recorder.

A normal run of the SEM II covers a period of about 10 min, usually consisting of 10 puffs from each of 30 cigarettes. The prototype evaluation has involved more than 200 such runs. It was demonstrated that the unit can rapidly detect machine malfunction or operator error that might endanger animal safety. All three measurements showed a high degree of reproducibility as well as proportionality to smoke concentration.

The basic design of the prototype monitor is acceptable, and a field test model of the monitor is being fabricated for testing in inhalation studies at Microbiological Associates. The field-tested model has been simplified by eliminating the hydrogen concentration measurement made with the prototype device. It was felt that the carbon monoxide measurement was adequate as a backup for the optical detector, both for safety and exposure documentation. The safety circuit and interlocks for the field test unit must incorporate features not provided in the prototype. In actual field practice, exposures to particular banks of animals alternate in regular short cycles. The monitor must not only detect abnormally high levels of particulates and carbon monoxide, but must also monitor the exposure time to make certain that both instantaneous and integrated exposures remain below the danger thresholds for the particular animals being exposed. While this complicates the design of the field test monitor, its routine operation has necessarily been kept simple in order to make it suitable for use by operating personnel. (*T. M. Gayle, C. E. Higgins, J. R. Stokely*)

Application of a light-scattering device for detection of smoke particulates in the Walton smoke exposure system. One of the critical requirements in the operation of any exposure system is that a homogeneous aerosol be presented to the test animals. Chemical determination of smoke concentration at any given exposure site in an exposure chamber is time consuming. The need for an analytical method for rapid and continuous measurement of smoke concentration led us to investigate the application of a light-scattering device. Operational results from use of the Walton inhalation exposure system have shown the device to be especially suited to rapid smoke concentration determinations. The sensor was used to prove the uniformity of smoke concentration in the Walton chamber, to investigate the effect of changing puff parameters on production

of particulate matter, and to establish the effect of stirring on aerosol concentration and settling in the exposure chamber.

The light-scattering sensor consists of a commercially available combination light-emitting diode (LED) phototransistor device mounted in one of the mouse exposure positions in the Walton chamber. Infrared light (900 nm) emitted by the LED element is scattered by the smoke aerosol, and the reflected light is detected by the phototransistor element. The phototransistor output is recorded to display the concentration of the aerosol in the immediate vicinity of the sensor. Typical readouts of the sensor for smoke in the Walton system are shown in Fig. 4.4. The response, which increases only slightly as the smoke ages and agglomerates, is directly proportional to the aerosol concentration. The specific response was found to be independent of cigarette type, with the exception of synthetic cigarettes.

Monitoring individual compounds in a given smoke is also feasible. We have found, for example, that sensor response and nicotine concentration in IRI smoke in the chamber are directly related and are independent of the puff being monitored. It appears, therefore, that monitoring smoke concentration could give a good indication of the amounts of particulate components to which animals have been exposed. An independent measurement establishing the ratio of each component to the total particulate matter from that cigarette is all that is required.

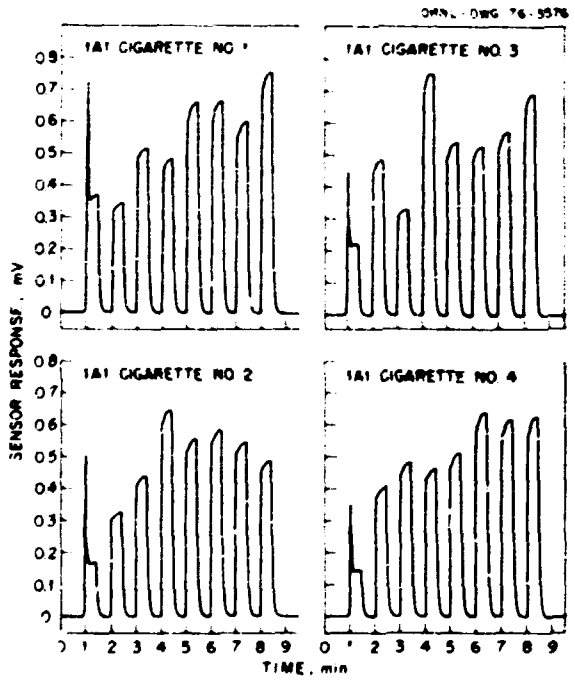

Fig. 4.4. Optical sensor response curves obtained on smoke in the Walton horizontal exposure system.

The light sensor has also been applied in studying the effects of changing puff parameters on particulate matter production. Three types of Walton puffs were tested: (1) constant duration, varying volume, (2) constant volume, varying puff time, and (3) varying puff time and volume. When 2-sec puff volumes were increased from 15 ml to 51 ml, the average sensor response per puff increased linearly more than threefold, while the total response increased from 1.9 mV to 4.4 mV. The total response represents particulate matter delivery for the entire cigarette. Putting the same volume (35 ml) of air through the cigarette over time intervals of 1 to 4 sec showed progressive, though not proportional, increases in particulate delivery with increasing length of puff. When the air flow necessary to produce a 35-ml puff in 2 sec was maintained for 1-, 2-, and 3-sec puffs, the average response per puff increased linearly from ~0.2 to 0.6 mV. The total response doubled only, since fewer puffs per cigarette resulted at the longer puff times. (*C. E. Higgins, J. R. Stokely*)

Particle size characteristics of tobacco smoke. Particle size distributions of tobacco smoke aerosols are being investigated using the methylcyanoacrylate (MCA) fixation technique.[23] Three aspects of this work will be discussed: (1) the methodology, including investigations into the validity of the results, (2) some general characteristics of tobacco smoke aerosols as determined by this technique, and (3) its application to the size distribution in specific smoking machines, particularly the Walton.

A simple syringe sampling technique is used to collect and fix smoke particles for microscopic observation. A syringe heated in an oven (60°C) is partially filled with air containing MCA vapor. The syringe is removed from the oven, and a smoke sample is injected into the warm MCA vapors. After a short reaction period the fixed particles are expelled onto a nucleopore filter, which is then processed for scanning-electron microscopic examination. There are losses of particles in the transfer of smoke aerosol to the filter, which can be severe under some circumstances. Agitation of the contents of the syringe to mix smoke and MCA promotes these losses. Plastic syringes have proved to be particularly

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

unreliable: as much as 80 to 90% of the smoke may be lost. These losses are size dependent, invalidating the sized distribution results.

Acceptably quantitative results are obtained, using glass syringes (with only turbulent mixing of smoke and MCA) and keeping the ratio of smoke to MCA vapor volume small; 80% or more of the gas-phase smoke particles are collected on the filter. When smoke is sampled in this way, particle size distributions show excellent reproducibility. One experiment, repeated seven times, gave a geometric mean diameter, d_r, of 0.404 ± 0.025 μm (standard deviation) and a geometric standard deviation, σ_r, of 1.396 ± 0.029. A quantitative sampling procedure has also allowed us to estimate the diameter bias introduced by the addition of MCA in the fixation of gas-phase particles. The data presented above were from the mid puffs of seven 2A1 cigarettes. From the measured diameters we calculated the average particle volume ($\propto d^3$), and from the particle density on the filters we calculated the number concentration of particles in the chamber at the time of sampling. From these we estimate the total particulate mass per puff to be 4.6 ± 0.9 mg. This is in reasonably close agreement with the value of 4.0 mg from conventional gravimetric (TPM) analyses. The indicated difference translated to a diameter basis is about 4%.

A large number of determinations of smoke particle size distributions were made in the past year. Quite generally we found that the distribution of sizes is adequately approximated by a logarithmic-normal distribution function. A typical distribution is shown in Fig. 4.5. The lower section of this figure shows a histogram of the fraction of particles in various size intervals and the fitted log-normal curve (the two parameters d_r and σ_r define this curve). The upper section is a cumulative percentage plot on logarithmic probability coordinates; the linearity of such a plot is often taken as evidence of log-normality. Statistical tests for log-normality are routinely made; reasonably often the measured distribution does not conform in a strict statistical sense. Nevertheless, the deviations (usually a slight negative skewness) are seldom large enough to invalidate the use of this distribution function for practical purposes.

Rather unexpectedly, we found an almost constant value of σ_g (1.4 ± 0.1) from experiment to experiment. For example, a sample of fresh 10% cigarette smoke may contain about 3×10^8 particles per ml with d_g = 0.30 μm and σ_g = 1.37. After aging for 60 sec, normal coagulation processes reduced the number tenfold and increased d_g to 0.70 μm, but σ_g = 1.40 changed insignificantly. We found the kinetics of coagulation

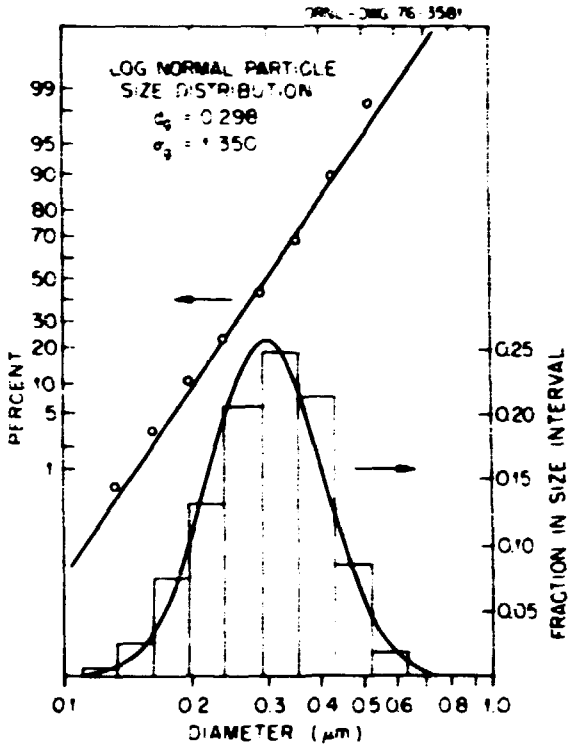

Fig. 4.5. Particle size distribution of unaged 1R1 cigarette tobacco smoke.

of an unstirred smoke aerosol to be second order with a rate constant of approximately 0.7×10^{-9} ml sec. This value is quite typical of aerosols in general.[24]

The particle size characteristics of tobacco smoke were studied by a variety of methods with a variety of results. Very often the work was directed to the question: What is the average particle size of tobacco smoke? As it leaves the butt of a cigarette, tobacco smoke is an extremely concentrated aerosol containing as many as 10^{10} particles per ml. The average size may double in the first second of existence. To measure the "initial" size, the smoke leaving the butt of the cigarette must be rapidly diluted to arrest the coagulation kinetics. We measured the size distributions of a number of cigarettes under conditions that approximate this rapid dilution requirement. A variety of initial sizes was found; the smallest, from a code 46 synthetic, was: d_g = 0.16 μm, σ_g = 1.41. Conventional cigarettes yielded diameters considerably larger: Kentucky 1R1, 0.26 μm; NCI code 15, 4th

24 H. L. Green and W. R. Lane, *Particulate Clouds*, Van Nostrand, Princeton, N.J., 1964, p. 140

series, 0.21 μm; Kentucky 2A1, 0.32 μm. No appreciable change in size with puff number was seen, but we have preliminary evidence that these initial sizes may depend on the manner in which the puff is taken.

Of practical interest are particle size characteristics of the tobacco smoke aerosol in existing smoke delivery systems, particularly with animals present in the system. The Walton horizontal exposure system was investigated, both with and without the presence of mice (12 acclimated black C-47 mice were used). Normally, animals are exposed to smoke for 30-sec periods. We extended this period to 60 sec in these experiments to accentuate particle size growth and possible changes from prolonged animal inhalation. The results, however, indicate no significant changes in size or size growth due to the presence of these animals. We found, on the basis of CO_2 analyses in the exposure chamber, that the respiration rates of the mice are severely curtailed on exposure to smoke. Based on Guyton's rule,[25] estimates are that 12 free-breathing mice should turn over about 70% of the contents in the exposure chamber in a 60-sec exposure. Measurements of comparative CO_2 gains indicate that they turn over only about 20% in the presence of smoke, an amount insufficient to appreciably perturb the particle size growth in the chamber. This result is supported by the measurements of number concentration of smoke particles in the chamber. Additionally, we note an insignificant increase in particle size from 30 to 60 sec. Presumably the Walton system with its high-velocity stirrer and its high surface-to-volume ratio perturbs the particulate cloud sufficiently to mask size growth by normal coagulation kinetics. (*R. W. Holmberg, L. B. Yeatts*)

BIOANALYTICAL METHODS AND PROJECTS

Separation and identification of rat urinary constituents. A general analytical procedure was developed for gas chromatographic profiling of biochemically significant compounds occurring in rat urine. Such "metabolic profiles" may aid in elucidating smoke-related pathology in rats chronically exposed to cigarette smoke. The rat urine specimens used in this work were obtained as part of the serial sacrifice portion of the chronic rat exposure study being conducted in the Biology Division. These specimens can be divided into four sets: (1) urine from aged nonsmoked rats (age controls), (2) urine from aged rats placed on smoking machines without smoking (stress or container controls), (3) urine from aged-smoked rats, and (4) urine from young nonsmoked rats.

The first step in the analysis of these samples is to fractionate the urine by gel chromatography, using Sephadex[26] G-25 as a stationary phase and eluting with 0.2 *M* ammonium acetate buffered at pH 5. This crude fractionation yields a three-peak chromatogram with the order of elution inversely related to molecular size. The eluted products were collected in two parts: (1) the fraction eluted in the void volume (macromolecules) and (2) the fraction that was retained by the stationary phase (peaks 2 and 3). Both fractions were concentrated to dryness by lyophilization. The macromolecular fraction was stored at 18°C for subsequent electrophoretic analyses. The second lyophilized fraction was dissolved in pyridine, derivatized with bis(trimethylsilyl)trifluoracetamine and separated by gas chromatography, employing 3% OV-17 on the stationary phase. Such gas chromatographic profiles obtained for the urine from young rats showed 32 distinct peaks. Profiles for different young rats were essentially the same, showing differences only in absolute peak heights. Most of these differences in absolute amounts can be attributed to the variation in the daily total urine volume excreted by individual animals.

Urinary constituents should vary with age. Accordingly, the profiles of seven urine samples from age-control rats exhibited 57 distinct peaks for each of the seven samples. Samples from the smoking rats and stressed rats (container controls) of the same age were separated by gel chromatography, lyophilized, and stored at 18°C. These samples will be derivatized and profiled in the near future.

Twenty-eight peaks in the profiles have been tentatively identified by use of retention indices or cochromatography with reference compounds. However, any distinct profile differences between smoking, stress, and age will be more carefully studied by preparing identical samples for GCMS examination. (*L. G. Farrar, J. E. Caton*)

Determination of nicotine and its metabolites. The analysis of nicotine and one or more of its metabolites in physiological fluids is of increasing interest to many "smoking and health" studies. Because of rapid

25. A. C. Guyton "Measurement of the Respiratory Volumes of Laboratory Animals," *Am. J. Physiol.* 150, 70 (1947).

26. Registered trademark, Pharmacia Fine Chemicals, Uppsala, Sweden.

pharmacokinetics, nicotine or cotinine (its principal metabolite in many species) levels in serum or urine are probably not good measures of smoke dose. However, periodic measurements of a parameter such as the chronic urinary level of cotinine in an experimental animal subjected to chronic smoke exposure may give an indication of continuing smoke insult. Any changes in urinary cotinine levels might indicate either a change in nicotine uptake or a change in the ability or mechanism of metabolizing nicotine. Thus, functional methods for the analysis of nicotine, cotinine, and other metabolites of nicotine would be useful tools to our support of chronic smoke exposure studies.

Analytical procedures for nicotine and its metabolites in physiological fluids are generally considered questionable because such compounds are difficult to handle analytically at the low levels present in physiological situations. In addition, nicotine is an almost ubiquitous compound under most conditions where a measurement is of interest. Thus, there are two requirements for the validation of analytical procedures: (1) some internal standard must be carried through the procedure in order to provide a reliable estimate of sample recovery, and (2) a blank is necessary to determine how much, if any, nicotine has been recovered from sources other than the sample.

Our general approach to this problem has been to use tracer quantities of ^{14}C-nicotine as an internal standard to estimate recoveries from both blanks and samples. After adding the tracer, samples of either serum or urine are extracted three times with volumes of benzene equal to twice the sample volume. The benzene extracts are pooled and concentrated to near dryness on a rotary evaporator. After evaporation, the samples are dissolved in a volume of ethanol equal to the original sample volume. Analysis of the recovered sample for ^{14}C activity indicates the amount of sample recovered; analysis by gas chromatography, using specific nitrogen detection, indicates the total amount present in the sample. This procedure has been shown to be effective for nicotine added to serum at the levels of interest (ng ml). However, there has been no validation of the procedure for metabolites because the metabolites of interest are not readily available.

Two of the principal metabolites of nicotine (cotinine and nicotine-1'-oxide) were synthesized according to published methods.[27,28] In each case the starting material for the preparation was nicotine, and gas chromatographic analysis of each product showed it to contain a small amount of nicotine and one major peak. Future efforts must be directed toward the synthesis of ^{14}C metabolites. Upon completion of such synthesis, the recovery after extraction and concentration must be established, followed by the characterization of the response of the specific nitrogen detector to each of these metabolites. *(J. E. Caton, B. F. Hirsch)*

Dosimetry in rats. A study is under way in the Biology Division that involves the chronic exposure of rats to inhalation of cigarette smoke. Two aspects of this study are: a serial sacrifice experiment in which rats were exposed for predetermined periods (12, 18, and 24 months) before sacrifice; and a lifetime study in which the rats will be exposed for the longest time interval consistent with viability and survival rate. Only a small amount of data was available for estimating dose in rats exposed on the system employed in this study. Thus the tracer dosimetry technique,[29] using cigarettes labeled with ^{14}C-dotriacontane (DTC), was applied to 40 rats exposed to two different smoke concentrations at two different times. Another dosimetry experiment was designed to ascertain the effect of containment on dose.

The results of a set of four rat dosimetry experiments with the Maddox-ORNL exposure system, smoking both one and two cigarettes at 30- and 40-sec puff exposure times, are summarized in Table 4.3. In this table the total exposure time is combined with smoke concentration as indicated to give a value called smoke exposure. Both the carboxyhemoglobin concentration in the blood and the amount of TPM deposited in the lung vary linearly with smoke exposure. The distribution of activity and, therefore, TPM within the rat was essentially the same for all exposures. The respiratory tract (exclusive of the upper airways) contained 65% of the total internal activity. The upper airways contained 10% of the internal activity; and the larynx, stomach, and remainder of the animal contained 8, 11, and 5%, respectively, of the total internal activity. The distribution of activity within the respiratory tract (excluding the upper airways) of the rat was also determined. Typical data for this distribution are

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27. F. C. Taylor and N. E. Boxer, "Pyridine-1-oxides. IV. Nicotine-1-oxide, Nicotine-1'-oxide, and Nicotine-1,1'-dioxide," *J. Org. Chem.* 24, 275 (1959).

28. F. R. Bowman and H. McKennis, "(−)-Cotinine," *Biochem. Prep.* 10, 36 (1959).

29. 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).

shown in Table 4.3. The various lobes of the lung are not the same size; thus the left lung (largest lobe) always had the greatest activity. However, when the deposition is normalized on the basis of lobe weight (Table 4.4), there appear to be sites of preferential deposition. Careful analysis of lung distribution data from 40 rats indicates that there is better than a 99% probability that the weight-normalized deposition in the right superior lobe is higher than that in any other lobe. The weight-normalized deposition in the right inferior lobe has a 98% probability of being lowest of any lung lobe. Values determined for the right media lobe, post-caval lobe, and left lung are probably the same.

Another set of experiments involving rats showed that the manner of animal restraint has a definite effect on the dose retained by the animal. The experiments involved 30 rats restrained by one of three different methods during exposure. The restraint methods were: (1) the regular containment method used in the chronic exposure studies in which the rat is held in place in the containment tube by a sponge (movement is almost completely restricted), (2) the rat is held in place in the containment tube by a slant-faced collar (within the containment tube, movement is relatively unrestricted), and (3) the rat is restrained in the containment tube simply by holding his nose in the chamber by means of a "tooth hook" with no other restrictions in the tube.

Two types of restraint were used in each of three different exposures of ten rats to % smoke from a code 16 cigarette generated by the Maddox-ORNL exposure device. Deposition in the lung was increased by 18% for the "tooth restraint" and by 10% for the slant-faced collar, relative to the regular containment. However, these differences may not be significant. Of more significance is the reduction (53% reduction for the slant face and 70% for the "tooth restraint," compared with the deposition for the regular containment) of deposition in the larynx for the restraint methods that are less restrictive of movement. Thus, some consideration of containment

Table 4.3. Smoke constituent uptake for various inhalation exposure conditions

Exposure time per puff[a] (sec)	Total exposure time (sec)	Smoke concentration (%)	Smoke exposure[b]	TPM deposited in lungs (μg)	Carboxyhemoglobin (%)
30	210	6.4	13.4	210	18.4 ± 2.5
40	320	5.8	18.6	340	20.4 ± 2.2
30	210	14.8	31.1	590	26.1 ± 2.2
40	320	13.5	43.2	980	28.9 ± 6.8

[a]Rats exposed to smoke from one code 16 cigarette on Maddox-ORNL exposure device.
[b]Smoke exposure = total exposure time × smoke concentration/100.

Table 4.4. Distribution of activity within the respiratory tract of rats[a]

Area	TPM (μg)	TPM/organ weight (μg/g)	Total activity in respiratory tract (%)
Trachea	27		4
Bifurcation	40		6
Left lobe	204	2.61	31
Post-caval lobe	66	2.94	10
Right inferior lobe	135	2.15	21
Right superior lobe	109	4.30	17
Right media lobe	73	2.49	11
Total	654		100

[a]Exposed for 30 sec/puff on Maddox-ORNL exposure device smoking code 16 cigarettes; smoke concentration was 14.8%.

method may be important in evaluating larynx pathology. (*J. E. Caton*)

Comparative dosimetry in hamsters and rats. Like rats, hamsters have been the subject of studies concerned with cigarette smoke aerosols generated by the Maddox-ORNL exposure device. Therefore, with adequate data available for both species, some comparison seems appropriate. The internal distribution of DTC activity is the same for both hamsters and rats. However, the total internal deposition per gram of body weight is significantly higher for hamsters in comparison with rats. This difference may be somewhat related to the method of restraint.

The standard restraint system for hamsters on the Maddox-ORNL device employs a collar and allows significant body movement within the containment tube. The standard restraint system for rats, however, limits movement severely and may possibly limit the depth of respiration by slightly restricting expansion of the chest cavity. In any case, the increased body movement of the hamster should stimulate respiration and thereby contribute to increased internal deposition of the exposure aerosol. In addition to greater deposition per unit body weight, the rate of increase in lung deposition with increasing smoke exposure is more than twice as great for hamsters as for rats. Another difference is the relative effect of exposure time and smoke concentration. In evaluating smoke exposure for rats, exposure time and smoke concentration can be weighted equally. For hamsters, lung deposition appears to be slightly more dependent on smoke concentration. Log-log plots of lung deposition in hamsters vs exposure time indicate that the time contribution to smoke exposure values must be weighted by some fractional exponential. Such variations can probably be attributed to breathing patterns, but other differences such as method of restraint, greater vigor of the hamster, and the hamster's greater tolerance of nicotine may play a role in this time dependence variation. The data conclusively demonstrate, however, that smoke doses to hamsters follow much different patterns than do smoke doses to rats exposed on the Maddox-ORNL exposure system. (*J. E. Caton*)

Dosimetry in mice. Studies of dosimetry using mice are carried out jointly with Microbiological Associates of Bethesda, Maryland, for the Council for Tobacco Research, USA. Our responsibilities in this effort include cigarette selection, cigarette labeling, tissue analysis, and data compilation. Animal conditioning and exposure are the responsibilities of Microbiological Associates. In contrast to our rat and hamster studies, these mouse exposures have been carried out on the Walton horizontal smoking machine, which has several basic differences from the Maddox-ORNL machine. The studies are quite comprehensive and involve large numbers of animals, which lends a high degree of statistical significance to the results. During the past year, experiments were completed to determine the effect on internal smoke particulate deposition of the following parameters: (1) exposure time, (2) smoke concentration, (3) sex of exposed mouse, (4) strain of exposed mouse, (5) type of animal containment, (6) retention period for three different tracer compounds (^{14}C-DTC, ^{14}C-nicotine, ^{14}C-BaP), and (7) comparative retention periods for two different mouse strains. In all, about 400 cigarettes were selected and labeled, and 6000 tissue samples were analyzed.

Internal deposition increased with per-puff exposure time as expected. However, analysis of the data indicated that increasing per-puff exposure time had an increasingly important effect on internal deposition for mice exposed on the Walton horizontal smoking machine. This was not true for rats and hamsters exposed on the Maddox-ORNL machine. The second experiment was designed to measure the variation in deposition of ^{14}C-DTC as a function of smoke concentration at a single per-puff exposure time (30 sec). Here the amount of internal tracer retention was a linear function of smoke concentration.

Comparative dose measurements were made on both sexes of five different strains (C3H Ant, DBA 2, C57BL 6, BC3F1, and B6C3F1) of mice. Some sex-dependent deposition was found for the C3H Ant and DBA 2 strains. This sex dependence, which is of doubtful significance, indicated an increased internal deposition in males compared with females. The effect of strain on deposition is significant, with the following order of decreasing deposition: C57BL 6 ≅ BC3F1 > DBA 2 > C3H Ant > B6C3F1. Mice were restrained by either a cone-shaped containment tube or a neck-restraining device in one experiment; the amount of internal deposition was the same for both methods of restraint.

The three experiments studying the retention period of tracer compounds showed some interesting results. In the case of DTC the body distribution changes very slowly over a 24-hr period. Even the total-body burden of DTC decreases by less than 20% over a 24-hr period. Thus, DTC appears to be an inert tracer capable of mapping the initial fate of deposited smoke particulate matter very well, especially when animals are sacrificed within 15 min after completion

of the exposure. The retention period experiments indicate that both ^{14}C-nicotine and ^{14}C-BaP are very poor tracers of the initial distribution of smoke particulates in the mouse. Immediately after smoke exposure, less than 25% of the total internal nicotine or BaP activity is located in the lung. Both compounds apparently have rapid pharmacokinetics in the lung after inhalation. In studies completed, less than half of the internal activity of either of these compounds can be assigned to specific areas. One can speculate that much of the nicotine may be in the circulatory system and other body fluids. However, a more careful mapping of the distribution of both compounds is needed. (*J. E. Caton*)

Evaluation of the use of an antibody to BaP to remove BaP from mainstream cigarette smoke. An antibody claimed to be specific for BaP was raised in goats by personnel at the University of Nebraska Medical Center at Omaha (UNMC). Subsequently, UNMC patented the idea of using the antiserum as a cigarette filter component that might remove BaP from the mainstream smoke. This laboratory, at the request of the NCI SHP, then assumed the role of assisting personnel from UNMC in evaluating the utility of this antiserum as a BaP scavenger in a cigarette filter.

The efficacy of the antiserum was tested by adding it to the cellulose filter of experimental filter cigarettes and by adding it to Aquafilters.[30] Subsequently, the relative amount of added ^{7,10}-^{14}C-BaP removed from the mainstream smoke was compared with the amount of BaP tracer removed by filters treated with normal saline solution. The goat-serum-treated cellulose filters were most efficient in removing the ^{14}C-BaP tracer from the smoke. It made little difference, however, whether or not the goat serum contained antibodies to BaP. Both serum-treated (with and without antibody) cellulose filters removed about 50% of the ^{14}C-BaP activity. The saline-treated cellulose filters removed about 30% of the activity. All Aquafilters removed about 30% of the ^{14}C-BaP; pretreatment with antibodies had no effect.

All studies indicate that the use of an antigen-antibody reaction to remove specific harmful components from mainstream cigarette smoke does not have great potential. However, serum proteins in general may add to the efficiency of a cellulose filter. (*J. E. Caton*)

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30. Trademark, Aquafilter Corporation, Southfield, Mich.

5. Quality Assurance, Safety, and Tabulation of Analyses

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

QUALITY ASSURANCE

The Quality Assurance (QA) program has been strengthened during this reporting period. Each section or group has developed a QA program appropriate to its work. These programs are described in the first division-wide report issued July 1, 1976. Future divisional QA reports will be issued semiannually to highlight changes in the QA program and to summarize what has been accomplished.

We have continued to maintain a quality control program within the Analytical Services Section. Customers have been supplied with control samples that can be bottled, labeled, and submitted for analysis along with real samples. We have also added a new control sample to the repertory: one that contains U, Mo, Cr, and Zr for use by the Transuranium Laboratory staff. We have also received the limits of error experienced in our quality control program over the past two years and have tightened a number of values, as indicated in Table 5.1.

For the National Uranium Resources Evaluation (NURE) Program, our calibration standard is 93% enriched ^{235}U from the National Bureau of Standards. For our internal quality control, NBS-1632 coal and NBS-1633 fly ash standard reference materials are used. Table 5.2 summarizes the quality control data.

Table 5.3 shows the quality level for each laboratory 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 5.4.

SAFETY

During the past year the Analytical Chemistry Division had eight first aid cases, most of which involved minor cuts or burns on fingers. The only case that could have been serious occurred when the bottom fell out of a gallon jug of chromic acid; fortunately, little acid struck the employee and the safety shower was used promptly. The Division had one medical treatment case when an employee was injured while removing the cap from a bottle. There were three unusual occurrences. Two involved radiation contamination, and both were cleaned up with no problems. The third unusual

Table 5.1. Revisions in limits of error for quality control program

Method	Limit of error (2σ)	
	Old	New
Carbon: Leco (high)	6	5
Chromium: colorimetric (low)	10	5
Fluoride: volumetric	4	2
Iron: colorimetric (low)	10	6
Sulfur: Leco	15	10
Thorium: colorimetric, low thorium, low uranium	4	3
Uranium: fluorimetric, General Analyses Laboratory	10	8
Nitrate nitrogen: Technicon	20	10
Ammonia nitrogen: Technicon	20	10

Table 5.2. Quality control results for the determination of uranium by delayed neutron counting

Control	No. of determinations	Average uranium (ppm)	Relative standard deviation (%)
High uranium	60	10.59	2
Low uranium	58	5.23	4
NBS-1632 1.40 ± 0.1 ppm uranium (7.1%)	41 (2d quarter)	1.403	4
NBS-1632	40 (3d quarter)	1.413	4
NBS-1633 11.6 ± 0.2 ppm uranium (1.7%)	41 (2d quarter)	11.52	2
NBS-1633	40 (3d quarter)	11.64	2

Table 5.3. Distribution by laboratory of control tests for October 1975–September 1976

Laboratory	Number of control results		Quality level[a] (%)	
	Total	Outside fixed limits	1975	1976
Environmental Analyses	612	22	94.52	96.41
Radioactive Materials	905	39	85.68	95.69
General Analyses	903	41	91.49	95.46
Totals	2420	102	90.94	95.79

[a]Control results within 2*S* limits

occurrence, fortunately, occurred at night. A pressure vessel seal failed and resulted in a steam explosion. The only damage was to the oven that contained the pressure vessel. The pressure vessel has been redesigned, and the new oven has been provided with backup temperature control.

We continue to maintain a safety program that is section or group oriented and is supplemented by routine quarterly inspections by the Safety Committee. Additionally, we have begun to emphasize training opportunities that relate to safety. For example, seven people completed a cardiovascular resuscitation course at ORNL.

The Bio-Organic Section conducted, after normal working hours, a drown-proofing course for its members. A number of Division staff members are scheduled to participate in the Laboratory's first aid course.

The 1976 Safety Committee was G. R. Wilson, chairman; H. W. Dunn; N. M. Ferguson; P. Gouge; J. Hackney; T. R. Mueller; and J. M. Peele.

SUMMARY OF ANALYSES RENDERED

Table 5.5 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 5.4. Distribution of control results (by method) for October 1975–September 1976

Method	Constituent	No. of programs	No. of results	Total for method
Atomic absorption	Cadmium	2	19	
	Calcium	2	70	
	Chromium	1	7	
	Copper	2	8	
	Iron	1	25	
	Lead	2	15	
	Lithium	1	33	
	Magnesium	1	60	
	Nickel	1	7	
	Potassium	1	42	
	Sodium	1	31	
	Zinc	2	33	350
Colorimetric	Beryllium	1	27	
	Chromium	2	30	
	Iron	2	38	
	Molybdenum	2	31	
	Nickel	2	25	
	Nitrogen	3	130	
	Phosphorus	1	98	
	Sulfate	1	67	
	Thorium	2	180	
	Uranium	2	114	
	Zirconium	1	34	774
Coulometric	Uranium	3	360	360
Flame emission	Lithium	1	14	
	Potassium	1	18	
	Sodium	1	28	60
Fluorimetric	Uranium	3	227	227
Gravimetric	Carbon	2	100	100
Infrared absorption	Carbon	1	90	90
Volumetric	Fluoride	1	38	
	Nitrate	1	32	
	Sulfur	1	50	
	Thorium	2	157	
	Uranium	1	182	459
Total		54		2420

Table 5.5. Summary of analytical work

Organization	Number of results reported by							Total
	Elemental Spectrometry	Mass Spectrometry Service Laboratory	General Analyses Laboratory	Radioactive Materials Analytical Laboratories	Environmental and Radiochemical Analyses Laboratory	Activation Analysis Laboratory	Physicochemical Laboratory	
ORNL divisions								
Analytical Chemistry	3,770	982	1,438	36	200		46	6,472
Chemical Technology	31,533	13,173	13,820	26,114	9,172	141	1,256	95,189
Chemistry	1,597	734	1,777	162	646	100	1,369	6,385
Energy							25	25
Engineering Technology	1,773	446	754	10	987	1,117		5,087
Environmental Sciences	718	87	1,235	589	43,998	3,414	504	50,545
Health	493							493
Health Physics	553	10	138	3	1,915	66	39	2,724
Inspection Engineering	257							257
Metals and Ceramics	15,336	316	6,365	706	2,410	499	280	25,892
Neutron Physics	22				21	10		53
Operations	1,154	678	1,138	5,610	5,114	153	40	13,887
Physics	221	24			4		33	282
Plant and Equipment		300						300
Solid State	3,558	233	142	81	15	92	309	4,430
Thermonuclear	302						12	314
Others								
K-25	102							102
Los Alamos Scientific Laboratory		36		10				46
Miscellaneous	290	219	230	150	746	204	279	1,520
NURE[a]						1,779		1,779
Protective Coating Testing				184	480			
Y-12	157	2,736	29	18				
Total	61,836	19,974	27,066	33,673	65,110	7,575	4,172	219,782

[a]National Uranium Resource Evaluation

6. 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 Department, E. I. duPont de Nemours and Co., Wilmington, Delaware.

V. A. Fassel, Deputy Director, Ames Laboratory, ERDA, and Professor of Chemistry, Iowa State University, Ames.

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

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, specializes in areas of electrochemistry and molten-salt research.

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. 7.

Dr. Henry Borella, Edge-e-tron, Germas and Greer, Santa Barbara, California.

Professor Edward Rinehart, Department of Physics, University of Wyoming, Laramie.

Dr. Ronald J. Pugmire, Vice-President for Research, University of Utah, Salt Lake City.

Dr. Harry S. Hertz, Chemical Division, National Bureau of Standards, Washington, D.C.

Dr. Charles D. Wagner, Shell Development Company, Houston, Texas

Dr. Eugene Barry, Department of Chemistry, University of Lowell, Lowell, Massachusetts.

Dr. Thomas Isenhour, Department of Chemistry, University of North Carolina, Chapel Hill

Dr. Peter W. Carr, Department of Chemistry, University of Georgia, Athens.

Dr. Philip D. LaFleur, Institute for Materials Research, National Bureau of Standards, Washington, D.C.

Dr. Lawrence W. Kessler, Sonoscan, Inc., Bensenville, Illinois

PARTICIPATION IN ORNL "IN-HOURS" PROGRAM

Gerald Goldstein taught a course in Liquid Chromatography, and W. Griest taught a course in Gas Chromatography as part of the Laboratory's "In-Hours" Continuing Education Program. One person from the Division completed the Liquid Chromatography course, and ten Divisional people completed the Gas Chromatography course.

Short Course in Interpretation of Mass Spectra

W. T. Rainey and D. C. Canada taught the American Chemical Society short course in Interpretation of Mass Spectra to six members of the Division staff.

GREAT LAKES COLLEGES ASSOCIATION (GLCA) EDUCATION PROGRAM

This cooperative program is now in its seventh year. Two students were assigned to the Division during the fall 1976 semester: S. V. Johanningsmeir from DePauw University in Greencastle, Indiana, to work with J. R. Stokely and W. H. Griest on a method for the determination of glycerol and other humectants in tobacco and tobacco smoke; and R. Q. Thompson from College of Wooster, Wooster, Ohio, to work with A. R. Jones on the liquid chromatographic fractionation of coal-derived oils.

SOUTHERN COLLEGES AND UNIVERSITIES UNION (SCUU) SCIENCE SEMESTER

Two undergraduate students were assigned to the Division as part of the SCUU cooperative program for the winter 1976 semester: J. D. Meyer from Centre College in Danville, Kentucky, worked with J. R. Stokely and J. H. Moneyhun to develop a gas chromatographic procedure for determining hydrogen cyanide in tobacco smoke; and D. H. Sikes from University of the South, Sewanee, Tennessee, worked with B. R. Clark on the isolation of organic compounds from water.

IAEA FELLOWSHIP PROGRAM

D. A. Batistoni, IAEA Fellow, Chemistry Department, National Atomic Energy Commission, Buenos Aires, Argentina, was assigned to the Division in August 1975 to work with C. Feldman on the evaluation of emission spectroscopy sources. He completed this assignment on November 18, 1976.

P. S. Murty, IAEA Fellow, Bhabha Atomic Research Center, Bombay, India, was assigned to the Division from June 1975 to September 30, 1976. He studied electron spectroscopy for chemical analysis under the direction of L. D. Hulett.

SUMMER PROGRAM

During the summer, the Division was host to representatives of several programs that have been developed to offer laboratory experience to college students and faculty members as well as to promising high school graduates. G. Goldstein served as "Dean" for these guests during their visit.

ORAU Summer Research Participant

Dr. W. M. Cooke, University of North Carolina at Charlotte, worked with W. H. Griest on the analysis of main- and side-stream tobacco smoke polynuclear aromatic hydrocarbons.

Dr. Wilmer J. Stratton, Earlham College, Richmond, Indiana, worked with H. H. Ross on new methods for trace metal analysis using a microwave emission detector. On September 1, 1976, he became a GLCA Visiting Faculty Participant and continued working on this project.

ORAU Summer Undergraduate Research Trainees

M. P. Barbalas, Rose-Hulman Institute of Technology, Terre Haute, Indiana, worked with W. R. Laing on coal liquefaction.

Lauren Duffey, College of Charleston, Charleston, South Carolina, worked with J. R. Stokely and W. H. Griest on the polyglycol anatysis of tobacco.

Franklin Hickman, Davidson College, Davidson, North Carolina, worked with W. R. Laing on fuel reprocessing.

D. H. Sikes from University of the South, Sewanee, Tennessee, worked with B. R. Clark on the isolation of organic compounds from water.

J. G. Tarter, Angelo State University, San Angelo, Texas, worked with L. D. Hulett on x-ray fluorescence.

Temporary Summer Graduate Student Employees

M. W. Brown, Centenary College of Louisiana, Shreveport, Louisiana, worked with H. Kubota on the analysis of polynuclear aromatic hydrocarbons.

Bernard Hale, Tusiegee Institute, Alabama, worked with J. S. Eldridge on gamma-ray spectrometry of environmental samples.

Jacqueline L. Kracker, Florida State University, Tallahassee, Florida, worked with J. E. Strain developing the high-power microwave plasma as an excitation source for spectroscopy.

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
Nominating Committee:	East Tennessee Section, ACS

J. E. Caton

Lecturer:	ORAU Traveling Lecture Program
Consultant:	National Cancer Institute

W. H. Christie

Lecturer:	ORAU Traveling Lecture Program
Member:	Committee E-42, Surface Analysis, ASTM

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

D. A. Costanzo

Member:	Committees C-26, Fuel, Control, and Moderator Materials for Nuclear Reactor Applications; and C-26.05, Methods of Test, ASTM

J. S. Eldridge

Recipient:	NASA Group Achievement Award, Apollo-Soyuz Test Project Experiments Team, Johnson Space Center, Sept. 16, 1975

C. Feldman

Consultant:	Trace Mercury Analysis, Almadén, Spain

J. C. Franklin

Member:	ERDA Mass Spectrometer Technical Group ASMS Committee VII, Studies of Solids

G. Goldberg

Member:	Committee D-1, Paint, Varnish, Lacquer, and Related Projects Subcommittee D01.43, Coatings for Power Generation Facilities, ASTM Advisory Board of Utilities Nuclear Coating Work Committee (UNCWC)
Secretary:	Rewrite "Suggested Tests for Codings for Nuclear and Power Generating Facilities," Subcommittee D01.43

G. Goldstein

Member:	NAS-NRC Committee on Specifications and Criteria for Biochemical Compounds
Chairman:	Subcommittee on Nucleotides and Related Compounds IUB-IUPAC Ad Hoc Committee on Radioactive and Isotopic Specifications of Labelled Compounds
Past-president:	Tennessee Institute of Chemists (AIC)

M. R. Guerin

Consultant:	National Cancer Institute
Member:	Tobacco Working Group, National Cancer Institute Smoking and Health Program Advisory Committee
Chairman:	Chemical Subgroup, Tobacco Working Group, National Cancer Institute Smoking and Health Program

R. W. Holmberg

Consultant:	National Cancer Institute

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*

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, 5th International Conference on Modern Trends in Activation Analysis
	ANS Isotopes and Radiation Division: Executive Committee; Program Chairman
Regional Editor:	*Journal of Radioanalytical Chemistry*
Associate Editor:	*Radiochemical and Radioanalytical Letters*
Special Consultant:	International Atomic Energy Agency, Applications of Nuclear Methods in Environmental Research, Vienna, Austria, March 1976
Invited Participant:	Workshop on Health and Environmental Effects of Coal Combustion Technology, for ERDA DBER, Knoxville, Tenn., Aug. 2–6, 1976

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

W. T. Rainey, Jr.

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

S. A. Reynolds

Member:	Committee D-19, Water, ASTM
	Committee E-10, Nuclear Applications and Measurement of Radiation Effects, ASTM
	Environmental Sciences Division, ANS
	Committee on Environmental Analytical Methodology, ACS
Secretary:	Subcommittee 4, Methods of Radiochemical Analysis

E. Ricci

Member:	Executive Committee, Isotope and Radiation Division, American Nuclear Society
Chairman:	Planning Committee, Isotopes and Radiation Division, American Nuclear Society

H. H. Ross

Member:	ORNL Graduate Student Selection Panel
Member:	ORNL Technology Utilization Committee

W. D. Shults

Cochairman:	Workshop on Health and Environmental Effects of Coal Combustion Technology, for ERDA DBER, Knoxville, Tenn., Aug. 2–6, 1976 (with R. I. Van Hook)
Coprincipal Investigator:	ORNL NSF EATC Program (with R. I. Van Hook) (until Dec. 31, 1976)
Analytical Chemistry Division Representative:	ORNL Coal Technology Program Steering Committee (until June 1, 1976)
Analytical Chemistry Division Representative:	ORNL Life Sciences Program: Coal Conversion Technology (until June 1, 1976)
Member:	ORNL "In-Hours" Continuing Education Committee
Editorial Board:	*Analytical Chemistry*
Secretary:	Fellowship Committee, Analytical Chemistry Division, American Chemical Society
Session Chairman:	General Spectroscopy, Second Annual FACSS Meeting, Indianapolis, Indiana, October 1975
Invited Participant:	ERDA DBER Workshop on Surrogate Standards for Use in Coal Conversion Studies, June 1976
Invited Participant:	NBS Workshop on a National Environmental Specimen Bank, August 1976
Chairman:	Analytical Program, Southeastern Regional American Chemical Society Meeting, October 1976

J. R. Soukoly

Member:	Committee D-22, Methods of Sampling and Analysis of Atmospheres, ASTM
Consultant:	National Cancer Institute

D. H. Smith

Coordinator:	Divisional Ph.D. recruiting

7. Presentation of Research Results

As in past years, the Division has actively responded to the changing priorities of the Laboratory 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 Laboratory divisions. Such persons are designated by an asterisk.

PUBLICATIONS

Contributions to Proceedings

AUTHOR(s)	TITLE	PUBLISHER
Bondietti, E. A.* S. A. Reynolds, M. H. Shanks*	"Interaction of Plutonium with Complexing Substances in Soils and Natural Waters"	*Transuranium Nuclides in the Environment*. IAEA, Vienna, 1976. p. 273
Carter, J. A., W. R. Wasick	"Platinum Metals in Air Particulates Near a Catalytic Converter Test Site as Measured by Isotope Dilution SSMS"	*Proc. Catalyst Research Program's Platinum Research Review Conference*, Rougemont, N.C., Dec. 3–5, 1975
Carter, J. A., R. L. Walker, R. F. Fry, C. A. Pritchard	"A Simplified Separation Method for Simultaneous U and Pu Isotopic Analysis with a Two-Stage Mass Spectrometer"	*Proc. Intern. Symp. on the Safeguarding of Nuclear Materials*, IAEA-SM-201/9, Vienna, 1976. p. 461
Carter, J. A., D. L. Donohue, J. C. Franklin, R. W. Stelzner	"Environmental and Fuel Materials Analyses by Multi-Element Isotope Dilution Spark Source Mass Spectrometry"	*Trace Substances in Environmental Health-IX*, D. D. Hemphill, ed., Univ. of Missouri, Columbia, 1975, p. 304
Carter, J. A.	(See Franklin, J. C.)	
Clark, B. R.	(See Guerin, M. R.)	
Costanzo, D. A.	(See Pruitt, M. E.)	
Dale, J. M.	(See Hulett, L. D.)	
Donohue, D. L.	(See Carter, J. A.) (See Franklin, J. C.)	

AUTHOR(s)	TITLE	PUBLISHER
Dunn, H. W.	(See Hulett, L. D.)	
Eby, R. E.	(See Carter, J. A.)	
Eldridge, J. S., G. D. O'Kelley,* K. J. Northcutt	"Primordial and Cosmogenic Radionuclides in Descartes and Taurus-Littrow Materials: Extension of Studies by Nondestructive γ-ray Spectrometry"	*Proc. 6th Lunar Science Conference*, 1975, p. 1407
Eldridge, J. S.	(See O'Kelley, G. D.)	
Emery, J.	(See Hulett, L. D.)	
Franklin, J. C.	(See Carter, J. A.)	
Franklin, J. C., J. A. Carter, D. L. Donohue, R. W. Stelzner	"Multielement Isotope Dilution Spark Source Mass Spectrometry"	*Proc. 23rd Annual Conference on Mass Spectrometry and Allied Topics*, Houston, Texas, 1975, p. 355
Griest, W. H.	(See Guerin, M. R.)	
	(See Kubota, H.)	
Guerin, M. R., J. L. Epler,* C.-h. Ho, B. R. Clark	"Determining Fugitive Emissions Measurement Needs for an Emerging Industry-Advanced Fossil Fuels Utilization"	*Proc. of Symp. on Fugitive Emissions Measurement and Control*, Hartford, Conn., 1976
Guerin, M. R.	(See Kubota, H.)	
Guerin, M. R.	"Tobacco Smoke Characterization: A Model for Coal Liquefaction-Analytical Research"	*Proc. Workshop on Analytical Needs of the Future as Applied to Coal Liquefaction*, Greenbo, Ky., Aug. 21-23, 1974, p. 170
Guerin, M. R., W. H. Griest, C.-h. Ho, W. D. Shults	"Chemical Characterization of Coal Conversion Pilot Plant Materials"	*Proc. Third ERDA Environmental Protection Conference*, Chicago, Ill., Sept. 23-26, 1975
Ho, C.-h.	(See Guerin, M. R.)	
Hulett, L. D., J. M. Dale, J. F. Emery, W. S. Lyon, W. Fulkerson*	"Techniques for Characterization of Particulate Matter: Neutron Activation Analysis, X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy"	*Proc. Workshop on Sampling, Analysis, and Monitoring of Stack Emissions*, Electric Power Research Institute, Palo Alto, Calif., April 1976, p. 241
Hulett, L. D., H. W. Dunn, J. M. Dale, J. F. Emery, W. S. Lyon, P. S. Murty*	"The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron, X-ray, and Nuclear Physics Methods"	*Proc. Measurement, Detection, and Control of Environmental Pollutants*, IAEA-SM-206/1, Vienna, 1976, p. 29

AUTHOR(s)	TITLE	PUBLISHER
Kerley, J. R.,* D. L. Manning, R. F. Clausing*	"Corrosion Resistance to Some Nickel-Base Alloys to Molten Fluoride Salts Containing UF_4 and Tellurium"	*Proc. Intern. Symp. on Molten Salts*, The Electrochemical Society, Inc., Washington, D.C., August 1976, p. 315
Kubota, H., W. H. Griest, M. R. Guerin	"Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples Trace Polynuclear Aromatic Hydrocarbons"	*Proc. 9th Annual Conference on Trace Substances in Environmental Health*, Columbia, Mo., June 9–12, 1976, p. 281
Lyon, W. S.	(See Hulett, L. D.)	
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Musick, W. R.	(See Carter, J. A.)	
Northcutt, K. J.	(See Eldridge, J. S.) (See O'Kelley, G. D.)	
O'Kelley, G. D.,* J. S. Eldridge, K. J. Northcutt	"Radionuclide Concentrations in KREEP Basalt Samples 15382 and 15386"	*Proc. Lunar Science VII*, Lunar Science Instit., Houston, Texas, 1976, p. 651
Pritchard, C. A.	(See Carter, J. A.)	
Pruett, M. E., A. W. Longest,* D. A. Costanzo, J. A. Conlin,* U. Gat,* B. D. Epstein*	"Tritium Monitoring System for the GB-10 GCFR Fuel Irradiation Experiment"	*Trans. Am. Nucl. Soc.* 23, 1976, p. 116
Reynolds, S. A.	(See Bondietti, E. A.)	
Rose, H. H.	"Theory and Application of Cerenkov Counting"	*Proc. of Liquid Scintillation Science and Tech.*, Academic Press, New York, 1976, p. 79
Shults, W. D.	(See Guerin, M. R.)	
Stelzner, R. W.	(See Carter, J. A.) (See Franklin, J. C.)	
Steff, L. R.,* R. B. Walton,* T. D. Reilly,* L. W. Fields,* R. L. Walker, W. T. Mullins,* J. J. Thomas*	"Neutron Measurements of ^{234}U Isotopic Abundance in UF_6 Samples"	*Proc. 16th Annual Meeting of Nuclear Materials Management*, Nucl. Mater. Manage., New Orleans, La., 1975
Walker, R. L.	(See Carter, J. A.) (See Steff, L. R.)	

AUTHOR(s)	TITLE	PUBLISHER
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Horton, A. D., R. F. Apple, A. S. Meyer, M. R. Guerin	"A Puff-Averaging Analytical Cigarette Smoking Device"	*Tobacco Sci.* XX, 22 (1975)
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Lee, D. A.	(See Carpenter, J. A.)	
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Meyer, A. S.	(See Horton, A. D.)	
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Moore, F. L., W. S. Groenier*	"Removal and Recovery of Cyanide and Zinc from Electroplating Wastes by Solvent Extraction"	*Plating and Surface Finishing* 63(8), 26 (1976)
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Payne, M. G.,* G. S. Hurst,* M. H. Nayfeh,* J. P. Judish,* C. H. Chen,* E. B. Wagner,* J. P. Young	"Kinetics of He (2^1S) Using Resonance Ionization Spectroscopy"	*Phys. Rev. Lett.* 35, 1154 (1975)

AUTHOR(s)	TITLE	PUBLISHER
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	(See Rao, T. K.)	
Scott, T. G.	(See Reynolds, S. A.)	
Scott, T. G., S. A. Reynolds	"Determination of Plutonium in Environmental Samples Part II. Procedures"	*Radiochem. Radioanal. Lett.* 23, 275 (1975)
Senn, David R.,* P. W. Carr,* L. N. Klatt	"Compensation for Thermal Drift in an Optical Feedback Stabilized"	*Chem. Instrum.* 7, 145 (1976)
Senn, David, R.,* P. W. Carr,* L. N. Klatt	"Determination of Nitrate Ion at the Part Per Billion Level in Environmental Samples with a Continuous Flow Immobilized Enzyme Reaction"	*Anal. Chem.* 48, 954 (1976)
Shaw, R. W., M. Nicol*	"Phosphorescence and Triplet-Triplet Absorption Spectra of Anthracene-*d*10 in Polymethylmethacrylate Under High Pressures"	*Chem. Phys. Lett.* 39, 108 (1976)
Smith, D. H.,	(See Christie, W. H.)	
	(See Gentry, R. V.)	
Stokely, J. R., H. A. Friedman*	"Electrochemical Studies on the Existence of Divalent Oxidation States of Selected Actinides in Acetonitrile Solution"	*Inorg. Nucl. Chem. Lett.* 12, 505 (1976)
Walker, R. L.	(See Gentry, R. V.)	
Young, J. P.	(See Finch, C. B.)	
	(See Payne, M. G.)	
Westgard, J. O.,* R. N. Carey,* D. H. Feldbriegge,* L. M. Jenkins	"Performance Studies on the Technicon SMAC Analysis: Precision and Comparison of Values with Methods in Routine Laboratory Service"	*Clin Chem.* 22, 489 (1976)

AUTHOR(s)	TITLE	PUBLISHER
	Theses	
Jenkins, R. A.	"The Electrochemical Oxidation of NADH and its Application to a Reagentless Lactate Sensor"	Ph.D., University of Wisconsin, Madison (1975)
Maddox, W. L.	"Analysis of Cigarette Smoke by Fourier Transform Infrared Spectrometry"	Ph.D., University of Tennessee, Knoxville (1976)

REPORTS

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Canada, D. C.	(See Lee, D. A.)	
Carter, J. A.	(See Lee, D. A.)	
	(See Smith, D. H.)	
	(See Walker, R. L.)	
Carter, J. A.	*Analytical Chemistry Division Research and Development Summary September 1976*	ORNL/CF-76/342 (October 1976)
Christie, W. H.	(See Rainey, W. T.)	
	(See Smith, D. H.)	
Corbin, L. T.	(See Shults, W. D.)	
Costanzo, D. A.	(See Goldberg, G.)	
	(See LaValle, D. E.)	
	(See Lee, D. A.)	
Dyer, F. F., R. P. Wichner,* W. J. Martin,* L. L. Fairchild,* R. J. Kedl,* H. J. de Nordwall*	*Post-Irradiation Examination of Peach Bottom HTGR Driver Fuel Element E06-01*	ORNL-5126 (April 1976)
Dickens, J. K.,* T. A. Love,* J. W. McConnell,* J. F. Emery, R. W. Peele*	*Fission Product Beta and Gamma Energy Release Quarterly Progress Report for October–December 1975*	ORNL/TM-5275 (February 1976)
	Fission Product Beta and Gamma Energy Release Quarterly Progress Report for January–March 1976	ORNL/NUREG/TM-23 (May 1976)
	Fission Product Beta and Gamma Energy Release Quarterly Progress Report for April–June 1976	ORNL/NUREG/TM-47 (September 1976)
	Fission Product Beta and Gamma Energy Release Quarterly Progress Report for July–September 1976	ORNL/NUREG/TM-65 (November 1976)
	Preliminary Fission Product Energy Release Measurements for Thermal Neutron Fission of ^{235}U	ORNL/TM-5273 (March 1976)
Eldridge, J. S.	(See Trombka, J. I.)	
Emery, J. F.	(See Dickens, J. K.)	

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Goldberg, G., D. A. Costanzo	*A Versatile Particle Size Analyzer*	ORNL/TM-5157 (November 1975)
Goldstein, G., J. E. Strain, J. L. Bowling*	*Environmental Applications of the Centrifugal Fast Analyzer*	ORNL/NSF/EATC-15 (December 1975)
Guerin, M. R.	*Analytical Chemistry Division Research and Development Summary October 1976*	ORNL/CF-76/407 (November 1976)
Judd, M. S.,* J. E. VanCleve, Jr.,* W. T. Rainey	*Recovery of Perchloroethylene Scrubbing Medium Generated in the Refabrication of High-Temperature Gas-Cooled Reactor Fuel*	ORNL/TM-5620 (November 1976)
Klatt, L. N., D. R. Senn,* P. W. Carr*	*An Enzyme Catalyzed Reaction for the Determination of Nitrate*	EPA Final Report, Grant R-800-858 (May 1976)
Laing, W. R.	*Analysis of ORNL Process Water from 1960 to Present*	ORNL/CF-76/148 (May 1976)
LaValle, D. E., D. A. Costanzo, W. J. Lackey,* A. J. Caputo*	*The Determination of Dejective Particle Fraction in HTGR Fuels*	ORNL/TM-5483 (September 1976)
LaValle, D. E., D. A. Costanzo, W. J. Lackey,* J. D. Sease*	*Technique for Differentiating Between Open and Closed Pores on a Microscopic Scale*	ORNL/TM-5100 (November 1976)
Lee, D. A., D. A. Costanzo, D. P. Stinton,* J. A. Carpenter,* W. T. Rainey, D. C. Canada, J. A. Carter	*In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer*	ORNL/TM-5579 (August 1976)
Lyon, W. S.	*Analytical Chemistry Division Research and Development Summary August 1976*	ORNL/CF-76/329 (September 1976)
McKown, H. S.	(See Smith, D. H.)	
Moore, F. L.	*Chemical Separations for Abatement Control of Energy Processes*	ORNL/NSF/EATC-20 (December 1975)
Mueller, T. R.	*Checkout and Test Procedure, Fluorophotometer*	ORNL/Q-5198A-ST (June 1976)
Pritchard, C. A.	(See Rainey, W. T.) (See Walker, R. L.)	
Rainey, W. T.	(See Judd, M. S.) (See Lee, D. A.)	
Rainey, W. T., W. H. Christie, C. A. Pritchard, W. Lijinsky*	Mass Spectra of N-Nitroso Compounds	ORNL/TM-5500 (September 1976)

AUTHOR(s)	TITLE	REPORT NO. AND DATE
Shults, W. D.	*Preliminary Results: Chemical and Biological Examination of Coal-Derived Materials*	ORNL/NSF/EATC-18 (March 1976)
Shults, W. D., L. T. Corbin	*Analytical Chemistry Division Research and Development Summary – November 1975*	ORNL/CF-75/12-2 (December 1975)
	Summary for December 1975	ORNL/CF-76/21 (January 1976)
	Summary for January 1976	ORNL/CF-76/48 (February 1976)
	Summary for February 1976	ORNL/CF-76/86 (March 1976)
	Summary for March 1976	ORNL/CF-76/111 (April 1976)
	Summary for April 1976	ORNL/CF-76/131 (May 1976)
	Summary for May 1976	ORNL/CF-76/199 (July 1976)
	Summary for July 1976	ORNL/CF-76/302 (August 1976)
Shults, W. D.	(See Van Hook, R. I.)	
Smith, D. H.	(See Walker, R. L.)	
Smith, D. H., H. S. McKown, W. H. Christie, R. L. Walker, J. A. Carter	*Instruction Manual for ORNL Tandem High Abundance Sensitivity Mass Spectrometer*	ORNL/TM-5485 (June 1976)
Strain, J. E.	(See Goldstein, G.)	
Trombka, J. I.,* J. S. Eldridge, et al.	*Crystal Activation-Experiment MA-151*	NASA/TMX-58173 (1976)
Van Hook, R. I.,* W. D. Shults	*EATC Progress Report October 1974 December 1975*	ORNL/NSF/EATC-22 (February 1976)
Walker, R. L.	(See Smith, D. H.)	
Walker, R. L., C. A. Pritchard, J. A. Carter, D. H. Smith	*Practical Aspects of the Resin Bead Technique for Mass Spectrometric Sample Loading*	ORNL/TM-5505 (July 1976)
Wilson, G. R.	*Statistical Quality Control Report, Analytical Chemistry Division, July through September 1975*	ORNL/CF-75/10-19 (October 1975)

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.

20th Annual ORNL Conference on Analytical Chemistry in Energy and Environmental Technology

This year's conference – the 20th – was again held at the Riverside Motor Lodge in Gatlinburg. Six sessions occupied the full three days October 12-14. Titles of these sessions were: Analytical Chemistry Related to Fossil Energy Technology (1), Analytical Chemistry Related to Fossil Energy Technology (2), Special Session on National Uranium Resources Evaluation (NURE), Nuclear and Radiochemical Methods, X-ray and Spectroscopic Methods, and Automation and New Instrumentation.

L. J. Brady was Conference Chairman; W. S. Lyon was Technical Program Chairman; and A. L. Harrod served as Treasurer and Exhibits Coordinator.

At Meetings of Professional Societies, Conferences, and the Like

AUTHOR(s)	TITLE	PRESENTED AT
Bondietti, E. A.,* S. A. Reynolds	"Field and Laboratory Observations on Plutonium Oxidation States"	Workshop on Actinide-Sediment Interactions, Seattle, Wash., Feb. 10-11, 1976
Bondietti, E. A.,* S. A. Reynolds, M. H. Shanks*	"Interaction of Plutonium with Complexing Substances in Soils and Natural Waters"	IAEA/ERDA Symposium on Transuranium Nuclides in the Environment, San Francisco, Nov. 17-21, 1975
Bostick, D. T.	"The Determination of Atmospheric Sulfate"	Symposium on Recent Developments in Sampling and Analysis of Atmospheric Sulfate and Nitrate, Research Triangle Park, N.C., Mar. 23, 1976
	"Studies of the Determination of Atmospheric Sulfate"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Bostick, D. T., W. D. Bostick*	"The Spectrokinetic Analysis of Sulfate Using the Miniature Centrifugal Fast Analyzer System"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12-14, 1976
Botts, J. L., D. A. Costanzo, D. E. LaValle, F. L. Layton	"Analytical Methods for the Chemical Characterization of HTGR Fuels"	78th Annual Meeting, American Ceramic Society, Cincinnati, Ohio, May 1-6, 1976
Carpenter, J. A.,* D. A. Lee	"TGA-DTA-Mass Spectrometer Observations of the Carbonization of Uranium-Loaded Weak Acid Resin Microspheres"	78th Annual Meeting, American Ceramic Society, Cincinnati, Ohio, May 1-6, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Carter, J. A., D. L. Donohue, J. C. Franklin	"Multielement Analysis by Isotope Dilution Spark Source Mass Spectrometry"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Carter, J. A., W. R. Mueck	"Platinum Metals in Air Particulates Near a Catalytic Converter Measured by Isotope Dilution SSMS"	Catalyst Research Program's Platinum Research Review Conference, Rougemont, N.C., Dec. 3–5, 1975
Caton, J. E.	"Cigarette Smoke Dosimetry in Mice"	Council for Tobacco Research Contractors Meeting, New Orleans, La., Apr. 1–3, 1976
	"Analytical Electrophoresis"	ORAU Traveling Lecture, Christian Brothers College, Memphis, Tenn., Feb. 18, 1976
	"Immunological Reagents in Analytical Chemistry"	ORAU Traveling Lecture, Tougaloo College, Tougaloo, Miss., Feb. 17, 1976
Caton, J. E., W. E. Dalbey,* P. Nettesheim,* M. R. Guerin	"Tobacco Smoke Inhalation Dosimetry"	Inhalation Toxicology Workshop, Tampa, Fla., Oct. 20–22, 1976
Christie, W. H.	"The Ion Microprobe Mass Analyzer as a Surface Analytical Technique – An Overview"	Surface Science and Heterogeneous Catalysis Conference, ORNL, Oak Ridge, Tenn., Nov. 9, 1976
	"Mass Spectrometry and Ion Microprobe Mass Analysis"	ORAU Traveling Lecture, Lowell University, Lowell, Mass., Nov. 16, 1976
Christie, W. H., D. H. Smith	"Applications of Ion Microprobe Mass Analysis"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Clark, B. R., M. R. Guerin, C.-h. Ho, I. B. Rubin, J. L. Epler*	"Chemical-Biological-Environmental Characterization of Fossil Fuel Conversion Materials"	Energy/Environment Workshop: SRM's for Coal Gasification and Liquefaction, Gaithersburg, Md., Jan. 20–21, 1976
	"Chemical-Biological Characterization of Coal Conversion Liquids"	81st National Meeting of the American Institute of Chemical Engineers, Kansas City, Mo., Apr. 13, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Clark, B. R., M. R. Guerin	"Chemical Characterization and Monitoring Studies of Effluents from Emerging Fossil Fuel Processes"	APCA Conference on Toxic Substances in the Air Environment, Cambridge, Mass., Nov. 7–9, 1976
	"ORNL Program to Screen for Health Hazards Associated with Coal Liquefaction"	National Research Council, National Academy of Sciences, Meeting of the Committee on Processing and Utilization of Fossil Fuels Ad Hoc Panel On Liquefaction of Coal, Washington, D.C., Mar. 9, 1976
Clark, B. R., C.-h. Ho	"Organic Contaminants in Aqueous Media Related to Oil Shale, Oil Refining, and Geothermal Sources"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Clark, B. R., J. A. Richards,* D. H. Evans*	"Infrared and NMR Spectroelectrochemistry"	149th Meeting of Electrochemical Society, Washington, D.C., May 2–7, 1976
Corbin, L. T.	"Service Activities of 1975"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Costanzo, D. A.	"Analytical Chemistry Division Research and Development Activities"	ORNL Chemical Technology Division Seminar, Oak Ridge, Tenn., Apr. 21, 1976
	"Analytical Chemistry in the GCR Program"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
	"Analytical Chemistry Support to the HTGR Base Program"	ORNL HTGR Fuel Development Program Seminar, Oak Ridge, Tenn., Mar. 17, 1976

AUTHOR(s)	TITLE	PRESENTED AT
	"Chemical Characterization of HTGR Fuel"	Information Exchange Meeting, General Atomic Company, San Diego, Calif., Aug. 24–27, 1976
	"Determination of the Defective Particle Fraction of HTGR Fuel"	ORNL/KFA (Germany) Information Exchange, ORNL, Oak Ridge, Tenn., Nov. 22–23, 1976
Donohue, D. L., J. A. Carter, J. C. Franklin	"Standards Requirements for Coal and Coal Products Analysis"	SRM's for Coal Gasification, National Bureau of Standards, Washington, D.C., Jan. 20–21, 1976
Donohue, D. L., J. C. Franklin	"Multielement Isotope Dilution Spark Source Mass Spectrometry"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Dunn, H. W., L. D. Hulett	"X-ray Fluorescence Quantative Analysis Using Fundamental Constants"	American Nuclear Society Workshop, Lynchburg, Va., Oct. 4–5, 1976
Dyer, F. F.	"From Beta Counting to Computers A Look at the Past of Neutron Activation Analysis"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Eldridge, J. S.	"Applications of Instrumental Gamma-Ray Spectrometry to a Variety of Environmental Problems"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12–14, 1976
	"Radionuclide Concentrations in KREEP Basalt Samples 15382 and 15386"	7th Lunar Science Conference, Houston, Tex., Mar. 15–19, 1976
Emery, J. F.	"On-Line Ge(Li) Gamma Spectrometry"	ORNL Gas-Cooled Fast Reactor Technical Review Meeting, Oak Ridge, Tenn., Aug. 26, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Farrar, L. G., J. R. Stokely, M. R. Guerin	"Polonium-210 in Commercial Cigarette Smoke Condensates"	30th Tobacco Chemists Research Conference, Nashville, Tenn., Oct 18–20, 1976
Feldman, C.	"Analytical Chemistry of Arsenic and Arsenicals Intermission"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Fellows, R. L.,* J. P. Young, J. R. Peterson,* R. G. Haire*	"Radioluminescence Spectra of Einsteinium-253 Trihalides"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Gentry, R. V.,* W. H. Christie, D. H. Smith, R. L. Walker, S. S. Cristy,* J. F. McLaughlin*	"Dwarf Radiohalos"	American Geophysical Union Annual Meeting, Washington, D.C., April 1976
Goldberg, G.	"Testing of Protective Coatings for the Nuclear Industry"	Utilities Nuclear Coatings Work Committee (UNCWC), Miami Beach, Fla., Mar. 1976
	"Testing of Coatings for the Nuclear Industry"	Southeastern Regional Meeting, National Association of Corrosion Engineers, Buena Vista, Fla., Nov. 9–13, 1975
Goldstein, G	"Liquid Chromatographic Study of Polycyclic Aromatic Hydrocarbons"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
	"Separation of Polycyclic Aromatic Hydrocarbons by Liquid Chromatography"	UT Chemistry Department Seminar, University of Tennessee, Knoxville, Feb. 17, 1976
	"A New Liquid Chromatographic Method for Separation of Polynuclear Aromatic Hydrocarbons Using Polyvinylpyrrolidone as Stationary Phase"	27th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, Mar. 1–5, 1976

AUTHOR(s)	TITLE	PRESENTED AT
	"Liquid Chromatography of Polycyclic Aromatic Hydrocarbons"	ORNL Analytical Chemistry Division Seminar, Oak Ridge, Tenn., Jan 13, 1976
Guerin, M. R.	"Gas Chromatographic Study of Polycyclic Aromatic Hydrocarbons"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Guerin, M. R., H. Kubota, M. R. Guerin	"PAH Profiling Analysis by GLC"	First ORNL Workshop on Polycyclic Aromatic Hydrocarbons: Characterization and Measurement with a View Toward Personnel Protection, Oak Ridge, Tenn., Feb. 26, 1976
Guerin, M. R., G. Oberach	"Multicomponent PAH Analysis and Blind Assay of Tobacco Smoke"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Guerin, M. R.	"Tobacco Smoke Chemistry"	National Cancer Institute Tobacco Working Group Meeting, Bethesda, Md., Mar. 10, 1976
	"Inhalation Dosimetry Monitoring"	National Cancer Institute Tobacco Working Group Meeting, Bethesda, Md., Mar. 10, 1976
	"Identification, Monitoring, and Control of Water-Soluble Effluents"	Symposium on Management of Residuals from Synthetic Fuels Production, Denver, Col., May 25–27, 1976
Guerin, M. R., J. L. Epler,* C.-h. Ho, B. R. Clark	"Determining Fugitive Emissions Measurements Needs for an Emerging Industry – Advanced Fossil Fuels Utilization"	Symposium on Fugitive Emissions: Measurement and Control, Hartford, Conn., May 17–19, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Guerin, M. R., J. R. Stokely	"Interaction of Proband, Machine, and Animal"	Inhalation Toxicology Workshop, Tampa, Fla., Oct. 20–22, 1976
Haire, R. G.,* J. P. Young, R. L. Fellows,* J. R. Peterson*	"Microchemical Techniques for the Synthesis and Study of ^{249}Bk, ^{249}Cf, and ^{253}Es Halides and Oxyhalides"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Higgins, C. E., T. M. Gayle,* J. R. Stokely	"A Light-Scattering Sensor for Detection of Tobacco Smoke Particulates in Exposure Systems"	30th Tobacco Chemists Research Conference, Nashville, Tenn., Oct. 18–20, 1976
Ho, C.-h., M. R. Guerin	"Determination of Organic Compounds in Manures"	Manure Corporation Research Reporting and Planning Meeting, Kansas City, Mo., Aug. 23, 1976
Ho, C.-h., B. R. Clark	"Chemical Characterization of Shale Oil and Shale Oil By-product Retort Water"	Coalab '76, Laramie, Wyo., July 19–23, 1976
	"Determination of Polynuclear Aromatic Hydrocarbons and n-Alkanes in Fossil Fuel Materials"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12–14, 1976
Holmberg, R. W.	"The Determination of Smoke Aerosol Particle Size"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Hulett, L. D., J. M. Dale	"Applications of Electron Spectroscopy"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
	"Electron Spectroscopy Facilities and Program in the Analytical Chemistry Division"	Surface Science and Heterogeneous Catalysis Conference, ORNL, Oak Ridge, Tenn., Nov. 9, 1976
Hulett, L. D., H. W. Dunn, J. M. Dale, J. F. Emery, W. S. Lyon, P. S. Murty*	"The Characterization of Solid Specimens from Environmental Pollution Studies Using Electron X-ray and Nuclear Physics Methods"	International Symposium on the Development of Nuclear-Based Techniques for the Measurement, Detection, and Control of Environmental Pollutants, Vienna, Austria, Mar. 15–19, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Hubert, L. D., C. J. Sparks	"Quantitative Analysis by X-ray Fluorescence Without Standards"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12-14, 1976
Jones, A. Russell	"A Preparative Scale Fractionation of Shale Oil"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12-14, 1976
Jungers, R. H.,* J. A. Carter, D. A. Clay,* J. E. Bumgarner*	"Trace Constituents in Fuels and Additives Determined by Isotopic Dilution Spark Source Mass Spectrometry and Neutron Activation Analysis"	American Chemical Society Centennial Meeting, New York, N.Y., Apr. 4-9, 1976
Keiser, J. R.,* D. L. Manning, R. E. Chumley*	"Corrosion Resistance of Some Nickel-Base Alloys to Molten Fluoride Salts Containing UF_4 and Tellurium"	Molten Salt Symposium, 149th Meeting of the Electrochemical Society, Washington, D.C., May 2-7, 1976
Klatt, L. N.	"A New Dielectric-Constant Detector for Liquid Chromatography"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
	"Applications of Enzymes to the Determination of Contaminants in Water"	Seminar, University of New Orleans, New Orleans, La., Mar. 24, 1976
	"Recent Developments in Liquid Chromatography"	Pensacola Section of the American Chemical Society, Pensacola, Fla., Mar. 25, 1976
	"A Universal Detector for Liquid Chromatography Based upon Dielectric Constant"	172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug. 30-Sept. 3, 1976
	"A Dielectric Constant Monitor for Liquid Chromatography"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12-14, 1976
Lang, W. R., L. J. Brady	"Coal and Analytical Chemistry"	ORNL Analytical Chemistry Division Seminar, Oak Ridge, Tenn., Feb. 10, 1976
Lee, D. A.	"In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spectrometer"	ORNL Analytical Chemistry Division Seminar, Oak Ridge, Tenn., May 17, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Lee, D. A., W. T. Rainey, Jr., D. C. Canada	"In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Using a Time-of-Flight Mass Spectrometer"	"5th Annual Meeting, American Ceramic Society, Cincinnati, Ohio, May 1 - 6, 1976
Lyon, W. S.	"Nuclear Methods in Environmental and Energy Related Research"	IAEA Advisory Group Meeting on Application of Nuclear Methods, Vienna, Austria, Mar. 22, 1976
Lyon, W. S., J. F. Emery	"Multielement Analysis by Instrumental Neutron Activation Analysis"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27 - 29, 1976
Maddox, W.	"Use of Fourier Transform Infrared Spectroscopy in Tobacco Smoke Chamber Analysis"	ORNL Analytical Chemistry Division Seminar, Oak Ridge, Tenn., Apr. 29, 1976
Maddox, W., G. Matamoros*	"Analysis of Cigarette Smoke by Fourier Transform Infrared Spectroscopy"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27 - 29, 1976
Manning, D. L., G. Matamoros*	"Recent Electroanalytical Studies in Molten Fluoride Salt Systems"	172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug. 30 - Sept. 3, 1976
Moore, F. L.	"Recent Studies on Pollution Control of Mercury and Cyanides"	Workshop for Technical Personnel from Arthur D. Little Company on Waste Management, Oak Ridge, Tenn., Apr. 8, 1976
	"Cyanide and Zinc Removal and Recovery from Electrofinishing Wastes"	Workshop for Technical Managers from Hydrocarbon Corp. on Waste Treatment, Oak Ridge, Tenn., Sept. 16, 1976
Nayfeh, M. H.,* J. P. Young, G. S. Hurst*	"Photoionization of Cs Excited States"	29th Annual Gaseous Electronics Conference, Cleveland, Ohio, Oct. 19 - 22, 1976
Peterson, J. R., R. L. Fellows,* J. P. Young, R. G. Haire*	"Absorption Spectroscopic and X-ray Diffraction Study of Dimorphism in $^{249}BkBr_3$"	172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug. 30 - Sept. 3, 1976

AUTHOR(s)	TITLE	PRESENTED AT
	"Study of the Solid-State Phase Transformation of $^{249}BkBr_3$ via Absorption Spectroscopy and X-ray Diffraction Techniques"	2nd International Conference on the Electronic Structure of the Actinides, Wroclaw, Poland, Sept. 13–16, 1976
Pruett, M. F.	"Tritium Measurements in GB-10"	ORNL Gas-Cooled Fast Reactor Technical Review Meeting, Oak Ridge, Tenn., Aug. 26, 1976
Pruett, M. F., A. W. Longest,* D. A. Costanzo, J. A. Coulon,* C. Gat,* B. C. Fjeldsted*	"Tritium Monitoring System for the GB-10 GCFR Fuel Irradiation Experiment"	American Nuclear Society Annual Meeting, Toronto, Canada, June 14–16, 1976
Ramey, W. T., D. C. Canada	"Organic Mass Spectrometry"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Ramey, W. T., D. C. Canada, C. A. Pritchard	"Use of Organic Mass Spectrometry in Energy-Related Programs"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976
Reynolds, S. A.	"Radioanalytical Methodology and Standards Needs at ORNL Relative to Uranium Mining and Milling"	Workshop on SRM's for Uranium Mining, National Bureau of Standards, Washington, D.C., Mar. 22, 1976
	"Plutonium and Actinides in the Environment"	ORAU College Faculty Institute on Radiotracer Techniques in Ecology, Oak Ridge, Tenn., Aug. 12, 1976
Reynolds, S. A., F. A. Bondietti,* T. G. Scott	"Environmental Alpha Emitters: Some Radiochemistry and Analysis"	22nd Annual Conference, Bioanalytical, Environmental, and Analytical Chemistry, Philadelphia, Pa., Oct. 7, 1976
Rees, H. H.	"Theory and Application of Cerenkov Counting"	International Conference on Liquid Scintillation Science and Technology, Banff, Alberta, Canada, June 16, 1976

AUTHOR(s)	TITLE	PRESENTED AT
Rubin, I. B., M. R. Guerin, J. L. Epler,* A. A. Hardigree*	"Fractionation of Fossil Fuel Conversion Products for Biotesting"	Gatlinburg Conference, Gatlinburg, Tenn., Oct. 12–14, 1976
Shults, W. D., J. A. Carter, M. R. Guerin, W. R. Laing	"Analytical Problems That Rest at the Energy-Environment Interface"	American Chemical Society Centennial Meeting, New York, N.Y., Apr. 4–9, 1976
Smith, D. H., W. H. Christie	"An Approach to SIMS Quantification Analysis of 10 NBS Glass Standards"	Workshop on Microstandards, National Bureau of Standards, Gaithersburg, Md., Jan. 22–23, 1976
Smith, D. H., H. S. McKown, W. H. Christie	"Two-Stage Mass Spectrometer for IAEA Safeguards Laboratory"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Stelzner, R. W., N. A. Betz,* J. S. Stanton*	"Computerized Data Management System"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Stokely, J. R.	"Characterization of the SEM Animal Inhalation Exposure System"	Council for Tobacco Research Contractors Meeting, New Orleans, La., Apr. 1–3, 1976
	"Review and Status of Inhalation Bioassay Monitering Activities"	National Cancer Institute Smoking and Health Program, Chemistry Subgroup Meeting, Rockville, Md., June 9, 1976
Stokely, J. R., M. R. Guerin	"Tobacco Smoke Inhalation Exposure Systems"	Inhalation Toxicology Workshop, Tampa, Fla., Oct. 20–22, 1976
Walker, R. L.	"Microbead Technique Applied to Burnup Analysis"	ORNL Analytical Chemistry Division Annual Information Meeting, Oak Ridge, Tenn., Mar. 11, 1976
Young, J. P., Haire, R. G.,* Fellows, R. L.,* Peterson, J. R.*	"Spectrophotometric Studies of Microgram Quantities of the Halides of Berkelium, Californium, and Einsteinium"	Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, Pa., Nov. 15–19, 1976

AUTHOR(s)	TITLE	PRESENTED AT
	"Spectrophotometric and X-ray Diffraction Studies of the Reaction of Hydrogen with Berkelium, Californium, and Einsteinium Bromide and Iodides"	Southeastern Regional ACS Meeting, Gatlinburg, Tenn., Oct. 27–29, 1976

Analytical Chemistry Division Seminars at ORNL

SPEAKER(s)	TITLE	DATE
Barry, E. F. University of Lowell Lowell, Mass.	"Selective Stationary Phases in Gas Chromatography"	Sept. 8, 1976
Borella, H. EG&G Santa Barbara, Calif.	"Energy and Environmental Monitoring"	Feb. 19, 1976
Carr, Peter W. University of Georgia Athens	"Analytical Application of Immobilized Enzyme Technology"	Oct. 26, 1976
Delhave, M. CNRS Laboratory University of Lille France	"Laser Microprobe Spectroscopy"	Nov. 19, 1976
Dooley, J. E. Bartlesville Energy Research Center Bartlesville, Okla.	"An Analytical Scheme for Characterization of Liquid Products from Coal"	Dec. 3, 1975
Evans, C. A. University of Illinois Urbana	"A Comparison of MeV-He^{+2} Back-Scattering with Other Methods of Surface Analysis"	Nov. 3, 1976
Goldstein, G. ORNL	"Liquid Chromatography of Polycyclic Aromatic Hydrocarbons"	Jan. 13, 1976
Hertz, H. S. NBS Washington, D.C.	"State of the Art Chromatographic Techniques Applied to ppb-Level Environmental Assessment"	June 17, 1976
Isenhour, Tom University of North Carolina Chapel Hill	"Minicomputer Text Searching Applied to Bibliographic and Spectroscopic Data Bases"	Sept. 30, 1976
Kessler, L. W. Sonoscan, Inc. Bensenville, Ill.	"Acoustic Microscopy"	Nov. 15, 1976
LaFleur, P. D. Institute for Materials Research NbS Washington, D.C.	"Standard Materials and Accurate Analysis"	Nov. 8, 1976
Laing, W. R., and L. J. Brady ORNL	"Coal and Analytical Chemistry"	Feb. 10, 1976

SPEAKER(s)	TITLE	DATE
Lee, D. A. ORNL	"In-Line Monitoring of Effluents from HTGR Fuel Particle Preparation Processes Using a Time-of-Flight Mass Spec[illegible]meter"	May 17, 1976
Maddox, W. L. ORNL	"Use of Fourier Transform Infrared Spectroscopy in Tobacco Smoke Chamber Anaiysis"	Apr. 20, 1976
McCrone, W. C. McCrone Research Institute Chicago, Ill.	"Sleuthing with the Microscope"	Dec. 10, 1975
Pugmire, R. J. University of Utah Salt Lake City	"Application of Carbon-13 NMR to Fossil-Derived Liquids"	May 20, 1976
Reynolds, S. A. ORNL	"Alpha Emitters in Environmental Materials"	Oct. 28, 1976
Rinehart, Edward University of Wyoming Laramie	"Microwave Spectroscopy"	Mar. 17, 1976
Wagner, C. D. Shell Development Co. Houston, Tex.	"Dual Anode ESCA: A New Approach to Chemical State Identification"	July 12, 1976

PATENTS

AUTHOR(s)	TITLE	PATENT NO.	DATE ISSUED
Anderson, N. G.,* J. E. Caton	"Rotor for Centrifugal Testing of Electrophoresis Gel"	3,927,826	Dec. 23, 1975
Mueller, T. R.	"Automatic Electrochemical Ambient Air Monitor for Chloride and Chlorine"	3,969,209	July 13, 1976
Mueller, T. R., H. H. Ross	"Automatic Ranging Circuit for a Digital Panel Meter"	3,958,178	May 18, 1976

ARTICLES REVIEWED OR REFEREED FOR PERIODICALS

Reviewer or referee	Number of articles reviewed or refereed for indicated periodical																								
	Acad. Press	*ACS Chem. Ser.*	*Anal. Chem.*	*Anal. Chim. Acta*	*Anal. Lett.*	*ASTM Methods*	*Biochim. Biophys.*	*Chem. Instrum.*	*Clin. Chem.*	*Environ. Sci. Technol.*	*J. Assoc. Anal. Chem.*	*J. Electroanal. Chem.*	*J. Electron. Spectros.*	*J. Lipid Res.*	*J. Nat. Cancer Inst.*	*J. Polym. Sci.*	*J. Radioanal. Chem.*	*Med. Phys.*	*Nucl. Sci. Eng.*	*Nucl. Technol.*	ORNL Reports	*Phys. Rev.*	Proposals	*Radiochem. Radioanal. Lett.*	*Tab. Int.*	Total
Bostic, D. A.			2																				1			3
Canada, D. C.																							1			1
Christie, W. H.		1																					1			2
Clark, B. R.											1															1
Costanzo, D. A.				1																2				1		4
Emery, J. F.			5																							5
Feldman, C.			5																							5
Griest, W. H.			1																				1			2
Guerin, M. R.															3								8		1	12
Holmberg, R. W.			1																							1
Hulett, L. D.													4			4		1				1	1			11
Klatt, L. N.			3									1									1		1			6
Laing, W. R.						7																				7
Lyon, W. S.			2							1						20							3	4		30
Maddox, W. L.	1																									1
Moore, F. L.			5																		1		1			7
Mueller, T. R.			3					1																		4
Rainey, W. T.							1		1					1												3
Reynolds, S. A.						5													1					1		7
Ross, H. H.																							2			2
Shaw, R. W.																							1			1
Shults, W. D.			1																				4			5
Stelzner, R. W.			1																							1
Walker, R. L.					1																		1			2
Walton, J. R.																					1					1
Young, J. P.					1																		2			3
Total	1	1	29	1	2	12	1	1	1	1	1	1	4	1	3	4	20	1	1	2	3	1	28	6	1	127

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